ANNUAL REPORT | 2019

PRADEEP RESEARCH GROUP

INDIAN INSTITUTE OF TECHNOLOGY MADRAS

CHENNAI 600 036, INDIA

During the visit of Prof. R. Graham Cooks, Purdue University and Prof. Thomas Thundat, University at Buffalo on December 12, 2019.

Pictured above are, from left to right: 1st row (sitting) – Subhashree Das, Amrita Chakraborty, A. Suganya, Biswajit Mondal, Swetashree Acharya, Prof. T. Pradeep, Anagha Jose, Deeksha, Dr. C. K. Manju, K. Priya, Prof. R. Graham Cooks, Prof. Thomas Thundat, Rabiul Islam.

2nd row (on knees) – Ananthu Mahendranath, Krisdevaraj, Dr. Angshuman Roychoudhary, Debasmita Ghosh, Shubadip Das, Soumya Samanta, Sanjit Gayen, K. S. Sugi, C. Sudhakar.

3rd row (standing) – Anil Kumar Avula, Anikit Nagar, Arijit Jana, Dr. Saurav Kanti Jana, Spoorthi B. K., Madhuri Jash, Dr. Papri Chakraborty, Dr. R. Sathya, Md. Bodiuzzaman, Sritama Mukherjee, Tripti Ahuja, Khadeeja Mubashira, Tanvi Gupte, Paulami Bose, S. Jenifer, E. Sundarraj, Sandeep Bose, Jyotirmoy Ghosh, Gaurav Vishwakarma, Jayoti Roy.

4th row (standing) - Asish Kurian, Dr. S. Vidhya, Dr. Abhijit Nag, Dr. P. Ganesan, Vishal Kumar, Srikrishnarka Pillalamarri, M. P. Kannan.

Not pictured: Ramesh Kumar, Dr. Krishnan Swaminathan, Esma Khatun, Mohd. Azhardin Ganayee, Pallab Basuri, Dr. Wakeel Ahmed Dar.

Please visit the links for annual reports of 2014, 2015, 2016, 2017 and 2018.

OUR TEAM

Thalappil Pradeep
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Deepak Parekh Institute Chair Professor and Professor of Chemistry
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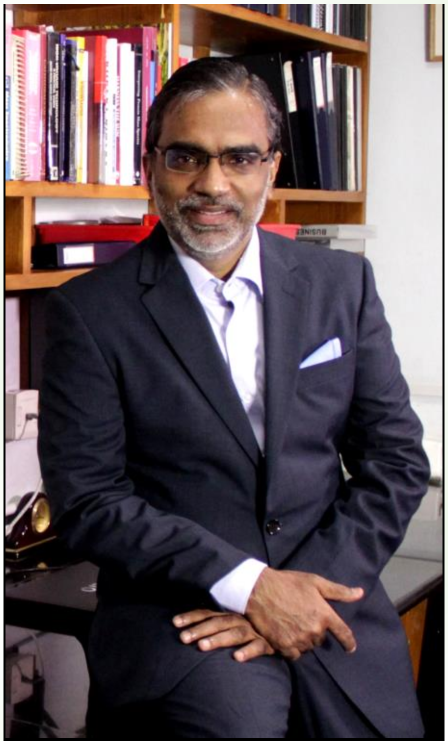
Web: www.dstuns.iitm.ac.in/pradeep-research-group.php



Our Struggle

Is To Be

Creative…

Today and

Everyday!

Ph.D. Students

- Amrita Chakraborty
- Anagha Jose
- Anil Kumar
- Ankit Nagar
- Arijit Jana
- Biswajit Mondal
- Debasmita Ghosh
- Esma Khatun
- Gaurav Vishwakarma
- Jayoti Roy
- Jyotirmoy Ghosh
- S. Jenifer *
- M. P. Kannan*
- Dr. Krishnan Swaminathan MD FRCP (Edin)*
- Madhuri Jash
- Md Bodiuzzaman
- Md Rabiul Islam
- Mohd. Azhardin Ganayee
- Pallab Basuri
- Paulami Bose
- Sandeep Bose
- Spoorthi B. K.
- Sritama Mukherjee*
- Sudhakar Chennu
- Suganya Arunan*
- K. S. Sugi
- Srikrishnarka Pillalamarri*
- Swetashree Acharya
- Tanvi Gupte*
- Tripti Ahuja
- Vishal Kumar*

*** Interdisciplinary/Joint students**

Postdoctoral/Research Associates

- Dr. P. Ganesan
- Dr. Sourav Kanti Jana
- Dr. Wakeel Ahmed Dar
- Dr. Angshuman RayChowdhuri
- Dr. Sathya Ramalingam
- Dr. Kartheek Joshua
- Dr. Papri Chakraborty
- Dr. Abhijit Nag

Project Associates

- Shubhasree Das

M.Sc. Students

- Deeksha
- Subhadeep Das
- Soumya Samanta
- Sanjit Gayen

B.Tech. Students

- Sathvik Ajay Iyengar
- Dasi Raaga Madhuri

Summer & Winter Student(s)/Fellow(s)

- Amrita P. Sandra
- Pooja Ajayan
- Devika
- V. S. Nishanthi
- Megha Maria Stanley
- Anjana Devi
- Khadeeja Mubashira

Administrative Officer

- K. Priya

Project Technicians

- E. Sundarraj
- Asish Kurian
- Devaraj. K

M.S. Students

- Ramesh Kumar
- Ananthu Mahendranath

Project Officer

- M. Bhaskar

WHAT'S INSIDE?

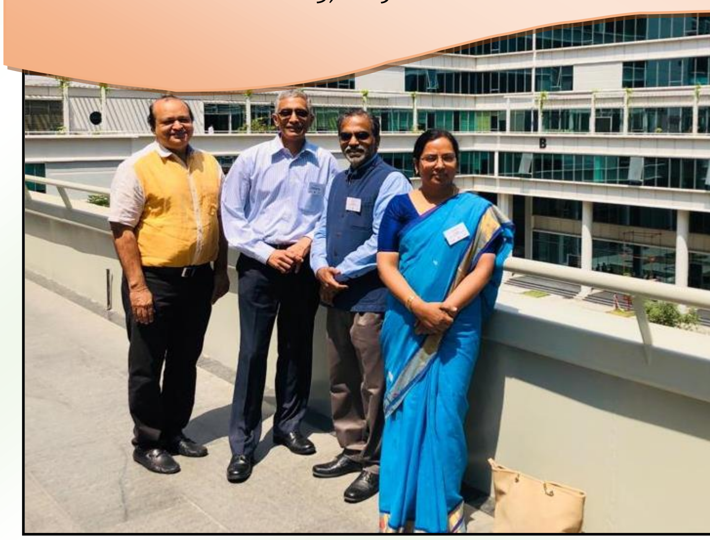
Glimpses of 2019

Prof. Pradeep briefing our clean water technologies to **PM Shri. Narendra Modi** during **Singapore-India Hackathon** on September 29, 2019 in IIT Madras, telecasted in DD News.

Mr. Deepak Parekh, HDFC chairman and his colleagues with **Prof. Pradeep** on the inauguration of **ICCW** on April 22, 2019 at IITM Research Park.

Scholars were excited to meet **Shri. T. K. A Nair**, Ex-Principal Secretary and later Advisor to Prime Minister of India from 2004-2014, when he visited the lab during May 24-25, 2019.

Prof. Pradeep with **Mr. Parameswaran Iyer**, Secretary, MDWS, **Ms. T. Radha**, IAS , Jt. Secretary, MDWS and **Mr. Rajendra Mootha**, CEO, IITM Research Park at ***Jal Samvaad*: Discussions on Clean Water** workshop conducted jointly by Ministry of Drinking Water and Sanitation (MDWS) and United Nations Children's Fund (UNICEF), partnering with Indian Institute of Technology, Madras (IITM) held at IITM Research Park on March 23, 2019.



Awards and Honors

1. Prof. Pradeep was elected as an Honoree on the Asian Scientist 100 list (2019) edition that celebrates the successes of Asia's brightest researchers and innovators, highlighting their achievements across a range of scientific disciplines.

2. Prof. Pradeep was felicitated at EFCS 2019- International conference for distinguished service to chemical sciences on December 13, 2019 held at Farook College, Calicut.

Prof. Pradeep with former ISRO Chairman **Dr. Kiran Kumar**, vice-chancellor **Dr. Jamshed Bharucha** and pro-VC **Dr. D. Narayana Rao** at SRM University, Amravati.

Inauguration of **awareness posters on Water, Sanitation and Hygiene (WASH)** by Ministry of Drinking Water and Sanitation during ***Jal Samvaad***: Discussions on Clean Water.

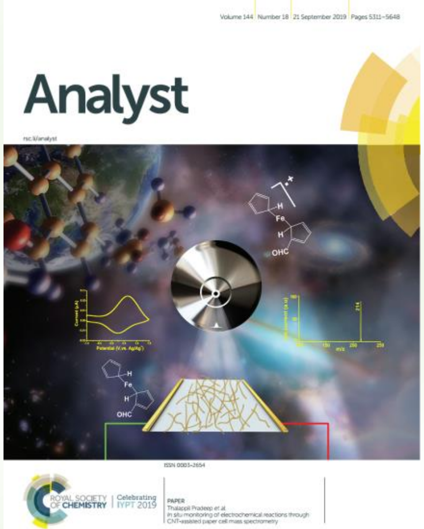
Publications

*Journal publications**

1. Nanocellulose reinforced organo-inorganic nanocomposite for synergistic and affordable defluoridation of water and an evaluation of its sustainability metrics, Sritama Mukherjee, Haritha Ramireddy, Avijit Baidya, A. K. Amala, Chennu Sudhakar, Biswajit Mondal, Ligy Philip, and, Thalappil Pradeep, ACS Sustain. Chem. Eng., 2019. (DOI: 10.1021/acssuschemeng.9b04822) (ARTICLE ASAP).

2. Formation of cubic ice via clathrate hydrate, prepared in ultrahigh vacuum under cryogenic conditions, Jyotirmoy Ghosh, Radha Gobinda Bhuin, Gaurav Vishwakarma, and, Thalappil Pradeep, J. Phys. Chem. Lett., 11 (2020), 26-32. (DOI: 10.1021/acs.jpclett.9b03063).

3. Intercluster reactions resulting in silver-rich trimetallic nanoclusters, Esma Khatun, Papri Chakraborty, Betsy Jacob, Ganesan Paramasivam, Mohammad Bodiuzzaman, Wakeel Dar, and, Thalappil Pradeep, Chem. Mater., 2019. (DOI: 10.1021/acs.chemmater.9b04530) (Just Accepted).



R. Narayanan et al., Analyst, 2019, 144, 5404-5412. **Inside front cover**

4. Internalization of a preformed atomically precise silver cluster in proteins by multistep events and emergence of luminescent counterparts retaining bioactivity, Debasmita Ghosh, Mohammad Bodiuzzaman, Anirban Som, Sebastian Raja, Ananya Baksi, Atanu Ghosh, Jyotirmoy Ghosh, Akshayaa Ganesh, Priyanka Samji, Sundarasamy Mahalingam, Devarajan Karunagaran, and, Thalappil Pradeep, J. Phys. Chem. C, 123 (2019), 48, 29408-29417. (DOI: 10.1021/acs.jpcc.9b07765).

5. Metal ion-induced luminescence enhancement in protein protected gold clusters, Jyoti Mohanty, Kamalesh Chaudhari, Chennu Sudhakar, and, Thalappil Pradeep, J. Phys. Chem. C, 123 (2019) 28969–28976. (DOI: 10.1021/acs.jpcc.9b07370).

6. Interparticle reactions between silver nanoclusters leading to product co-crystals by selective co-crystallization, Wakeel Ahmed Dar, Mohammad Bodiuzzaman, Debasmita Ghosh, Ganesan Paramasivam, Esma Khatun, Korath Shivan Sugi, and, Thalappil Pradeep, ACS Nano, 13 (2019) 13365–13373 (DOI: 10.1021/acsnano.9b06740).

7. Mechanistic elucidation of the structure and reactivity of bare and hydride protected Ag_{17}^{+} clusters, Ananya Baksi, Madhuri Jash, Soumabha Bag, Sathish Mudedla, Mohammad Bodiuzzaman, Debasmita Ghosh, Ganesan Paramasivam, Venkatesan Subramanian, and Thalappil Pradeep, J. Phys. Chem. C, 123 (2019) 28494-28501. (DOI: 10.1021/acs.jpcc.9b09465).

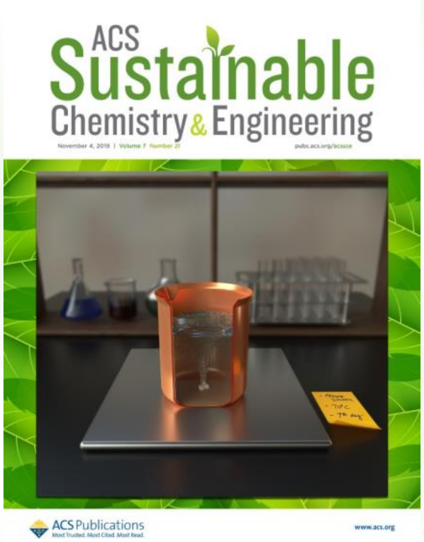
8. Enhancing the sensitivity of point-of-use electrochemical microfluidic sensors by ion concentration polarisation - A case study on Arsenic, Vidhya Subramanian, Sangjun Lee, Sanjoy Jena, Sourav Kanti Jana, Debdutta Ray, Sung Jae Kim, and Thalappil Pradeep, Sensors & Actuators: B. Chemical, 304 (2020) 127340 (DOI: 10.1016/j.snb.2019.127340).

9. Ambient electrospray deposition Raman spectroscopy (AESD RS) using soft landed preformed silver nanoparticles for rapid and sensitive analysis, Tripti Ahuja, Atanu Ghosh, Sandip Mondal, Pallab Basuri, Jenifer Shantha Kumar, Pillalamarri Srikrishnarka, Jyoti Sarita Mohanty, Sandeep Bose, and Thalappil Pradeep, Analyst, 144 (2019) 7412-7420 (DOI: 10.1039/C9AN01700C).

10. Crystallization of a supramolecular coassembly of an atomically precise nanoparticle with a crown ether, Papri Chakraborty, Abhijit Nag, Korath Shivan Sugi, Tripti Ahuja, Babu Varghese, and Thalappil Pradeep, ACS Materials Lett., 1 (2019) 534–540 (DOI: 10.1021/acsmaterialslett.9b00352).

11. Tribochemical degradation of polytetrafluoroethylene in water and generation of nanoplastics, Abhijit Nag, Ananya Baksi, Jyotirmoy Ghosh, Vishal Kumar, Soumabha Bag, Biswajit Mondal, Tripti Ahuja, and Thalappil Pradeep, ACS Sustain. Chem. Eng., 7 (2019) 21, 17554-17558 (DOI: 10.1021/acssuschemeng.9b03573).

12. Waterborne fluorine-free superhydrophobic surfaces exhibiting simultaneous CO_2 and humidity sorption, Avijit Baidya, Anagha Yatheendran, Tripti Ahuja, Chennu Sudhakar, Sarit Kumar Das, Robin H.A. Ras, and Thalappil Pradeep, Adv. Mater. Interfaces, 6 (2019) 9990–10000 (DOI: 10.1002/admi.201901013).



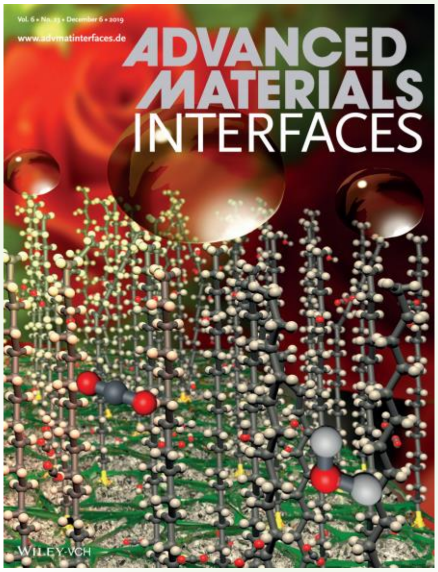
Abhijit Nag et al., ACS Sustain. Chem. Eng., 2019 (Article ASAP). **Cover page**

13. In-situ monitoring of electrochemical reactions through CNTs-assisted paper cell mass spectrometry, Rahul Narayanan, Pallab Basuri, Sourav Kanti Jana, Ananthu Mahendranath, Sandeep Bose and Thalappil Pradeep, Analyst, 144 (2019) 5404 (DOI: 10.1039/C9AN00791A).

14. Highly-sensitive As^{3+} detection using electrodeposited nanostructured MnO_x and phase evolution of the active material during sensing, Tanvi Gupte, Sourav Kanti Jana, Jyoti Sarita Mohanty, Srikrishnarka Pillalamarri, Sritama Mukherjee, Tripti Ahuja, Chennu Sudhakar, Tiju Thomas, and Thalappil Pradeep, ACS Appl. Mater. Interfaces, 11 (2019) 28154–28163 (DOI: 10.1021/acsami.9b06023).

15. Conformational changes of protein upon encapsulation of noble metal clusters: An investigation by hydrogen/deuterium exchange mass spectrometry, Debasmita Ghosh, Sathish Kumar Mudedla, Md Rabiul Islam, Venkatesan Subramanian, and Thalappil Pradeep, J. Phys. Chem. C, 123 (2019) 17598–17605 (DOI: 10.1021/acs.jpcc.9b04009).

16. Spontaneous formation of tetrahydrofuran hydrate in ultra-high vacuum, Jyotirmoy Ghosh, Radha Gobinda Bhuin, Gopi Ragupathy, and Thalappil Pradeep, J. Phys. Chem. C, 123 (2019) 16300–16307 (DOI: 10.1021/acs.jpcc.9b04370).

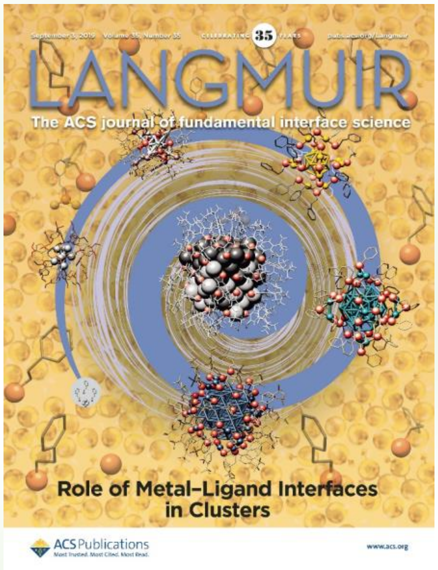


Avijit Baidya et al., Adv. Mater. Interfaces, 6 (2019) 9990–10000. **Inside back cover**

17. Geologically-inspired monoliths for sustainable release of essential minerals into drinking water, Swathy Jakka Ravindran, Ananthu Mahendranath, Srikrishnarka Pillalamarri, Anil Kumar Avula, Md Rabiul Islam, Sritama Mukherjee, Ligy Philip, and Thalappil Pradeep, ACS Sustain. Chem. Eng., 7 (2019) 11735-11744 (DOI: 10.1021/acssuschemeng.9b01902).

18. Surface treated nanofibers as high current yielding breath humidity sensors for wearable electronics, Sathvik Iyengar, Srikrishnarka Pillalamarri, Sourav Jana, Md Rabiul Islam, Tripti Ahuja, Jyoti Sarita Mohanty, and Thalappil Pradeep, ACS Appl. Electron. Mater., 1 (2019) 951–960 (DOI: 10.1021/acsaelm.9b00123).

19. Reply to Choukroun et al.: IR and TPD data suggest the formation of clathrate hydrates in laboratory experiments simulating ISM, Jyotirmoy Ghosh, Rabin Rajan J. Methikkalam, Radha Gobinda Bhuin, Gopi Ragupathy, Nilesh Choudhary, Rajnish Kumar, and Thalappil Pradeep, Proc. Natl. Acad. Sci. U.S.A., 29 (2019) 14409-14410 (DOI: 10.1073/pnas.1905894116).



K. R. Krishnadas et al., Langmuir, 35 (2018) 11243-11254. **Cover page**

20. The emerging interface of mass spectrometry with materials, Papri Chakraborty, and Thalappil Pradeep, NPG Asia Materials, 11 (2019) 1095 (DOI: 10.1038/s41427-019-0149-3).

21. Formation of a NIR emitting Ag34S3SBB20(CF3COO)62+ cluster from a hydride protected silver cluster, C. K. Manju, Debasmita Ghosh, Mohammad Bodiuzzaman, and Thalappil Pradeep, Dalton Trans., 48 (2019) 8664-8670 (DOI: 10.1039/C9DT01533G).

22. Sub-ppt level detection of analytes by superhydrophobic pre-concentration paper spray ionization mass spectrometry (SHPPSI MS), Pallab Basuri, Avijit Baidya and Thalappil Pradeep, Anal. Chem., 91 (2019) 7118-7124 (DOI: 10.1021/acs.analchem.9b00144).

23. Confining an Ag10 Core in an Ag12 Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization, Esma Khatun, Md Bodiuzzaman, Korath Sugi, Papri Chakraborty, Ganesan Paramasivam, Wakeel Dar, Tripti Ahuja, Sudhadevi Antharjanam, and Thalappil Pradeep, ACS Nano., 13 (2019) 5753-5759 (DOI: 10.1021/acsnano.9b01189).

24. A covalently linked dimer of [Ag25(DMBT)18]-, Md Bodiuzzaman, Abhijit Nag, Raghu Narayanan Pradeep, Ankush Chakraborty, Ranjit Bag, Paramasivam Ganesan, Ganapati Natarajan, G. Sekar, Sundargopal Ghosh and Thalappil Pradeep, Chem. Commun., 55 (2019) 5025-5028 (DOI: 10.1039/C9CC01289C).

25. Electrospray deposition-induced ambient phase transition in copper sulphide nanostructures, Arijit Jana, Sourav Kanti Jana, Depanjan Sarkar, Tripti Ahuja, Pallab Basuri, Biswajit Mondal,

Sandeep Bose, Jyotirmoy Ghosh, and Thalappil Pradeep, J. Mater. Chem. A, 7 (2019) 6387-6394 (DOI: 10.1039/C9TA00003H).

26. Spatial distribution mapping of molecules in the grains of different rice landraces, using desorption electrospray ionization mass spectrometry, Arunan Suganya, Debal Deb and Thalappil Pradeep, Rapid Commun. Mass Spectrom., 33 (2019) 727–736 (DOI: 10.1002/rcm.8397).

27. Clathrate hydrates in interstellar environment, Jyotirmoy Ghosh, Rabin Rajan J. Methikkalam, Radha Gobinda Bhuin, Gopi Ragupathy, Nilesh Choudhary, Rajnish Kumar, and Thalappil Pradeep, Proc. Natl. Acad. Sci. U.S.A., 116 (2019) 1526-1531 (DOI: 10.1073/pnas.1814293116).

28. Approaching materials with atomic precision using supramolecular cluster assemblies, Papri Chakraborty, Abhijit Nag, Amrita Chakraborty and Thalappil Pradeep, Acc. Chem. Res., 52 (2019) 2–11 (DOI: 10.1021/acs.accounts.8b00369).

Publications with other groups

29. Effects of chloride concentration on the water disinfection performance of silver containing nanocellulose-based composites, Janika Lehtonen, Jukka Hassinen, Riina Honkanen, Avula Anil Kumar, Heli Viskari, Anu Kettunen, Nikolaos Pahimanolis, Thalappil Pradeep, Orlando J. Rojas, and Olli Ikkala, Sci. Rep., 9 (2019) 19505 (DOI: 10.1038/s41598-019-56009-6).

30. Nano-Gymnastics: Visualisation of inter-cluster reactions by high resolution trapped ion mobility mass spectrometry, Ananya Baksi, Erik Schneider, Patrick Weis, Kumaranchira Krishnadas, Debasmita Ghosh, Horst Hahn, Thalappil Pradeep, and, Manfred Kappes, J. Phys. Chem. C, 121 (2019) 13421–13427 (DOI: 10.1021/acs.jpcc.9b08686).

*Some of these papers will appear in 2020. Some were listed in the Annual Report of 2018, without page numbers.

Patent Applications

Indian

1. A compact, modular and scalable continuous-flow greywater sink for potable and non-potable uses, Thalappil Pradeep and Ankit Nagar, 201941028155, July 12, 2019.
2. Composition for sustained release of minerals and carbonate in water and a water purification device based on the same, Thalappil Pradeep; Swathy J .R.; Nalenthiran Pugazhenthiran, 201943029174, July 17, 2019.
3. Method for generating different phases of copper sulphide nanostructures using electrospray deposition (ESD) under ambient conditions, Thalappil Pradeep; Arijit Jana; Sourav Kanti Jana; Depanjan Sarkar; 201941032379, August 9, 2019.
4. Tribochemical method for degradation of polymers in water, Thalappil Pradeep. Abhijit Nag, Ananya Baksi, Jyotirmoy Ghosh, Vishal Kumar, Soumabha Bag, Biswajit Mondal and Tripti Ahuja, TEMP/E-1/34612 /2019-CHE, 201941032757, August 13, 2019.

5. A green method for preparing robust and sustainable cellulose-polyaniline based nanocomposite for effective removal of fluoride from water and a purifier thereof, Thalappil Pradeep; Sritama Mukherjee; Haritha Ramireddy, 201941046691, November 15, 2019.
6. A method for facile, rapid and industrially scalable preparation of metal hydroxide composition, Hydromaterials Private Limited & Indian Institute of Technology Madras (IIT Madras), 201941054546, December 30, 2019.

PCT

1. A modified surface for condensation, T Pradeep; Ankit nagar; Ramesh Kumar, PCT/IN2019/50078, February 2, 2019.
2. An enhanced carbon dioxide sorbent nanofiber membrane and a device thereof, Thalappil Pradeep; Anagha Yatheendran; Ramesh Kumar; Arun Karthik S, PCT/IN2019/050555, July 30, 2019.

Patents Granted

Indian

1. Anti-gravity water filter cartridge, Design patent number 260460, filed on February 19, 2014, Issued October 18, 2019.
2. Water purification cartridge attached to container, Design patent application, TEMP/D-1/5729/2016-KOL, October 18, 2016 Patent number 287785, Issued June 21, 2019.
3. Composition for sustained release of carbonate and a water purification device based on the same with enhanced biocidal activity, 7026/CHE/2015, December 29, 2015, granted as patent no. 314266 on June 17, 2019.

PCT

1. Detection of quantity of water flow using quantum clusters, T. Pradeep, Leelavathi A, M. Udhaya Sankar, Amrita Chaudhary, Anshup, T. Udayabhaskararao, 1521/CHE/2012, April 17, 2012. Issued in China with patent number CN104520706 B. Issued US patent no. US 10041925 B2, issued on August 7, 2018. Issued in Japan patent no. JP6367182 B2 on August 8, 2018, Issued in Mexico patent no. MX362092 B on October 7, 2019, Issued in Ireland patent no. IL20130235206 on December 31, 2014.

Graduation

PhD (viva completed, 2019)

1. **Shridevi S. Bhat,** Department of Chemistry, IIT Madras, 2019.

   ‘Investigations of mono and bimetallic clusters of iridium’.
2. **Papri Chakraborty**, Department of Chemistry, IIT Madras, 2019.

'Chemical interactions of noble metal nanoclusters: Dynamics, aggregation and supramolecular complexation'.

3. **Abhijit Nag**, Department of Chemistry, IIT Madras, 2019.
   'Consequences of molecular interactions of noble metals in the bulk and nanoscale'.
4. **Swathy Ravindran,** Department of Chemistry (Interdisciplinary), IIT Madras, 2019.
   'Employing common ions and molecules for sustainable clean water'.
5. **Manju C. K.,** Department of Chemistry, IIT Madras, 2019.
   'Investigations of new atomically precise metal chalcogenide clusters'.
6. **Jyoti Sarita Mohanty**, Department of Chemistry, IIT Madras, 2019.
   'Atomically precise clusters in protein templates: Synthesis and applications'.
7. **S. Vidhya**, Department of Biotechnology, IIT Madras, 2019.
   'Integrating technologies to create modular sensors for water quality monitoring'.

M.Sc. (graduated in 2019)

1. **Atanu Ghosh**, Department of Chemistry, IIT Madras, 2019. 'Ambient Electrospray coupled Raman Spectroscopy (AE RS): A tool for rapid analyte detection and probing molecular orientations in real time'.
2. **Shibalik Mukherjee**, Department of Chemistry, IIT Madras, 2019. 'Ligand shell modifications in atomically precise silver nanoclusters and their consequences'.
3. **Subhashree Das**, Department of Chemistry, IIT Madras, 2019. 'New Ionization Techniques: Promoting the Journey of Mass Spectrometry from an Analytical Method to a Synthetic Tool'.
4. **Pratishtha**, Department of Chemistry, IIT Madras, 2019.'Desalination using modified thin film composite reverse osmosis membranes'.
5. **Manav Biren Shah***, Ahmedabad University, 2019 (iMSc). 'Colorimetric determination of fluoride in water using nanocages'.
6. **Harsh Dave***, Ahmedabad University, 2019 (iMSc). 'Plasmonic-luminescent nanocomposite as a probe for dual mode imaging'.
7. **Devika Rajan***, Calicut University, 2019 (M.Sc.). Reduced graphene oxide-hydrogel composite for atmospheric water harvesting'.

***From other institutions**

Lectures Delivered

1. Nanotechnologies for clean water, 9th General Body Meeting distinguished lecture, Water Quality India Association, Renaissance Hotel, Ahmedabad, January 10, 2019.
2. Atomically precise nanoparticles, Indian Association for the Cultivation of Science, Kolkata, January 16, 2019.
3. Clathrate hydrates in interstellar environment, Chemical Research Society of India, 24th NSC, CSIR-CLRI, Chennai February 8-10, 2019.
4. Water for Life – through materials, IIT Madras Technologies for Social Impact, IITM, February 16, 2019.
5. Clathrate hydrates in interstellar environment, ChemPhysMat, SAMat, JNCASR, Bengaluru, February 20-22, 2019.
6. Nanotechnologies for clean water, Centre for Environmental Studies (CES), Anna University, March 8, 2019.
7. Atomically precise nanoparticles, Frontiers in Materials from Basic Science to Real time Applications, Jain University, Bengaluru, March 14, 2019.
8. Science – A way of life, Gemini Ganesan Memorial Lecture, Madras Christian College, March 18, 2019.
9. From Materials to Clean Water: Science, Technology and Industry, National Technology Day Function, CSIR-SERC, CSIR Campus, Taramani, Chennai, May 10, 2019.
10. Materials with atomic precision, Department of Chemistry, Hanyang University, Seoul, May 16, 2019.
11. Atomically precise noble metal nanoparticles, Seoul National University, May 16, 2019.
12. Isotopic Exchange in Nanoparticles, Frontiers of Translational Materials Science, Department of Chemistry, Hanyang University, Seoul, May 17-18, 2019.

13. From Materials to Clean Water: Science, Technology and Industry, IIT Bombay Institute Colloquium, June 6, 2019.
14. Nanomaterials, clean water and ice, UON-India Symposium at IIT Madras, June 20-21, 2019.
15. Qingdao International Academician Park, Qingdao, China, June 25 – 29, 2019.

Prof. Pradeep with our lab alumnus Dr. C. Subramaniam and his students in his lab at IIT Bombay.

16. Nanoparticles with atomic precision, 26th International Symposium on Metastable, Amorphous and Nanostructured Materials, Chennai, July 8-12, 2019.
17. Isotopic Exchange in Nanoparticles, 2nd ACS-CRSI Meeting, IIT Kanpur, July 18, 2019.
18. Nanoparticles with atomic precision, Saint-Gobain Research India, IIT Madras Research Park, July 23, 2019.
19. Water in crisis: Survival, sustainability and opportunities, CSIR HeadQuarters, New Delhi, August 8, 2019.
20. Atomically precise noble metal nanoparticles, 8th ChinaNANO, Beijing, August 17-19, 2019.
21. Isotopic Exchange in Nanoparticles, 2nd Asian Symposium on Nanoscience and Nanotechnology, Beijing, August 18, 2019.
22. Atomically precise noble metal nanoparticles, Tsinghua University, Beijing, August 19, 2019.
23. From small to ultra-small: Nanoparticles to clusters, Science Academies' Lecture Workshop, Ramaiah Institute of Technology, Bengaluru, August 29, 2019.

Prof. Pradeep with our lab alumni Dr. C. Subramaniam and Dr. Sreekumaran Nair.

24. Nanomaterials to clean water: Science, technology and industry, Science Academies' Lecture Workshop, Ramaiah Institute of Technology, Bengaluru, August 29, 2019.
25. From materials to clean water: Science, technology and industry, Tech Fest, SRM University - AP Amaravati, September 28, 2019.

26. Isotopic Exchange in Nanoparticles, Advances in Mass Spectrometry, IISER Tirupati, November 19, 2019.
27. Nanoparticles are Molecules, ISMAS 2019, BARC, Mumbai, November 27-30, 2019.
28. From materials to clean water: Making affordable sensors for clean water, One day interactive session on sensors, ICCW, December 10, 2019.
29. Nanoparticles are Molecules, International Conference on Recent Advances in Nanoscience and Nanotechnology - ICRAN'19, Stella Maris College, Chennai, December 11-12, 2019.

During a lecture at NIT Calicut.

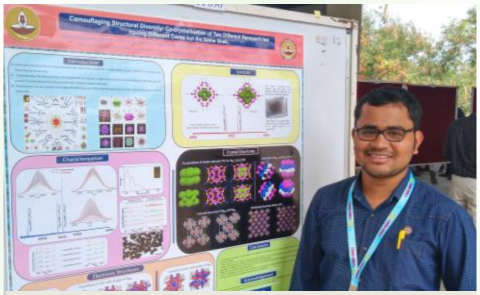
30. Clathrate hydrates in interstellar environment, Emerging Frontiers in Chemical Sciences (EFCS) - 2019, Farook College, December 13-15, 2019.
31. Nanoparticles are Molecules, National Symposium on Convergence of Chemistry & Materials (CCM-2019), BITS-Pilani, Hyderabad Campus, December 17-18, 2019.
32. Nanoparticles are Molecules, National Conference on Recent Trends in Materials Science and Technology (NCMST-2019), Institute of Space Science and Technology, Thiruvananthapuram, December 18-20, 2019.
33. Nanoparticles with atomic precision, National Conference on Nanomaterials for Energy, Environment and Health Care, National Institute of Technology Calicut, December 27-28, 2019.
34. Nanoparticles with atomic precision, International Conference on Nanoscience and Photonics for Medical Applications, MAHE, December 28-30, 2019.

Prof. Pradeep and colleagues in Qingdao International Academician Park, Qingdao, China.

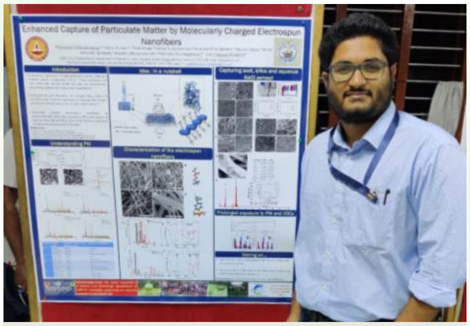
Student Activities

National Conferences:

1. ‘Fullerene-functionalized atomically precise silver nanoclusters’ by **Papri Chakraborty** in 13th RSC-CRSI joint symposium, February 7, 2019, held at IITM (Invited lecture).



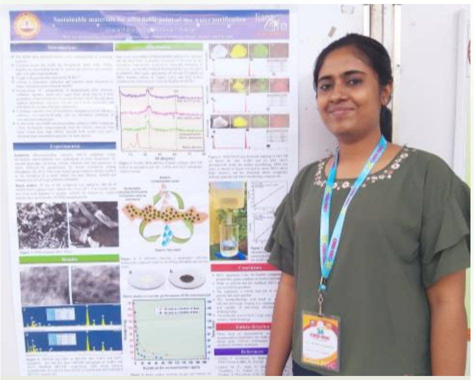
Bodiuzzaman@CRSI.



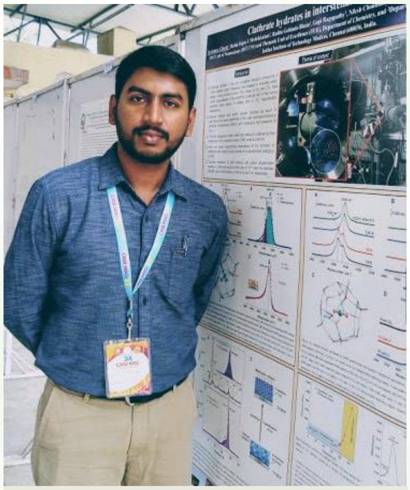
Srikrishnarka@ICRAN.

2. ‘Camouflaging Structural Diversity: Co-crystallisation of two different nanoparticles having different cores but the same shell’ by **Mohammad Bodiuzzaman** in 24th Chemical Research Society of India (CRSI) National Symposium in Chemistry, Central Leather Research Institute, Feb 08-10, 2019 .

3. ‘Surface treated electrospun nanofibers for a wearble breath humidity sensor’ by **Pillalamarri Srikrishnarka** in 24th Chemical Research Society of India (CRSI) National Symposium in Chemistry, Central Leather Research Institute, Feb 08-10, 2019.



Sritama@CRSI.



Jyotirmoy@CRSI.

4. ‘Sustainable materials for affordable point-of-use water purification’ by **Sritama Mukherjee** in 24th Chemical Research Society of India (CRSI) National Symposium in Chemistry, Central Leather Research Institute, Feb 08-10, 2019.
5. ‘Clathrate hydrates in interstellar environment’ by **Jyotirmoy Ghosh** in 24th Chemical Research Society of India (CRSI) National Symposium in Chemistry, Central Leather Research Institute, Feb 08-10, 2019.
6. ‘Clathrate hydrates in interstellar environment’ by **Jyotirmoy Ghosh** in Chemistry-in house Symposium, Department of Chemistry, IIT Madras, India, 2019 (oral presentation).

7. 'Synthesis and Characterization of Atomically Precise Silver Cluster Co-Crystals' by **Wakeel Ahmed Dar**, in 24th Chemical Research Society of India Symposium, CRSI 2019, CSIR-CLRI, Chennai, February 8-10, 2019.

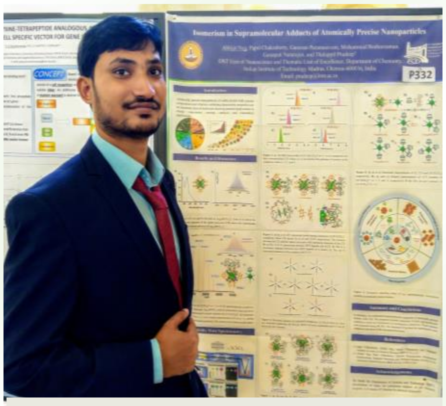
8. Chemistry of Atomically Precise Noble Metal Nanocluster Co-crystals' by **Wakeel Ahmed Dar** in 5th International Conference on Nanotechnology for Better Living, ICNBL-2019, National Institute of Technology, Srinagar, April 7-11, 2019.

9. 'Co-crystallization of Atomically Precise Noble Metal Silver Cluster by **Wakeel Ahmed Dar** in International Conference on Advanced Materials, ICAM 2019, Jamia Millia Islamia, New Delhi, March 6-7, 2019.

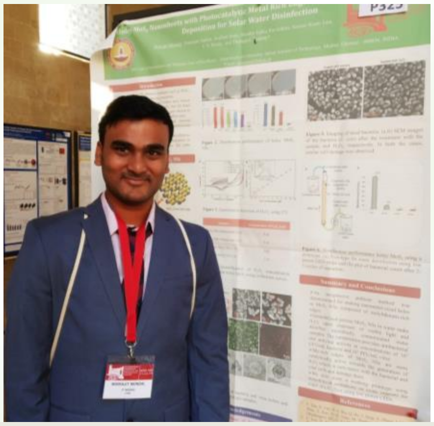
Wakeel@ICAM.

International Conferences:

1. 'Isomerism in supramolecular adductsof atomically precise nanoparticles' by **Abhijit Nag** in 14th International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC2019), Lecce, Italy, on 2–6 June, 2019.



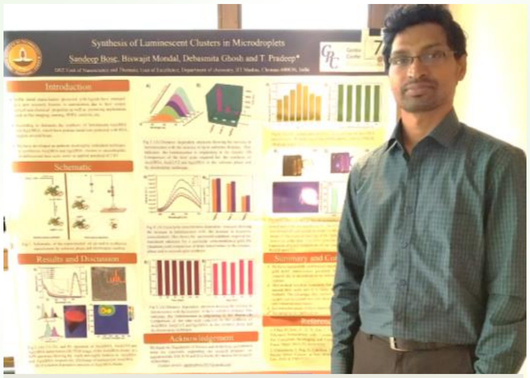
Abhijit@ISMSC.



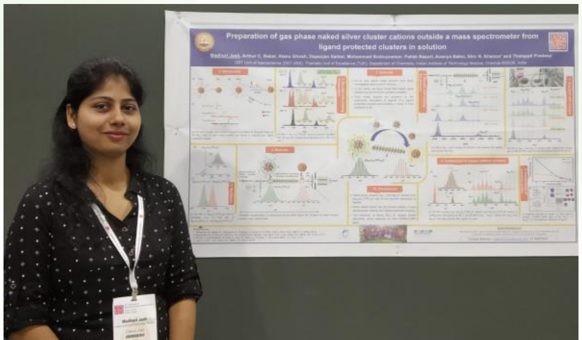
Biswajit@ISMSC.

2. 'Holey MoS2 nanosheets with photocatalytic metal rich edges by ambient electrospray deposition for solar water disinfection by **Biswajit Mondal** in 14th International Symposium on Macrocyclic and Supramolecular Chemistry (ISMSC), Lecce, Italy, on June 2-6, 2019.

3. 'Synthesis of luminescent clusters in microdroplets)' by **Sandeep Bose** in Gordon research conference on nanocluster and nanoparticles, Les Diabrelets, Switzerland on June 16-21, 2019.



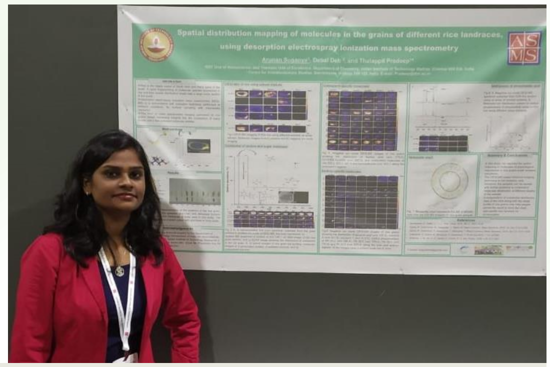
Sandeep@GRC.



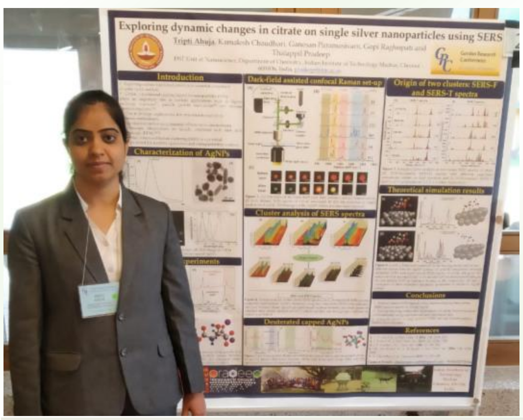
Madhuri@ASMS.

4. 'Preparation of gas phase naked silver cluster cations outside a mass spectrometer from ligand protected clusters in solution' by **Madhuri Jash** in 67th ASMS Conference on Mass Spectrometry and Allied Topics, Georgia World Congress Center, Atlanta, GA, USA, June 2-6, 2019.

5. 'Spatial distribution mapping of molecules in the grains of different rice landraces, using desorption electrospray ionization mass spectrometry' by **Suganya Arunan** in 67th ASMS Conference on Mass Spectrometry and Allied Topics, Georgia World Congress Center, Atlanta, GA, USA, June 2-6, 2019.

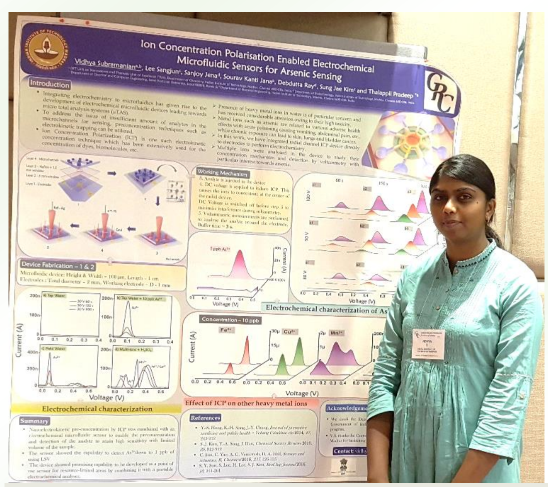


Suganya@ASMS.



Tripti@GRC.

6. 'Exploring dynamic changes in citrate on single silver nanoparticles using SERS' by **Tripti Ahuja** in Gordon research conference on nanocluster and nanoparticles, Les Diabrelets, Switzerland on June 16-21, 2019.
7. Oral presentation on 'Ambient Electrospray Deposition Raman Spectroscopy (AESD RS) using Soft Landed Preformed Silver Nanoparticles for Rapid and Sensitive Analysis' by **Tripti Ahuja** in Recent advances in material sciences and nanotechnology held in Stella Maris, Chennai, 2019.



Vidhya@GRC.

8. 'Ion concentration polarization enabled microfluidic sensors for arsenic sensing' by **S. Vidhya** in Gordon Research Seminar (GRS) and Gordon Research Conference (GRC) on Physics and Chemistry of Microfluidics, Hong Kong. June 15 – 21, 2019.

Recognition

Students

1. **Papri Chakraborty** won the best poster awards at CRSI, February 7 -9, 2019, held at CLRI, Chennai.

2. **Papri Chakraborty** won the Prof. Langmuir Prize for the best Ph.D. thesis in physical and theoretical chemistry, IIT Madras, 2019.

3. **Pallab Basuri** received the Overseas Visiting Doctoral Fellowship by SERB to work at Purdue. From left-> Pallab Basuri, Prof. Cooks, Dr. Praveen Kumar Somasundaram (OVDF head scientist), Ms. Heidi Arola and Ms. Madhu Wadhavan Sinha (Director of Finance).

4. **Anil Kumar Avula** received the Indo-US Science and Technology Forum (IUSSTF) Research Internship Program in Water Advanced Research and Innovation (WARI 2019) supported by the Department of Science and Technology, Govt. of India, UNL and IUSSTF.

5. **Pillalamarri Srikrishnarka** received best poster award at ICRAN, 2019 held at Stella Maris College, Chennai.

Alumni News

1. **Dr. Vidhya Subramanian** has joined International Centre for Clean Water (ICCW) as Project Scientist.

2. **Mr. Vaishnav Davey** has got appointed as the Chief Operating Officer at Theway Membranes.
3. **Dr. Rabin Rajan** has been placed as Assistant Professor, Department of Chemistry, Mar Ivanios College, Trivandrum.
4. **Dr. Habeeb Muhammed M. A.** has been placed as Assistant Professor, Department of Chemistry, TKM College of Engineering, Kollam, Kerala.
5. **Dr. Avijit Baidya** has joined as Biomaterials Sub-group leader, Khademhosseini Lab, Center for Minimally Invasive Therapeutics (CMIT) California NanoSystems Institute, UCLA.
6. **Dr. Sajanlal R. Panikkanvalappil** has joined as Scientist II, Dana-Farber Cancer Institute/Harvard Medical School, 27 DryDock Avenue, Floor 4, Room 66U, Boston, MA 02210, USA.
7. **Dr. Gopi Ragupathy** has received the Lady Davis Postdoctoral fellow for 2019-20 at The Institute of Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, Givat Ram, Jerusalem, 91904, Israel.
8. **Dr. Venkataramanan Mahalingam** has got promoted to Professor, Department of Chemistry, IISER Kolkata, India.
9. **Dr. Amitava Srimany** has joined as Assistant Scientist at Centre of Excellence in Rice Value Addition, International Rice Research Institute - South Asia Regional Centre, Varanasi, Uttar Pradesh, India.
10. **Dr. Swathy Ravindran** has joined as Assistant Manager in R&D labs of Eureka Forbes Ltd., Bangalore, India.
11. **Dr. Udayabhaskararao Thumu** has got appointed as Professor in Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China.
12. **Dr. N. Sandhyarani** has got promoted to Professor, NIT Calicut.
13. **Dr. G. Velmurugan** has joined as Scientist at KMCH Research Foundation, Kovai Medical Center & Hospital, Coimbatore, India.

Ongoing Research Grants

1. Understanding surface properties of atomically engineered cluster-assembled solids, SPARC project with Robin Ras and Olli Ikkala, Aalto, Finland with Tiju Thomas, IITM, Rs. 66. 3 lakhs (principal investigator).
2. VAJRA project with Pulickel M. Ajayan, Rice University, Rs. 9.75 lakhs.
3. Capacitive deionization technology for the extraction of germanium and selenium: two elements of strategic relevance, Ministry of Mines, Rs. 30 lakhs (principal investigator).
4. SUTRAM for EASY water, DST, Rs. 890 lakhs (co-principal investigator with Prof. Ligy Philip).
5. Affordable clean water in arsenic affected areas, Millennium Alliance, 2018-2020, Rs. 50 lakhs (principal investigator along with Ramesh Kumar).
6. Thematic project on frontiers of nanoscience and nanotechnology (TPF), DST, Rs. 541 lakhs (principal investigator).
7. Dust free glass, Saint-Gobain Resaerch India Ltd. Rs. 36 lakhs (principal investigator with Prof. R. Nagarajan).
8. Arsenic free South 24 Parganas district, DST, Rs. 374.88 lakhs (principal investigator)
9. Cluster composite nanofibre membranes for rapid, ultra-trace detection of waterborne contaminants, India-German Science and Technology Forum, Total funds Rs. 191.324 lakhs (principal investigator along with InnoNano Research Pvt. Ltd.).

Others such as JC Bose Fellowship, R&D Awards, technology development and instrument maintenance activities are managed as projects.

Grants Sanctioned in 2019

1. Identification and investigation of efficacy of potential biochemical molecules for extraction of gold and other noble metals from tailings and waste sources, Ministry of Mines, Rs. 34.64 lakhs (principal investigator).
2. Chemical transformations of clathrate hydrates under ultra-high vacuum, DST, Rs. 76.5 lakhs (principal investigator).

Visitors - 2019

1. Dr. Saji George, Associate Professor, McGill University, Canada, on June 20, 2019.
2. Mr. Sivaram Dhara (IITM alumni), President, Global Catalyst KK, Tokyo, Japan, on August 29, 2019.
3. Prof. Umesh Waghmare, Jawaharlal Nehru Center for Advanced Scientific Research (JNCASR), Bangalore, India.
4. Mr. Dhandapani, Indian Institute of Science and Education and Research (IISER) Berhampur, Odisha.
5. American Chemical Society (ACS) Team on July 15, 2019:
    - Professor Phil Savage, Penn State University, USA, Editor in Chief, Industrial and Engineering Chemistry Research
    - Professor Chris Jones, Georgia Tech University, USA, Editor in Chief, ACS Catalysis
    - Dr. Deeksha Gupta, Associate Director, India (Editorial, Society Programs and Services)
    - Dr. Sanchita Mukherjee, Development Editor, Editorial Outreach
    - Dr. Ajay Jha, Development Editor, ACS Omega
    - Ms. Deiji Deori, Associate, ACS Membership Outreach
6. Dr. Frank Brigano, Marmon Water, West Haven, Connecticut, USA, and Mr. Nishant Kulkarni, Filtrex Technologies, Bengaluru, India, on August 5, 2019.
7. Mr. S. Nagarajan, IAS, Director, Entrepreneurship Development and Innovation Institute, Chennai, Tamil Nadu, India, on July 23, 2019.
8. Ms. Meenakshi Raman & Mr. K. K. Raman (IITM alumni), Advisor, ICCW, on July 25, 2019.
9. Mr. Vikram Gulecha, Founder, OCEO Water, on August 13, 2019.
10. Ms. Shanta Sheela Nair, Retired IAS, and Mr. Sekar Raghavan, Director, Rain Center, Adyar, Chennai, on August 16, 2019.
11. Mr. T. M. Nagarajan, Vice President, Ms. Sugata Kadam and Mr. Barath Vasudevan, Territory Sales Manager, Wipro Water, Navi Mumbai, India, on August 19, 2019.
12. Students from SSN College, Chennai, India, on September 20, 2019.

13. Dr. Sabu Thomas, Vice-Chancellor, MG University, Kottayam, India, on September 23, 2019.
14. Ms. Paula Mariwala & Mr. Ravi Mariwala, Investor & Water Industrialist, along with Dr. Hadas and Dr. Rajnish Kumar, IITM, on October 4, 2019.
15. Prof A. M. Kannan, Arizona State University, Tempe, Arizona, US, on October 10, 2019.
16. Dr. Rakesh Kumar Sharma, Department of Chemistry, IIT-Jodhpur, Rajasthan, India, on September 20, 2019.
17. Ms. Divya Yachamaneni, Chief Executive Officer, and Mr. Abhishek Vaidianathan, Technical Head from Naandi Community Water Services (NCWS), on September 16, 2019.
18. Dr. Stefan Diederich, RWTH Aachen University, Germany, with Ms. Rupa Pandit, International Relations, IITM Research Park, on October 22, 2019.
19. Dr. Narasimha M. Rao, Chief Digital Officer, Buckman International, and Dr. Divagar Lakshmanan, Digital Services Innovation Manager, Buckman Laboratories India, on November 4, 2019.
20. Mr. Sharukh R. Taraporewala, Senior Vice President - Corporate Social Responsibility, Yes Bank, Ms. Vani Saxena from BSR & Associates, and Mr. Vipul Jain, Consultant at KPMG India, Mumbai, India, on November 6, 2019.
21. Mr. Perola Wictor, Mr. Henrik Lindgren, from Baxter, Sweden along with Mr. Guru Honawad, Mr. Ganesh Chandan Gangadharan, Mr. Nothing Kandiyil, from Baxter Bangalore, on November 7, 2019.
22. Dr Nonappa, from Aalto University, Finland, on November 12, 2019.
23. Mr. Avinash Thakur, CEO, and Prof. Dheeraj G. Agrawal from D Y Patil University, on November 15, 2019.
24. Mr. Vikram Nanwani and Mr. Shailesh Devani from Xylem, on November 18, 2019.
25. Mr. M. G. Madan Kumar, DCS Techno Services and Mr. Ashish, InnoDI, on November 21, 2019.
26. Dr. Bhaskar Harita, with Mr. Subramanium, on November 21, 2019.
27. IOCL team, on November 22, 2019.
28. Professor Rahul Nair and colleagues from Manchester, along with Dr. Pradeep, on November 22, 2019.
29. Mr. Gurjinder Singh and Mr. Devinder Bansal, on November 27, 2019.
30. Ms. Divya Yachamaneni, CEO, and Mr. Abhishek Vaidianathan, NCWS, on November 28, 2019.
31. Visitors from Kerala, from various Universities, on November 28, 2019.

32. Members from the interactive session on redesigning RO water purification systems, on November 29, 2019.
33. Dr. Mohammed Sherafatmand, Hydroleap, Singapore, on November 30, 2019.
34. Dr. Abdullah Alodhayb and Dr. Hamad Albrithen from King Saudi University, on December 10, 2019.
35. Mr. Harinder S Sikka - director of the Piramal conglomerate, on December 3, 2019.

Visiting Faculty

- Prof. R. Graham Cooks of Purdue University and a Distinguished Professor of IITM visited our lab during December 6-12, 2019.
- Prof. Thomas Thundat of University at Buffalo and a Distinguished Professor of IITM visited our lab during December 7-13, 2019.

Service 2019

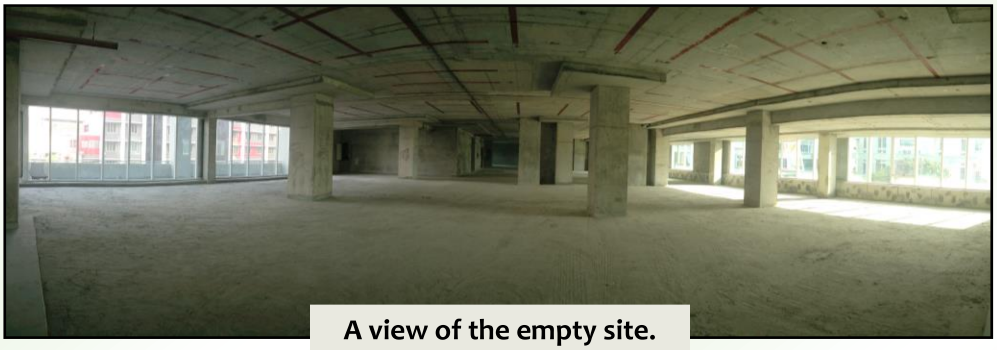
1. Member, Editorial Board of the journals, Chemistry of Materials, ACS Nano, Scientific Reports (Nature Group), Nanoscale, Particle, Surface Innovations, International Journal of Water and Wastewater Treatment, Chemistry of Materials and Nanoscale Advances.
2. Prof. Pradeep was appointed by Ministry of Jal Shakti as a member of the 'Technical committee for examination and use of innovations and technologies in drinking water and sanitation sector'.
3. Associate Editor of the journal, ACS Sustainable Chemistry & Engineering.
4. Visiting Professor, Manipal University, 2018 onwards.
5. Member, Program advisory committee of inorganic and physical chemistry, DST, 2018 onwards.
6. Member, Industry relevant R & D expert committee, DST, 2018 onwards.
7. Member, DST JSPS committee.
8. Member, Governing Council, Technology Information, Forecasting & Assessment Council (TIFAC).

9. Member, Research Advisory Council, Manipal Academy of Higher Education, Manipal.
10. Research Advisory Board, Pandit Deendayal Petroleum University.
11. Member, Research Advisory Committee, IIT Ropar.
12. Co-opted Member, Program Advisory Committee of SERB-SUPRA.
13. Member, Technical Committee for examination and use of innovations and technologies in drinking water and sanitation sector, Department of Drinking Water and Sanitation, Ministry of Jal Shakti, 2019-2024.

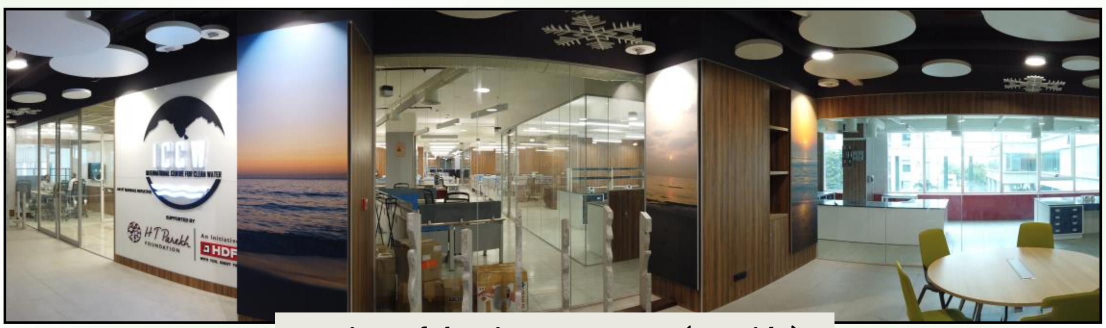
One day discussion meeting on sensors with various eminent scientists of India and abroad, organized at IIT Madras (ICCW) on December 10, 2019.

A New Initiative - ICCW

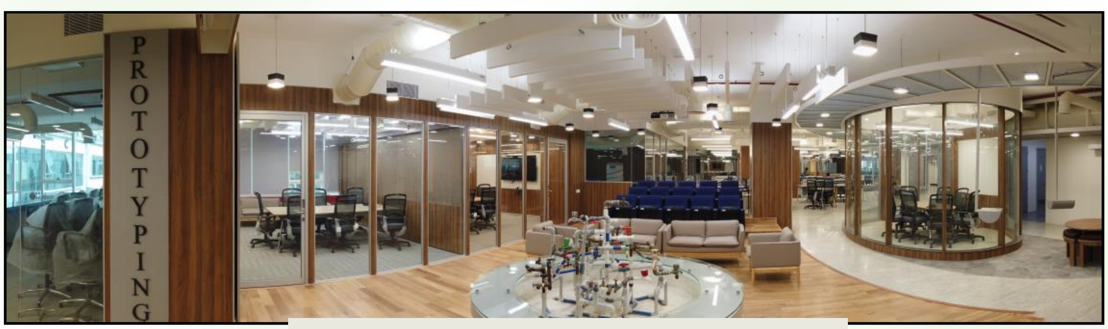
A new initiative to build the International Centre for Clean Water (ICCW) had begun in 2018. Inauguration of ICCW took place on World Earth Day, April 22, 2019. It was inaugurated by Mr Deepak Parekh, Chairman HDFC, and Professor Bhaskar Ramamurthi, Director, along with Professor T Pradeep and a group of dignitaries. ICCW aims to be one of the best ecosystems of its kind in the world to ideate, nurture and translate disruptive technologies for sustainable clean water, with collective participation of the global community, delivering first rate science, leading to wealth and social good simultaneously, in the process building water professionals of tomorrow. Glimpses of the empty site and the furnished sites are below.



A view of the empty site.



A view of the site at present. (Outside)



An inside view of the site at present.

Incubation

VayuJal Technologies Private Limited, has received initial funding needed for its activities. VayuJal has now built 7 units and has provided more than 85000 litres of drinking water from air.

InnoDI Water Technologies Private Limited wins the IMPACT MAKER AWARD AT XYNTEO EXCHANGE/INDIA2022, for the CDI technology. Over 100+ CDI units have been installed in India.

AquEasy Innovations Private Limited has been established to create efficient water transport solutions. Its prototypes have been tested.

Vayujal exhibited at L&T, during an event for World Environment Week.

Hydromaterials Private Limited is run by experienced water professionals with participation of IIT Madras and Prof. T. Pradeep. Company specializes in development and implementation of advanced technologies such as affordable technology for salt removal from water.

Arsenic and iron removal technologies are now delivering clean water to 900,000 people each day.

In Punjab, the community purifier has crossed accumulative water output of 10 million liters each day.

All are co-owned by IIT Madras.

Popular Science (Media Reports)

Big Breakthrough! IIT Madras degrades plastic in eco-friendly way

FINANCIAL EXPRESS — Read to Lead

By: Ribhu Mishra
Published: September 16, 2019 6:10:11 PM

Arjun Ram Meghwal urged the Indian Institute of Technology, Madras to invent an alternative to th single-use plastic.

IIT Madras organised a Conclave on September 15 of which the MoS Arjun Ram Meghwal was Keynote speake

THE HINDU

SCIENCE

IIT Madras: Breath humidity sensors for wearable electronics

R. Prasad

It detects ethanol, acetone in oral breath of alcoholics, diabetics, respectively

SCIENCE

Silver atoms of nanoparticles are mobile, IIT Madras team finds

THE HINDU

The rapid exchange of silver atoms in solution might have implications in real-life situations

விகடன்

செய்திகள் | இதழ்கள் | விகடன் ஸ்பெஷல் | சினிமா

Published: 15 Nov 2019 11 AM Updated: 15 Nov 2019 11 AM

'பிளாஸ்டிக்கும் கரையும்!'

PTFE பிளாஸ்டிக்கை சிதைவுறச் செய்ய முடியும் என்று கண்டுபிடித்துள்ளது, ஐஐடி மெட்ராஸைச் சேர்ந்த வேதியியல் குழு!

பேராசிரியர் பிரதீப் மற்றும் மாணவர் அஜித் நாக்

Tuesday, January 8, 2019 — DECCAN HERALD 9

Nation

Origin of life: Hydrates in interstellar space may throw new light

Kalyan Ray

NEW DELHI, DHNS: Gas hydrates, a potential source of energy on Earth, may be present in abundance in interstellar space, suggests new research by scientists at IIT-Madras.

The startling discovery may open up a completely new window to look at a fundamental query in science – how life began on Earth.

Hydrates or clathrate hydrates are molecules like methane, carbon dioxide, etc., trapped in well-defined cages of water molecules forming crystalline solids.

They are formed at places with high pressures and low temperatures such as the ocean floor. They are also found in the glaciers of Siberia.

Such hydrates, especially that of methane, are thought to be the future sources of fuel. Several countries, including India, have government-funded programmes to explore and harvest the hydrates lying hundreds of metres below the sea level.

Researchers from IIT-Madras formed such hydrates in a vacuum, 1,000 billion times below the atmospheric pressure called ultra-high vacuum and temperature close to -263 degree Celsius (10 Kelvin). These are the conditions present in deep space. "The findings open up the possibility of having entirely new chemistry in space. All small molecules in space should now be looked at as caged (hydrate) entity and reaction between two such molecules can give rise to new chemistry," Thalappil Pradeep, lead author of the study and a professor of chemistry at IIT-Madras, told *DH*.

The researchers created an environment in the laboratory to simulate the condition found in interstellar space.

"Since cages of water are not expected to form under such conditions, nothing surprising was seen initially. Then I thought why not wait for days and keep observing the changes; after all ice and methane have been sitting in the space for millions of years. The excitement happened after three days when new features started coming. Then of course, several experiments were done under controlled conditions," Pradeep said.

The research has been published on the December 7 issue of the journal Proceedings of the National Academy of Sciences. "The findings may have an impact on both astronomy and chemistry," the researchers reported.

While hydrates are being chased on the Earth as a futuristic source of energy, Pradeep ruled out any such use for an interstellar spacecraft with the current level of technology. Also, the space being too vast, it would be impossible to know where such hydrates can be found. A far more exciting option would be to search for new chemistry and tailor the space-probe instruments like spectroscopes to look for those signatures as there is still no answer as to how molecules formed in space and life came into being on Earth, he said.

(From left) Prof Rajnish Kumar, Jyotirmoy Ghosh and Prof Pradeep around their ultrahigh vacuum instrument.

THE HINDU BusinessLine

Mimicking space, IIT-M scientists cage methane in water

May be a crucible for unique chemical reactions that led to origin of life

(From left) Prof Rajnish Kumar, Jyotirmoy Ghosh and Prof T Pradeep around their ultra-high vacuum instrument

TECHNOLOGY

HOME | NEWS | APPS | SCIENCE AND FUTURE | #SUSTAINABILITY

HOME > TECHNOLOGY > NEWS > IIT Madras Team Finds Greener Way To Break Down Plastic, But Has Bad News On Plastic C

IIT Madras Team Finds Greener Way To Break Down Plastic, But Has Bad News On Plastic Cookware

Gwyn D'Mello | Updated: Sep 17, 2019, 13:17 IST

Professor Thalappil Pradeepand his students from the Chemistry Department at IIT Madras, have been working on something for a while. About three years ago, they noticed that silver dissolves in a glucose solution when heated to 70-degrees celsius. So they decided to experiment with that phenomenon, to see if it would also work with plastics.

NDTV

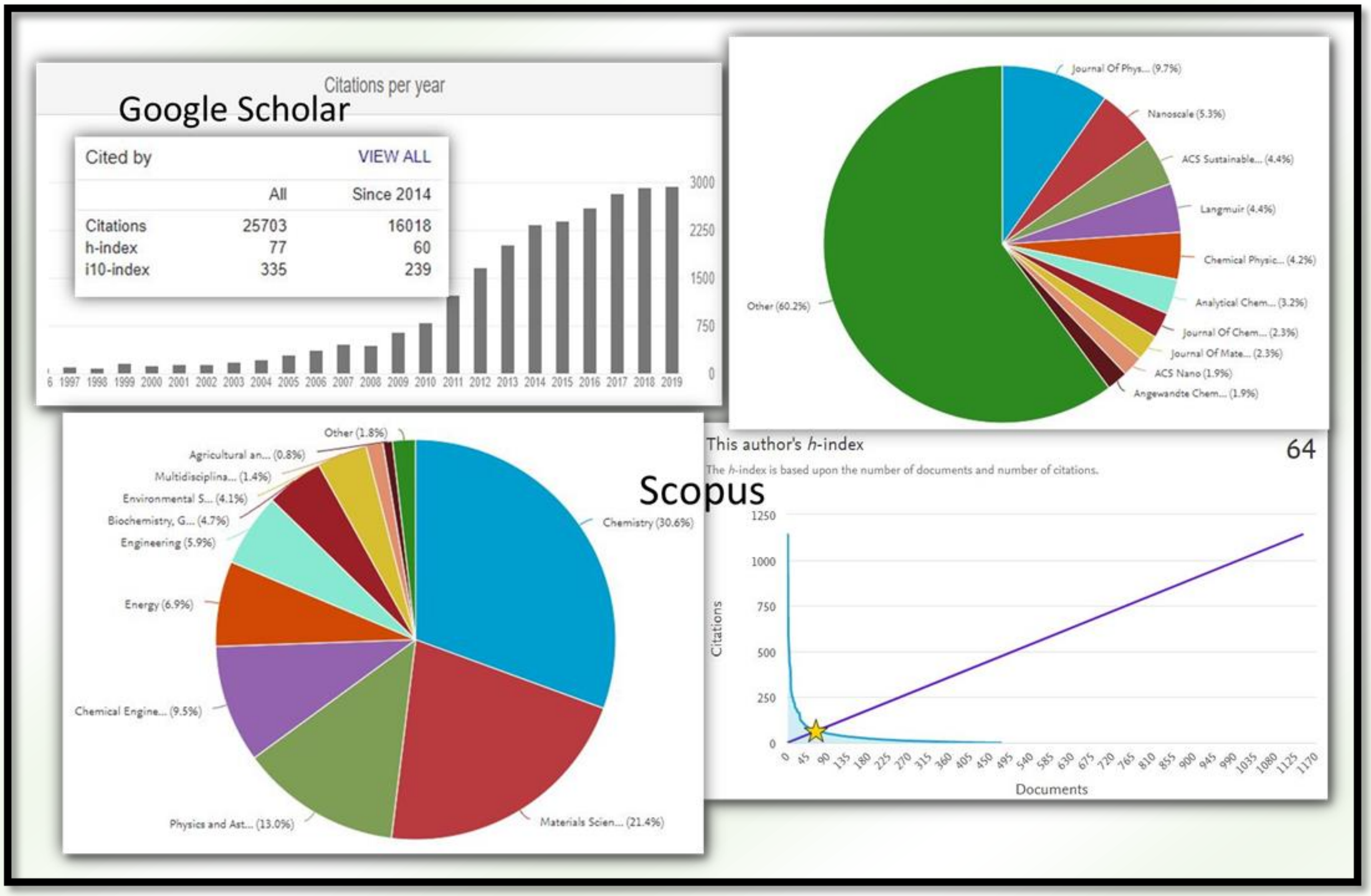
Home > Science > Methane Can Exist In Interstellar Atmosphere: IIT Madras Researchers

Methane Can Exist In Interstellar Atmosphere: IIT Madras Researchers

Gas hydrates such as methane hydrate can release combustible gases which could be used as a fuel, the IIT-M said.

Science | Indo-Asian News Service | Updated: January 08, 2019 06:05 IST

Publication Analysis



Sources:

1. Scopus, *visited on December 30, 2019.*
2. Google Scholar, *visited on December 30, 2019.*

Pradeep Research Group Year : 2019 Academic Output

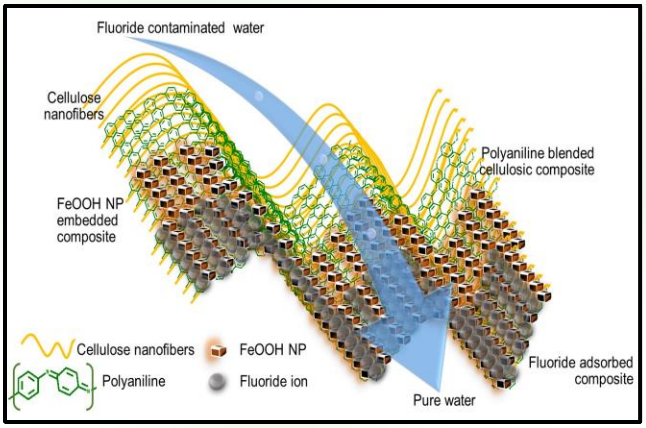
ABSTRACTS AT A GLANCE

Nanocellulose reinforced organo-inorganic nanocomposite for synergistic and affordable defluoridation of water and an evaluation of its sustainability metrics

Sritama Mukherjee, Haritha Ramireddy, Avijit Baidya, A. K. Amala, Chennu Sudhakar, Biswajit Mondal, Ligy Philip, and Thalappil Pradeep*

ACS Sustain. Chem. Eng., (2020) 8, 139-147. (DOI: 10.1021/acssuschemeng.9b04822) (ARTICLE ASAP).

Abstract: Fluoride (F-) is one of the common naturally occurring anions present in groundwater worldwide that may be beneficial or detrimental depending on the total amount ingested and the duration of exposure. Among all the remediation techniques, adsorption using nanomaterials show superior efficiency and the process can be eco-friendly and economical. We report cellulose nanofiber-polyaniline templated ferrihydrite (CNPFH) nanocomposite synthesized by a green one-pot process where the iron precursor not only acts as an oxidant for polymerization of aniline to give emaraldine base-emaraldine salt (EB-ES) form of polyaniline (PANI), but also forms 2-line ferrihydrite (FeOOH) nanoparticles in-situ. These nanoparticles get embedded into the cellulose-PANI blend to give a granular nanocomposite having double action sites for adsorption and robustness which also prevent nanoparticle leaching. Doped PANI and FeOOH act as synergistic adsorption sites for F- removal which results in an enhanced uptake capacity. The materials' adsorption mechanism and removal performance have been evaluated by diverse analytical techniques. The investigations concluded that the material is suitable to be used as adsorption media in the form of simple cartridges for gravity-fed water purification. In addition, the impact of such materials on the environment has been assessed by evaluating the relevant sustainability metrics and socio-economic parameters.

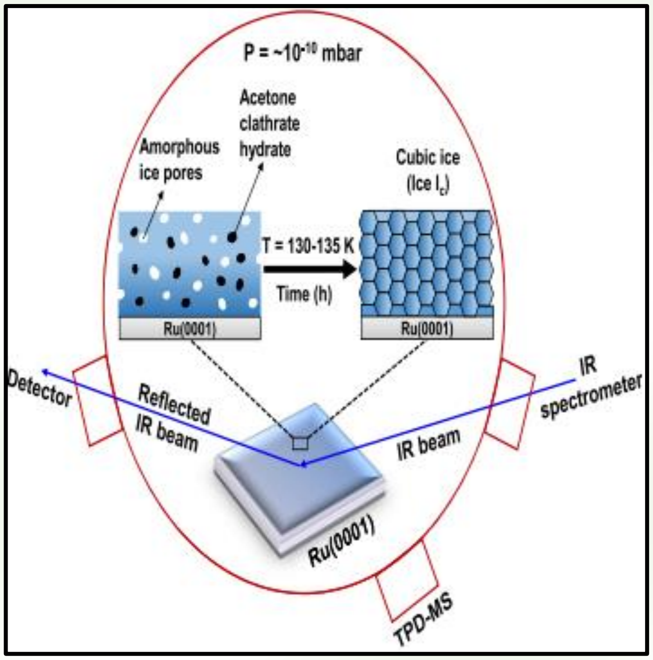


Formation of Cubic Ice via Clathrate Hydrate, Prepared in Ultrahigh Vacuum under Cryogenic Conditions

Jyotirmoy Ghosh, Radha Gobinda Bhuin, Gaurav Vishwakarma, and T. Pradeep*

J. Phys. Chem. Lett. (2020) 11, 26-32 (DOI: 10.1021/acs.jpclett.9b03063)

Abstract: Cubic ice (ice I_c) is a crystalline phase of solid water, which exists in the earth's atmosphere and extraterrestrial environments. We provide experimental evidence that dissociation of acetone clathrate hydrate (CH) makes ice I_c in ultrahigh vacuum (UHV) at 130–135 K. In this process, we find that crystallization of ice I_c occurs below its normal crystallization temperature. Time-dependent reflection absorption infrared spectroscopy (RAIRS) and reflection high-energy electron diffraction (RHEED) were utilized to confirm the formation of ice I_c. Associated crystallization kinetics and activation energy (E_a) for the process were evaluated. We suggest that enhanced mobility or diffusion of water molecules during acetone hydrate dissociation enabled crystallization. Moreover, this finding implied that CHs might exist in extreme low-pressure environments present in comets. These hydrates, subjected to prolonged thermal annealing, transform into ice I_c. This unique process of crystallization hints at a possible mechanistic route for the formation of ice I_c in comets.

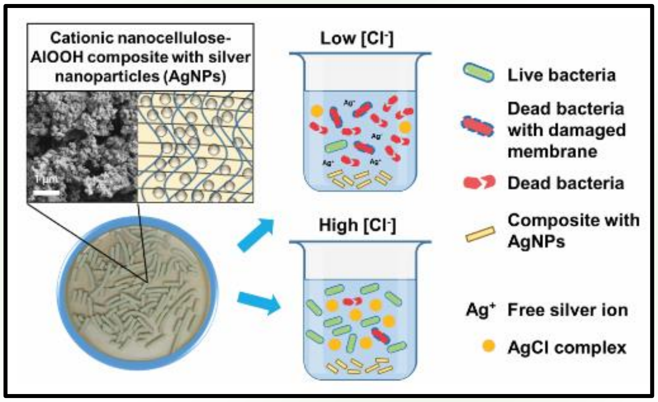


Effects of Chloride Concentration on the Water Disinfection Performance of Silver Containing Nanocellulose-based Composites

Janika Lehtonen, Jukka Hassinen, Riina Honkanen, Avula Anil Kumar, Heli Viskari, Anu Kettunen, Nikolaos Pahimanolis, Thalappil Pradeep, Orlando J. Rojas, and Olli Ikkala

Sci. Rep. 9, (2019) 19505 (DOI: 10.1038/s41598-019-56009-6)

The availability of microbially-safe drinking water is a challenge in many developing regions. Due to the well-known antibacterial effect of silver ions, materials used for their controlled release have been widely studied for point-of-use water disinfection. However, even if it is in principle known that chloride anions can suppress the antibacterial efficiency of silver, the majority of previous studies, surprisingly, have not focused on chloride concentrations relevant for freshwaters and thus for practical applications. Here, we prepared low-cost nanocellulose-aluminum oxyhydroxide nanocomposites functionalized with silver nanoparticles. Field samples obtained from Chennai, India were used as a guideline for choosing relevant chloride concentrations for the antibacterial studies, i.e., 10, 90 and 290 ppm. The antibacterial performance of the material against Escherichia coli and Bacillus subtilis was demonstrated and the influence of chloride concentration on the antibacterial effect was studied with E. coli. A 1 h contact time led to bacterial reductions of 5.6 log 10 , 2.9 log 10 , and 2.2 log 10 , respectively. This indicates that an increase of chloride concentration leads to a substantial reduction of antibacterial efficiency, even within chloride concentrations found in freshwaters. This work enables further insights for designing freshwater purification systems that utilize silver-releasing materials.

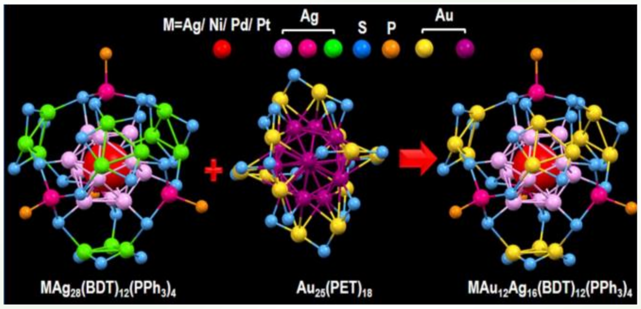


Intercluster Reactions Resulting in Silver-rich Trimetallic Nanoclusters

Esma Khatun, Papri Chakraborty, Betsy Jacob, Ganesan Paramasivam, Mohammad Bodiuzzaman, Wakeel Dar, and, Thalappil Pradeep*

Chem. Mater., 2019 (Just Accepted) (DOI: 10.1021/acs.chemmater.9b04530)

Abstract: Herein, we present an intercluster reaction leading to new trimetallic nanoclusters (NCs) using bimetallic and monometallic NCs as reactants. Dithiol protected bimetallic $MAg_{28}(BDT)_{12}(PPh_3)_4$ (BDT= 1, 3-benzenedithiol and M= Ni, Pd or Pt) and monothiol protected $Au_{25}(PET)_{18}$ (PET= 2-phenylethanethiol) were used as model NCs. A mixture of trimetallic $MAu_xAg_{28-x}(BDT)_{12}(PPh_3)_4$ (x = 1-12) and bimetallic $Ag_xAu_{25-x}(PET)_{18}$ (x = 1-7) NCs were formed during the reaction as understood from time-dependent electrospray ionization mass spectrometry (ESI MS). Detailed studies of inter-cluster reaction between $Ag_{29}(BDT)_{12}(PPh_3)_4$ and $Au_{25}(PET)_{18}$ were also performed. Although both $MAg_{28}(BDT)_{12}(PPh_3)_4$ (M = Ag, Ni, Pd or Pt) and $Au_{25}(PET)_{18}$ contain 13 atoms icosahedral core, only a maximum of 12 Au doped NCs were formed for the former as major product and not the 13 Au doped one, unlike the previous reports of intercluster reaction. The transfer of Ni, Pd or Pt atom from the centre of icosahedron of $MAg_{28}(BDT)_{12}(PPh_3)_4$ to $Au_{25}(PET)_{18}$ was not observed which suggests that the central atom is not involved in the reaction. Density functional theory (DFT) calculations were performed to know structures and properties of the formed NCs. This study demonstrates the use of inter-cluster reaction as an effective synthetic protocol to make multimetallic alloy NCs.

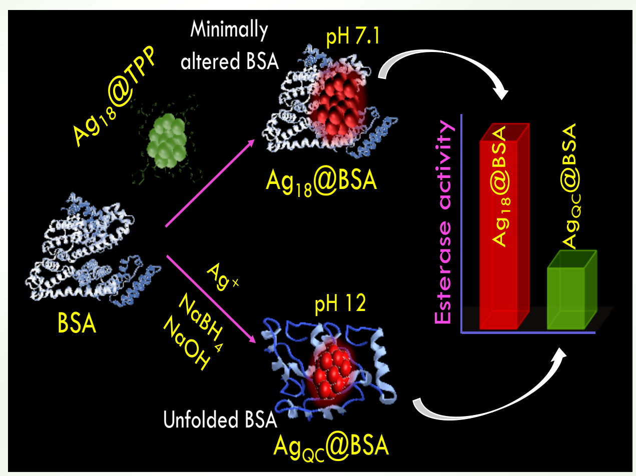


Internalization of a preformed atomically precise silver cluster in proteins by multistep events and emergence of luminescent counterparts retaining bioactivity

Debasmita Ghosh, Mohammad Bodiuzzaman, Anirban Som, Sebastian Raja, Ananya Baksi, Atanu Ghosh, Jyotirmoy Ghosh, Akshayaa Ganesh, Priyanka Samji, Sundarasamy Mahalingam, Devarajan Karunagaran, and, Thalappil Pradeep

J. Phys. Chem. C (2019) 123, 48, 29408-29417. (DOI: 10.1021/acs.jpcc.9b07765)

Abstract: A new synthetic protocol is introduced which preserves the secondary structure of protecting proteins encapsulating a luminescent atomically precise silver cluster. This was achieved by using a preformed triphenylphosphine (TPP) protected silver cluster as the precursor forming bovine serum albumin (BSA) and human serum albumin (HSA) protected Ag_{18} clusters. This is the first example of the formation of luminescent protein protected clusters in a neutral medium, without using any reducing agent, which results in minimal alteration of the protein structure during cluster growth. The cluster formed showed exceptional stability, unlike other silver clusters of this class. The formation of these red luminescent clusters was visualized by UV-vis and photoluminescence spectroscopy. The identification of Ag_{18} core was made through matrix assisted laser desorption ionization mass spectrometry (MALDI MS) and a plausible mechanism of the formation was identified by monitoring the systematic growth of the cluster core by time-dependent MALDI MS experiments and electrospray ionization mass spectrometry (ESI MS) of the reaction mixture. The cluster was successfully employed as a luminescent probe for cancer cell imaging. Retention of protein conformation in the clusters was confirmed through circular dichroism (CD) spectroscopy and the same was reflected in the retention of 89% of the esterase activity of BSA in the Ag_{18}@BSA clusters synthesized by this method, compared to only 28.7% for AgQC@BSA clusters synthesized using previous protocols, conducted in basic medium.



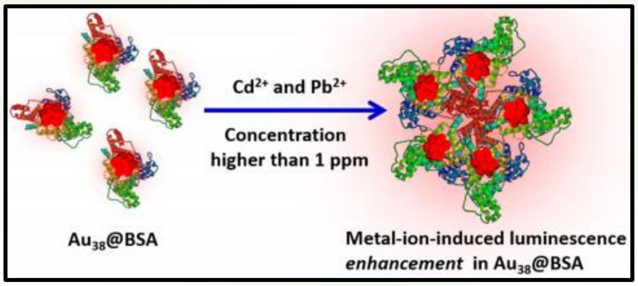
Metal ion-induced luminescence enhancement in protein protected gold clusters

Jyoti Mohanty, Kamalesh Chaudhari, Chennu Sudhakar, and T. Pradeep*

J. Phys. Chem. C, 123 (2019) 28969−28976 (DOI: 10.1021/acs.jpcc.9b07370)

Abstract: We probed the interaction between Au_{38}@BSA and various heavy metal ions using luminescence spectroscopy. Interestingly, Au_{38}@BSA showed luminescence enhancement upon interaction with Cd^{2+} and Pb^{2+} at concentrations higher than 1 ppm, due to the formation of cluster aggregates. Such aggregates were detected by dynamic light scattering (DLS) and high resolution electron microscopy (HRTEM) studies. Luminescence enhancement of Au_{38}@BSA

in the presence of Cd^{2+} was due to the interaction of Cd^{2+} with the cluster core, while Pb^{2+}-induced luminescence enhancement was due to BSA-Pb^{2+} interaction. Observations were further supported by X-ray photoelectron spectroscopy (XPS) studies. This kind of phenomenon has been observed in protein protected clusters for the first time. We believe that such metal-ion-induced luminescence enhancement can be used to synthesize cluster systems with enhanced optical properties and different ion–cluster interactions can be used to develop metal ion sensors using Au_{38}@BSA.

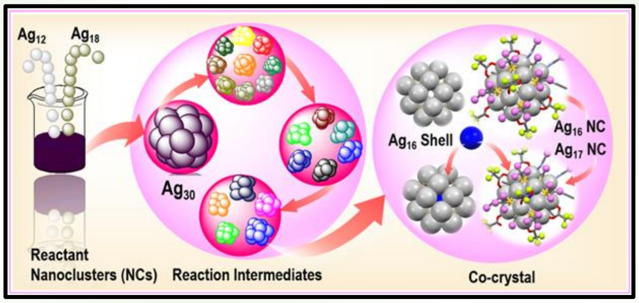


Interparticle reactions between silver nanoclusters leading to product co-crystals by selective co-crystallization

Wakeel Ahmed Dar, Mohammad Bodiuzzaman, Debasmita Ghosh, Ganesan Paramasivam, Esma Khatun, Korath Sugi, and T. Pradeep*

ACS Nano, 13 (2019) 13365−13373 (DOI: 10.1021/acsnano.9b06740)

Abstract: We present an example of an interparticle reaction between atomically precise nanoclusters (NCs) of the same metal, resulting in entirely different clusters. In detail, the clusters $[Ag_{12}(TBT)_8(TFA)_5(CH_3CN)]^+$ (TBT = tert-butylthiolate, TFA = trifluoroacetate, CH_3CN = acetonitrile) and $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ (TPP = triphenylphosphine) abbreviated as Ag_{12} and Ag_{18}, respectively, react leading to $[Ag_{16}(TBT)_8(TFA)_7(CH_3CN)_3Cl]^+$ and $[Ag_{17}(TBT)_8(TFA)_7(CH_3CN)_3Cl]^+$, abbreviated as Ag_{16} and Ag_{17}, respectively. The two product NCs crystallize together as both possess the same metal chalcogenolate shell, composed of $Ag_{16}S_8$, making them indistinguishable. The occupancies of Ag_{16} and Ag_{17} are 66.66 and 33.33%, respectively, in a single crystal. Electrospray ionization mass spectrometry (ESI MS) of the reaction product and a dissolved crystal show the population of Ag_{16} and Ag_{17} NCs to be in a 1:1 and 2:1 ratio, respectively. This suggests selective crystallization in the cocrystal. Time-dependent ESI MS was employed to understand the formation of product clusters by monitoring the reaction intermediates formed in the course of the reaction. We present an unprecedented growth mechanism for the formation of silver NCs mediated by silver thiolate intermediates.

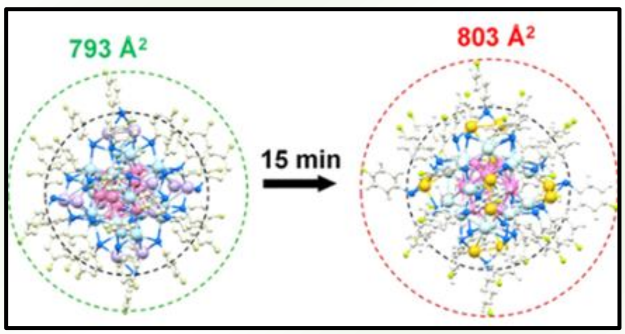


Nano-Gymnastics: Visualisation of inter-cluster reactions by high resolution trapped ion mobility mass spectrometry

Ananya Baksi, Erik Schneider, Patrick Weis, Kumaranchira Krishnadas, Debasmita Ghosh, Horst Hahn*, T. Pradeep*, and, Manfred Kappes*

J. Phys. Chem. C, 121 (2019) 13421−13427 (DOI: 10.1021/acs.jpcc.9b08686)

Abstract: Although single-crystal X-ray diffraction is a proven technique to determine the structure of monolayer-protected coinage metal clusters in solid state, it is not readily applicable to the characterization of such cluster structures in solution. The complexity of the characterization problem increases further when intercluster reactions are studied, in which two reactive cluster ions interact to form final products using a sequence of structural changes involving exchange of metal atoms and ligands. Here, we present the first time-resolved structural study of such processes which occur when solutions of $[TOA]^{+}[Au_{25}(PET)_{18}]^{-}$ and $[PPh_4]_4^{4+}[Ag_{44}(FTP)_{30}]^{4-}$ react upon mixing (PET: phenylethanethiolate; FTP: 4-fluorothiophenolate; and TOA: tetraoctylammonium ion). This is achieved using high-resolution trapped ion mobility mass spectrometry (TIMS). Specifically, we have used electrospray transfer to the TIMS apparatus followed by ion mobility measurements to probe the time-dependent structure of mass-selected $Au_xAg_{44-x}(FTP)_{30}^{4-}$ (x = 0–12) exchange products, with limited FTP for PET exchanges, formed in the reaction medium. Over the roughly 40 min reaction time before equilibration, with a product distribution centered around $Au_{12}Ag_{32}(FTP)_{30}^{4-}$, we observe intermediate species, $Au_xAg_{44-x}(FTP)_{30}^{4-}$, whose collision cross sections (CCSs) at a given x increase first relative to that of the $Ag_{44}(FTP)_{30}^{4-}$ parent and decrease subsequently. We attribute this to an energy-driven migration of the incorporated Au atoms from the ligated "staples" at the cluster surface to its icosahedral core. Upon collisional heating of $Au_xAg_{44-x}(FTP)_{30}^{4-}$, analogous back-migration of the heavier Au atoms from the core to the staples was observed in tandem mass spectrometry. To support our experimental observations, several isomeric structures (with all ligands) were calculated using density functional theory, and their CCS values were modeled using trajectory method calculations.

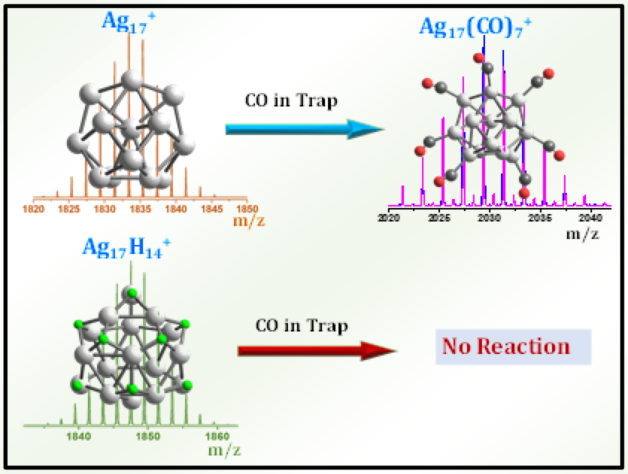


Mechanistic elucidation of the structure and reactivity of bare and hydride protected Ag_{17}^{+} clusters

Ananya Baksi, Madhuri Jash, Soumabha Bag, Sathish Mudedla, Mohammad Bodiuzzaman, Debasmita Ghosh, Ganesan Paramasivam, Venkatesan Subramanian, and T. Pradeep*

J. Phys. Chem. C, 123 (2019) 28494-28501 (DOI: 10.1021/acs.jpcc.9b09465)

Abstract: We report an approach to create bare silver cluster Ag_{17}^{+} and hydride-rich $Ag_{17}H_{14}^{+}$ separately, as pure species uncontaminated with other entities, in the gas phase starting from a solution-phase monolayer-protected cluster, $Ag_{18}H_{16}(PPh_3)_{10}^{2+}$. These clusters can be synthesized just by applying a small potential on the cone of the mass spectrometer, during electrospray mass spectral analysis. Both the clusters were trapped and reacted with reactive gases like carbon monoxide and acetylene. Unusual products like $Ag_{17}(CO)_7^{+}$ were observed when Ag_{17}^{+} was reacted with CO in the trap. No intermediate species were found. Transfer of H from acetylene to the cluster during reaction was observed, which later reduced acetylene. All of the structures formed were calculated using density functional theory and show interesting facts about the composition of the products and the mechanism of their formation. Most of the structures were observed for the first time.

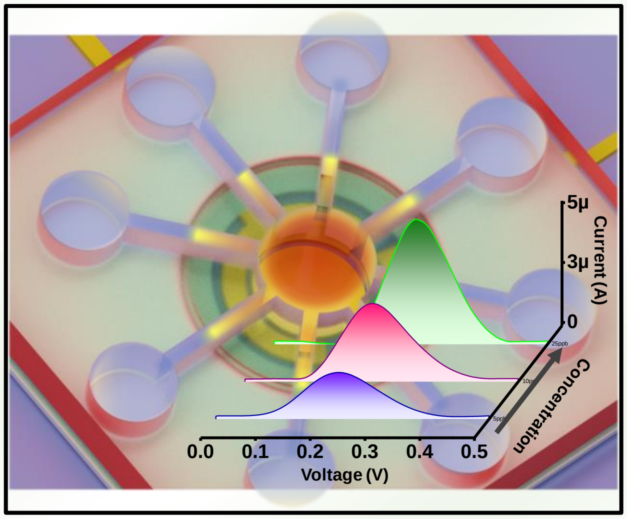


Enhancing the sensitivity of point-of-use electrochemical microfluidic sensors by ion concentration polarisation - A case study on Arsenic

Vidhya Subramania, Sangjun Lee, Sanjoy Jena, Sourav Kanti Jana, Debdutta Ray, Sung Jae Kim, and T. Pradeep*

Sensors & Actuators: B. Chemical 304 (2020) 127340 (DOI: 10.1016/j.snb.2019.127340)

Abstract: Point of use (POU) sensors are extremely relevant, being capable of providing fast and reliable analysis in remote and resource-limited settings. Of all the diverse techniques utilised for POU sensors, a combination of electrochemistry and microfluidics may have the greatest potential towards quantitative assessment of heavy metal ions. The major challenge in combining these for sensing applications lies in the complexity of fabricating integrated devices and the insufficient quantity of analytes in the sample volume. To address these issues, we have developed a radial microfluidic device capable of electrokinetic preconcentration by ion concentration polarization (ICP) and integrated it with electroactive surfaces. The proposed sensor is the first demonstration of concentration of heavy metal ions by ICP and its quantitative assessment by voltammetry. Utilising the integrated sensor, we have shown the sensing of As^{3+} down to 1 ppb by linear sweep voltammetry with ~40 µL of sample. The sensor was also tested successfully for



sensing As^{3+} in a field sample from an arsenic affected region of India. The sensor was also tested for the detection of other metal ions too. This work would facilitate the development of highly sensitive POU hand-held sensors for water quality monitoring in resource-limited areas.

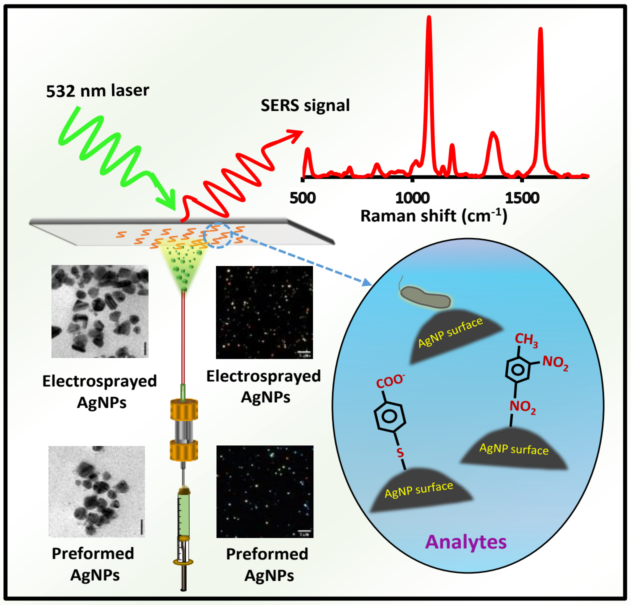
Ambient electrospray deposition Raman spectroscopy (AESD RS) using soft landed preformed silver nanoparticles for rapid and sensitive analysis

Tripti Ahuja, Atanu Ghosh, Sandip Mondal, Pallab Basuri, Jenifer Shantha Kumar, Pillalamarri Srikrishnarka, Jyoti Sarita Mohanty, Sandeep Bose, and T. Pradeep*

Analyst, 144 (2019) 7412-7420 (DOI: 10.1039/C9AN01700C)

Abstract: We introduce a technique called ambient electrospray deposition Raman spectroscopy (AESD RS) for rapid and sensitive surface-enhanced Raman scattering (SERS) based detection of analytes using a miniature Raman spectrometer. Using electrospray, soft landing of preformed silver nanoparticles (AgNPs) was performed for 30–40 seconds for different concentrations of analytes deposited on conducting glass slides. Using AESD RS, SERS signals were collected within 4–6 minutes, including sample preparation. Transmission electron microscopy (TEM) and dark-field microscopy (DFM) were used to characterize the preformed AgNPs before and after electrospray. We achieved the nanomolar and micromolar detection of p-mercaptobenzoic acid (p-MBA) and 2, 4-dinitrotoluene (2, 4-DNT), respectively. In this work, 0.3 µL of preformed AgNPs were used, which is ~33 times less in volume than the quantity needed for conventional SERS. Quantitation of unknown concentration of analytes was also possible.

A similar amount of electrosprayed AgNPs was utilized to characterize Escherichia coli (E. coli) bacteria of different concentrations. Viability of bacteria was tested using fluorescence microscopic imaging. Besides reduced analysis time and improved reproducibility of the data in every analysis, which is generally difficult in SERS, the amount of AgNPs required is an order of magnitude lower in this method. This method could also be used to probe the real-time changes in molecular and biological species under ambient conditions.

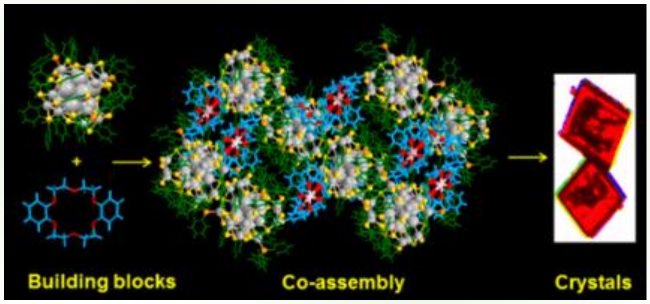


Crystallization of a supramolecular coassembly of an atomically precise nanoparticle with a crown ether

Papri Chakraborty, Abhijit Nag, Korath Shivan Sugi, Tripti Ahuja, Babu Varghese, and T. Pradeep*

ACS Materials Lett., 1 (2019) 534−540 (DOI: 10.1021/acsmaterialslett.9b00352)

Abstract: We report the crystal structure of a supramolecular coassembly of a red luminescent silver cluster, $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ (referred to as Ag_{29}) (BDT, 1,3-benzene dithiol; TPP, triphenyl phosphine), with dibenzo18-crown-6 ($DB_{18}C_6$). The structure may be viewed as crystallization-induced self-organization of DB18C6 molecules into cage-like hexamers in the interstitial spaces of the lattice of trigonal Ag_{29} (Ag_{29}T) clusters, which resulted in an anisotropic expansion of the Ag_{29}T lattice along its z axis. This structure corresponds to a new family of "lattice inclusion" compounds in nanoclusters. Supramolecular forces guide the assembly of the clusters and the crown ethers, which pack into complex hierarchical patterns in their crystal lattice. We identified the effect of such a coassembly on the solid-state luminescence of the cluster. The crystals containing the coassembly were ~3.5-fold more luminescent than the parent Ag_{29}T crystals. We also used high-resolution electrospray ionization mass spectrometry to get further insights into the nature of the complexation between Ag_{29} cluster and $DB_{18}C_6$. This study provides a new strategy for designing cluster-assembled functional materials with enhanced properties.

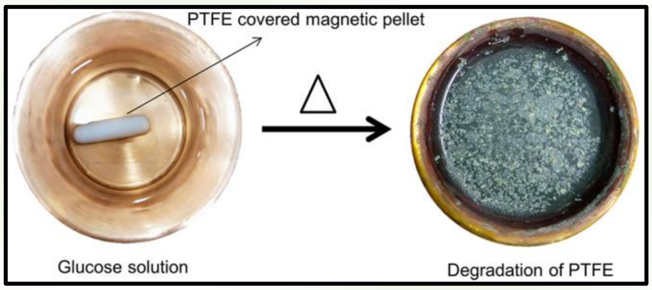


Tribochemical degradation of polytetrafluoroethylene in water and generation of nanoplastics

Abhijit Nag, Ananya Baksi, Jyotirmoy Ghosh, Vishal Kumar, Soumabha Bag, Biswajit Mondal, Tripti Ahuja, and T. Pradeep*

ACS Sustain. Chem. Eng., 2019, 7, 21, 17554-17558 (DOI: 10.1021/acssuschemeng.9b03573)

Abstract: Polytetrafluoroethylene (PTFE) is probably the most extensively used chemically inert and thermally stable polymer. We report the degradation of PTFE in water in the presence of common metals and carbohydrates resulting in polymeric fragments. About 53 mg of solid materials consisting of polymeric fragments and copper was separated from a copper vessel in 15 days when a PTFE pellet of about 920 mg was stirred with 1000 ppm glucose in 70 mL of water at 70 °C. Degradation produced fluorocarbon species in water were detected by high-resolution electrospray ionization mass spectrometry. Triboelectric charging of the PTFE surface during stirring and consequent interaction of the charged surface with the metal ions, brought to solution by carbohydrate induced corrosion, is attributed to this phenomenon. We show that such a process can be extended to other polymers such as polypropylene. The study suggests important



consequences of nanoplastics to environment and health, including impact of such chemistry to cooking.

Waterborne fluorine-free superhydrophobic surfaces exhibiting simultaneous CO_2 and humidity sorption

Avijit Baidya, Anagha Yatheendran, Tripti Ahuja, Chennu Sudhakar, Sarit Kumar Das, Robin H.A. Ras, and T. Pradeep*

Adv. Mater. Interfaces, 6 (2019) 9990−10000 (DOI: 10.1002/admi.201901013)

Abstract: Recent progress in the field of superhydrophobic materials has proven their potential to solve many problems of the contemporary society. However, the use of such materials to capture moisture and CO_2 from air, to help reduce the impact of global climate change is not explored. In addition, most of the time, fabrication of these materials needs organic solvents and fluorinated molecules involving multiple steps that hinder the use of nonwettable materials in everyday life. Herein, a waterborne, fluorine-free, robust superhydrophobic material synthesized at room temperature through a one-step chemical-modification process is reported, which exhibits moisture and CO_2 capturing capability. While covalently grafted low surface energy hydrocarbon molecules control the bulk superhydrophobicity, the incorporated amine functionalities facilitate moisture and CO_2 adsorption as these molecules (H_2O and CO_2) can easily diffuse through hydrocarbon assemblies. Being polar, H_2O molecules are observed to readily interact with amine groups and favor the adsorption process. Synthesized material shows an approximate CO_2 adsorption of 480 ppm (10.90 mmol L−1) in ambient conditions having 75% humidity. Multifunctionality along with durability of this material will help expand the applications of superhydrophobic materials.

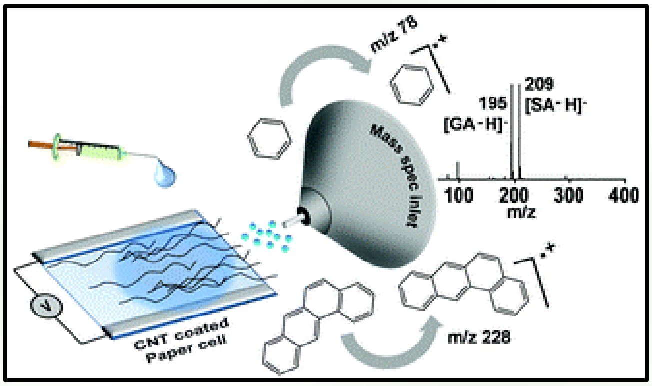
In-situ monitoring of electrochemical reactions through CNTs-assisted paper cell mass spectrometry

Rahul Narayanan, Pallab Basuri, Sourav Kanti Jana, Ananthu Mahendranath, Sandeep Bose and T. Pradeep*

Analyst, 144 (2019) 5404 (DOI: 10.1039/c9an00791a)

Abstract: A novel method of coupling electrochemistry (EC) with mass spectrometry (MS) is illustrated with a paper-based electrochemical cell supported by carbon nanotubes (CNTs). The electrochemically formed ions, created at appropriate electrochemical potentials, are ejected into the gas phase from the modified paper, without the application of additional potential. The electrochemical cell was fabricated by using a rectangular CNT-coated Whatman 42 filter paper with printed electrodes, using silver paste. This was used for studying the electrochemical conversion of thiols to disulfides, and the functionalization of polycyclic aromatic hydrocarbons (PAHs), which involve S–S and C–C bond formations, respectively.

We also demonstrate the versatility of the set-up by utilizing it for the detection of radical cations of metallocenes, monitoring the oxidation of sulfides through the detection of reactive intermediates, and the detection of radical cations of PAHs, all of which occur at specific applied potentials. Finally, the applicability of this technique for qualitative and quantitative analyses of environmentally relevant molecules has been demonstrated by studying the electrochemical oxidation of glucose (Glu) to gluconic acid (GlcA) and saccharic acid (SacA).

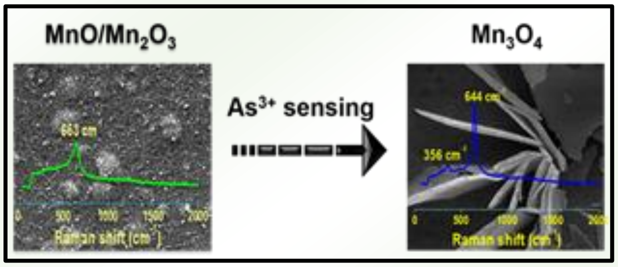


Highly-sensitive As^{3+} detection using electrodeposited nanostructured MnO_x and phase evolution of the active material during sensing

Tanvi Gupte, Sourav Kanti Jana, Jyoti Sarita Mohanty, Srikrishnarka Pillalamarri, Sritama Mukherjee, Tripti Ahuja, Chennu Sudhakar, Tiju Thomas, and T. Pradeep

ACS Appl. Mater. Interfaces, 11 (2019) 28154−28163 (DOI: 10.1021/acsami.9b06023)

Abstract: A simple, one-step electrodeposition approach has been used to fabricate MnO_x on an indium-doped tin oxide substrate for highly sensitive As^{3+} detection. We report an experimental limit of detection of 1 ppb through anodic stripping voltammetry with selectivity to As^{3+} in the presence of 10 times higher concentrations of several metal ions. Additionally, we report the simultaneous phase evolution of active material occurring through multiple stripping cycles, wherein MnO/Mn_2O_3 eventually converts to Mn_3O_4 as a result of change in the oxidation states of manganese. This occurs with concomitant changes in morphology. Change in the electronic property (increased charge transfer resistance) of the material due to sensing results in an eventual decrease in sensitivity after multiple stripping cycles. In a nutshell, this paper reports stripping-voltammetry-induced change in morphology and



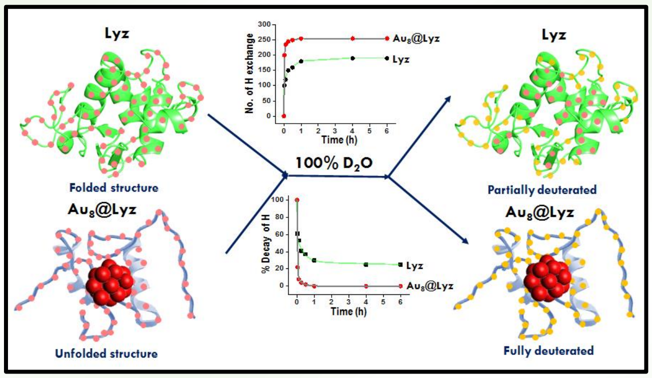
phase of as-prepared Mn-based electrodes during As sensing.

Conformational changes of protein upon encapsulation of noble metal clusters: An investigation by hydrogen/deuterium exchange mass spectrometry

Debasmita Ghosh, Sathish Kumar Mudedla, Md Rabiul Islam, Venkatesan Subramanian, and T. Pradeep*

J. Phys. Chem. C, 123 (2019) 17598−17605 (DOI: 10.1021/acs.jpcc.9b04009)

Abstract: Hydrogen/deuterium exchange mass spectrometry was employed to probe the conformational changes in lysozyme (Lyz) during the course of formation of a protein protected atomically precise Au_8 cluster. MALDI MS showed the protein, Lyz, to be present in a denatured state in the cluster. Detailed ESI MS analysis of the Au-attached Lyz adducts, an intermediate of cluster formation, confirmed that these conformational changes are brought about by Au–S bond formation and a similar conformation is retained in the final cluster. These results were supported by computational results, which showed an increase in solvent accessible surface area upon the formation of the adducts. Infrared spectroscopy established that change in the rate as well as the extent of the hydrogen/deuterium exchange observed in the cluster was due to the change in the amide II region of the encapsulating protein. Hydrogen/deuterium exchange ESI MS of Cu adducts of Lyz showed a lower degree of denaturation than their Au counterparts. XPS analysis revealed that Cu binds differently to Lyz than it does with Au, which is likely because of the stronger soft–soft Au–S interaction. Alkali metal ion binding, on the other hand, does not affect the protein conformation because such ions do not affect the disulfide bonds.

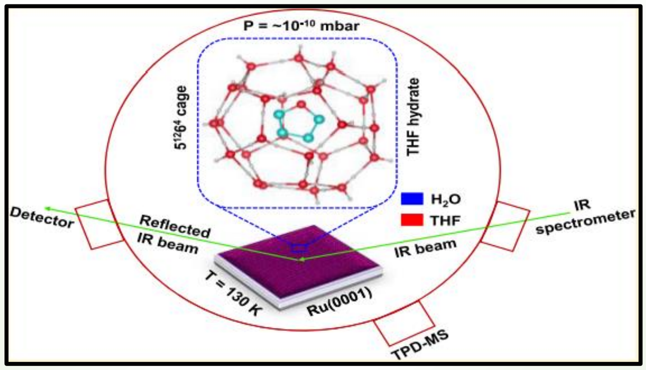


Spontaneous formation of tetrahydrofuran hydrate in ultra-high vacuum

Jyotirmoy Ghosh, Radha Gobinda Bhuin, Gopi Ragupathy, and T. Pradeep*

J. Phys. Chem. C, 123 (2019) 16300−16307 (DOI: 10.1021/acs.jpcc.9b04370)

Abstract: Clathrate hydrates (CHs) typically nucleate under high-pressure conditions, but their existence in ultrahigh vacuum (UHV) is an open question. Here, we report the formation of tetrahydrofuran (THF) hydrate in UHV, using reflection absorption infrared spectroscopy (RAIRS). Annealing both sequentially and co-deposited mixtures of THF and H_2O to 130 K for adequate time, originally prepared at 10 K, led to the formation of THF hydrate, at 10−10 mbar. Nucleation of THF hydrate was associated with the crystallization of amorphous solid water. Crystallization kinetics was examined through isothermal kinetic measurements using RAIRS in the temperature range of 120−130 K. The kinetic measurements revealed that the THF hydrate formation was a diffusion-controlled process and the overall activation energy for the process was found to be ∼23.12 kJ mol^{-1}.This considerably lower activation energy as compared to that for the crystallization of pure ice established the spontaneity of the process. The results provide valuable insights into the low-pressure characteristics of CHs and associated thermodynamics.

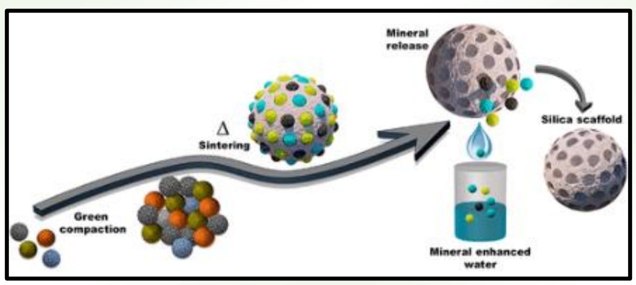


Geologically-inspired monoliths for sustainable release of essential minerals into drinking water

Swathy Jakka Ravindran, Ananthu Mahendranath, Srikrishnarka Pillalamarri, Anil Kumar Avula, Md Rabiul Islam, Sritama Mukherjee, Ligy Philip, and T. Pradeep*

ACS Sustain. Chem. Eng., 7 (2019) 11735-11744 (DOI: 10.1021/acssuschemeng.9b01902)

Abstract: Decreasing mineral content in drinking water is a serious concern especially due to the proliferation of desalination technologies. We present an approach to remineralize water with essential minerals such that their concentrations are at the recommended daily dose. We accomplished this using composite materials whose composition and surface area were tuned to achieve constant release of minerals into water over a prolonged period of time. We developed a nature-mimicking tectosilicate porous composite matrix and used it as a structural framework to incorporate leachable minerals to the extent of 40% of the whole mass, which were released into the water during its functional working life.



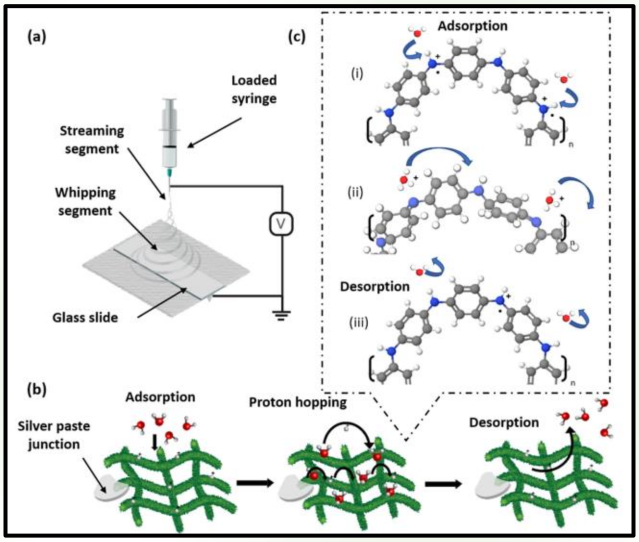
Release of not only the common macro minerals but also the vital trace minerals was possible in this work. Compacted composites of this kind have been used to create mineralization cartridges. The greenness of these composites evaluated from several sustainability metrics shows that the manufacturing process has minimum or negligible carbon emission, E-factor, and energy consumption. This methodology may be extended to encompass all the essential minerals expected to be present in water.

Surface treated nanofibers as high current yielding breath humidity sensors for wearable electronics

Sathvik Iyengar, Srikrishnarka Pillalamarri, Sourav Jana, Md Rabiul Islam, Tripti Ahuja, Jyoti Sarita Mohanty, and T. Pradeep*

ACS Appl. Electron. Mater., 1 (2019) 951−960 (DOI: 10.1021/acsaelm.9b00123)

Abstract: As wearable electronics have gained momentum in the past few years, there is a dire need for smart, responsive, and, most importantly, affordable sensors for biological monitoring. One such noninvasive method to gauge body metabolism is via breath analysis. In a successful attempt to sense and record relative humidity levels (%RH) in nasal and oral breath, this work presents an economical route to fabricate a wearable humidity sensor with high sensitivity and a response time of ~1 s. The sensor consists of a flexible backbone of electrospun poly(vinylidene fluoride)/reduced graphene oxide (PVDF/rGO) nanofibers which have been selectively sensitized to humidity via surface polymerization of aniline using the inexpensive successive ionic layer adsorption and reaction (SILAR) technique. We report a high sensitivity and a full response range (0−95% RH) supported by a low working voltage and minimalistic circuitry as an attractive feature for integration into wearable electronics. Moreover, as the device sensitivity is adequate even up to 95% RH, it is conducive to detect nasal breath and saturated humidity conditions accurately. As the method utilizes electrospinning, this work involves the preparation of such humidity sensors on a large scale (up to 400 units using 8 mg of rGO) with the benefit of having affordable and cost-effective devices.



Reply to Choukroun et al.: IR and TPD data suggest the formation of clathrate hydrates in laboratory experiments simulating ISM

Jyotirmoy Ghosh, Rabin Rajan J. Methikkalam, Radha Gobinda Bhuin, Gopi Ragupathy, Nilesh Choudhary, Rajnish Kumar, and T. Pradeep*,

Proc. Natl. Acad. Sci. U.S.A., 29 (2019) 14409-14410 (DOI: 10.1073/pnas.1905894116)

Abstract: In their letter, Choukroun et al. (1) caution against our results (2) as definitive evidence for the formation of clathrate hydrates (CHs) in the interstellar medium (ISM). We show the emergence of an infrared (IR) feature at 3,017 cm^{-1} in vapor-deposited CH_4–water mixture upon ~25 h of annealing, at 30 K in ultrahigh vacuum (2). We attribute the blue-shifted feature (with respect to the 3,009 cm−1 peak of condensed CH_4) to CH_4 hydrate of the 5^{12} structure. Dartois et al. (3) also suggested a blue shift for CH_4 trapped in the 5^{12} cage. A microsecond molecular dynamics simulation of CH_4 hydrate (4) predicted preferential formation of 5^{12} cages during CH nucleation. In our experiment (2), the trapped CH_4 desorbs along with the collapse of 5^{12} cages, increasing the intensity of molecular volcano of CH_4 at ~140 K in temperature programmed desorption (TPD). This is unexpected without CH being present. Thus, IR results, along with TPD and computations, support CH formation (2).

The emerging interface of mass spectrometry with materials

Papri Chakraborty, and T. Pradeep*

NPG Asia Materials (Just accepted)

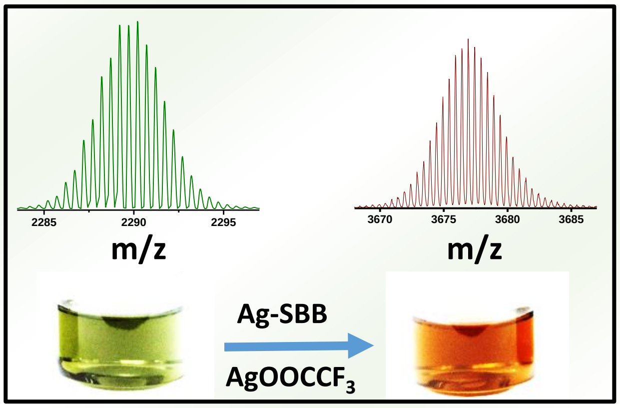
Abstract: Mass spectrometry (MS), a hundred-year-old subject, has been a technique of profound importance to molecular science. Its impact in solid-state materials science has not been evident, although many materials of modern science, such as fullerenes, have their origins in MS. Of late, mass spectrometric interface with materials is increasingly strengthened with advances in atomically precise clusters of noble metals. Advances in instrumentation along with recent developments in synthetic approaches have expanded the chemistry of clusters, and new insights into matter at the nanoscale are emerging. High-resolution MS coupled with soft ionization techniques enable efficient characterization of atomically precise clusters. Apart from that, techniques such as ion mobility, tandem MS, etc. reveal structural details of these systems. Growth, nucleation, and reactivity of clusters are also probed by MS. Some of the recent advancements in this field include the development of new hyphenated techniques. Finer structural details may be obtained by coupling MS with spectroscopic tools, such as photoelectron spectroscopy, vacuum ultraviolet spectroscopy, etc. With such advancements in instrumentation, MS can evolve into a universal tool for the characterization of materials. The present review captures highlights of this area.

Formation of a NIR emitting $Ag_{34}S_3SBB_{20}(CF_3COO)_6^{2+}$ cluster from a hydride protected silver cluster

C. K. Manju, Debasmita Ghosh, Mohammad Bodiuzzaman, and T. Pradeep*

Dalton Trans., 48 (2019) 8664-8670 (DOI: 10.1039/C9DT01533G)

Abstract: Recent reports have shown that the intercluster reaction is a new synthetic strategy to prepare alloy clusters. In this work, we performed an intercluster reaction between silver clusters and produced highly ionizable Ag–S-type clusters; we examined their formation by mass spectrometry. $[Ag_{18}(TPP)_{10}H_{16}]^{2+}$ (Ag_{18}), a highly reactive hydride and phosphine-protected silver cluster, was used as a sacrificial cluster in this synthesis. An intercluster reaction between Ag_{18} and smaller silver-chalcogenolate clusters (SCC) resulted in a new cluster, $[Ag_{34}S_3SBB_{20}(CF_3COO)_6]^{2+}$. The cluster showed an NIR emission at around 1100 nm. The cluster composition was confirmed by high-resolution electrospray ionization mass spectrometry (ESI-MS), thermogravimetry (TGA), and X-ray photoelectron spectroscopy (XPS).

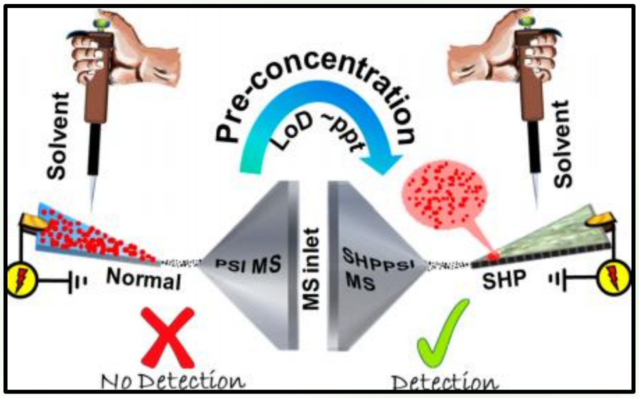


Sub-ppt level detection of analytes by superhydrophobic pre-concentration paper spray ionization mass spectrometry (SHPPSI MS)

Pallab Basuri, Avijit Baidya, and T. Pradeep*

Anal. Chem., 91 (2019) 7118-7124 (DOI: 10.1021/acs.analchem.9b00144)

Abstract: A new kind of ambient ionization method named superhydrophobic preconcentration paper spray ionization mass spectrometry (SHPPSI MS) is introduced, where superhydrophobicity and paper spray mass spectrometry (PS MS) are coupled. The SHPPSI MS requires only microliter amounts of analyte solutions, allows easy sampling procedure, and provides high sensitivity for a diverse array of analytes. It can be used to detect food adulteration at extremely low concentrations. The experimental methodology involves modifying one of the surfaces of a triangularly cut filter paper to make it acquire low surface energy by drop casting a green and ecofriendly superhydrophobic coating material over it followed by drying. A micrometer scale defect was made at close proximity to one of the tips of the paper using a pin. Preconcentration of the sample was accomplished by allowing a 10 µL droplet of an aqueous solution of the analyte to stand at the defect followed by drying naturally. The dried paper was used as the substrate for paper spray mass spectrometry by eluting the analyte with a suitable solvent. This novel technique was used to detect melamine in adulterated milk, whose detection at the ppt level in milk normally needs sophisticated instruments, a larger amount of sample, and a complex sampling procedure, including further purification and separation. The SHPPSI MS detects melamine directly from milk at the sub-ppb level by simply putting a microdroplet of adulterated milk at the substrate and eluting the sample with methanol. This paper-based technique can be a promising tool for direct sensing of analytes such as drugs in body fluids, pesticides in water and soil, etc.

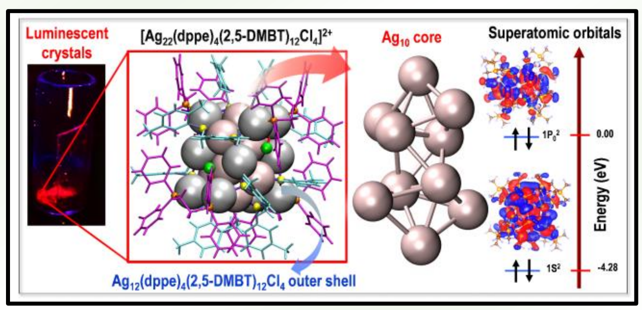


Confining an Ag_{10} Core in an Ag_{12} Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization

Esma Khatun, Md Bodiuzzaman, Korath Sugi, Papri Chakraborty, Ganesan Paramasivam, Wakeel Dar, Tripti Ahuja, Sudhadevi Antharjanam, and T. Pradeep*

ACS Nano., 13 (2019) 5753-5759 (DOI: 10.1021/acsnano.9b01189)

Abstract: We introduce a cluster coprotected by thioland diphosphine ligands, $[Ag_{22}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane; 2,5-DMBT= 2,5-dimethylbenzenethiol), which has an Ag_{10} core encapsulated by an $Ag_{12}(dppe)_4(2,5\text{-}DMBT)_{12}Cl_4$ shell. The Ag_{10} core comprises two Ag_5 distorted trigonal bipyramidal units and is uncommon in Au and Ag nanoclusters. The electrospray ionization mass spectrum reveals that the cluster is divalent and contains four free electrons. An uncommon crystallization-induced enhancement of emission is observed in the cluster. The emission is weak in the solution and amorphous states. However, it is enhanced 12 times in the crystalline state compared to the amorphous state. A detailed investigation of the crystal structure suggests that well-arranged C–H···π and π···π interactions between the ligands are the major factors for this enhanced emission. Further, in-depth structural elucidation and density functional theory calculations suggest that the cluster is a superatom with four magic electrons.



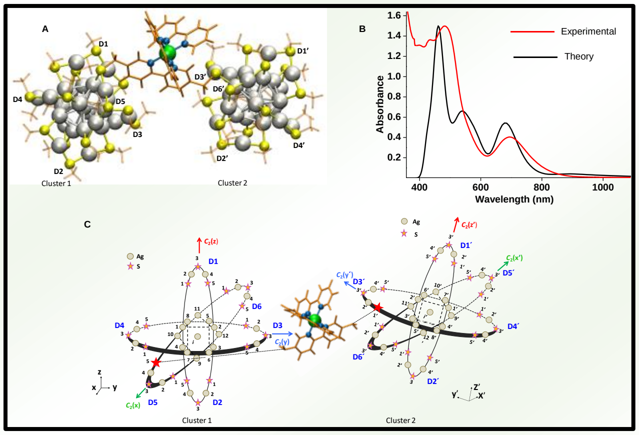
A covalently linked dimer of $[Ag_{25}(DMBT)_{18}]^-$

Md Bodiuzzaman, Abhijit Nag, Raghu Narayanan Pradeep, Ankush Chakraborty, Ranjit Bag, Paramasivam Ganesan, Ganapati Natarajan, G. Sekar, Sundargopal Ghosh, and T. Pradeep*

Chem. Commun., 55 (2019) 5025-5028 (DOI: 10.1039/C9CC01289C)

Abstract: We report the first example of a covalently bound dimer of monolayer protected atomically precise silver nanocluster $[Ag_{25}(DMBT)_{18}]$ (DMBT stands for 2,4-

dimethylbenzenethiol). Covalently linked dimers could be important to design new cluster assembled materials with composite properties. Recently, synthesis of new superstructures by assembly of molecular pieces of metals has attracted great attention. The creation of superstructures by clusters without changing the original structure of the building block is a challenging task. Ligand exchange reaction is suitable in this regard and various studies have been done on gold clusters to create



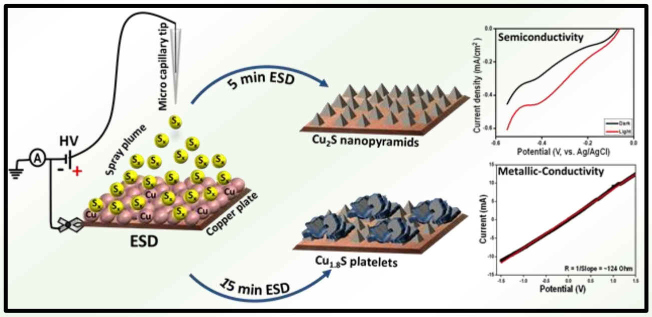
superstructures. Ligands containing two reactive rigid thiol groups can be efficient to create the assembly of building blocks. This aspect of creating superstructures has not been explored in the case of silver nanoclusters. In this regard, we report the first example of a covalently bound dimer of monolayer protected atomically precise silver nanocluster, $[Ag_{25}(DMBT)_{18}]^-$ (DMBT stands for 2, 4-dimethylbenzenethiol). The products were characterized by optical absorption spectroscopy, infrared spectroscopy and detailed high resolution electrospray ionization mass spectrometry (HR ESI MS). Covalently linked dimers could be important to design new cluster assembled materials with composite properties.

Electrospray deposition-induced ambient phase transition in copper sulphide nanostructures

Arijit Jana, Sourav Kanti Jana, Depanjan Sarkar, Tripti Ahuja, Pallab Basuri, Biswajit Mondal, Sandeep Bose, Jyotirmoy Ghosh, T. Pradeep*

J. Mater. Chem. A, 7 (2019) 6387-6394 (DOI: 10.1039/C9TA00003H)

Abstract: We introduce a new and simple method for synthesizing different phases of copper sulphide nanostructures using electrospray deposition (ESD) of molecular sulphur in the form of droplets on metallic copper surfaces under ambient conditions. Different phases of copper sulphide nanostructures were created by controlling the deposition time. Time dependent electron microscopy reveals conversion of the Cu_2S nanopyramids to $Cu_{1.8}S$ platelets during the course of ESD. In the beginning of deposition, direct



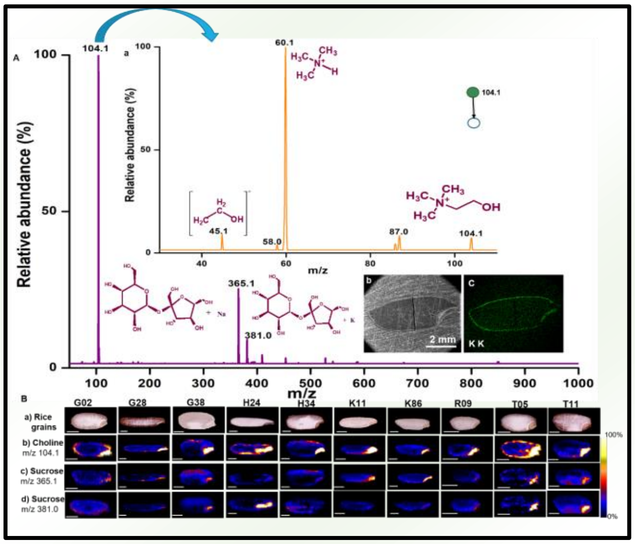
interaction between sulphur ions and metallic copper creates Cu_2S nanopyramids followed by subsequent slow diffusion of sulphur leading to the formation of copper deficient $Cu_{1.8}S$ platelets. A detailed characterization of both the nanostructures was performed by using different microscopic and spectroscopic tools such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, powder X-ray diffraction (PXRD) and X-ray photoelectron spectroscopy (XPS). We have also studied the optical properties of these nanostructures in both UV-Vis and near infrared (NIR) regions. The characteristic broad peaks in the UV-Vis region of Cu_2S nanopyramids indicate the photosensitive nature of the material. A positive photocurrent response was observed from the Cu_2S nanopyramids under electrochemical conditions, while $Cu_{1.8}S$ nanostructure shows an intense localized surface plasmon (LSPR) peak in the NIR region indicating its metallic nature. Current–voltage (I–V) measurements showed metallic conductivity in them.

Spatial distribution mapping of molecules in the grains of different rice landraces, using desorption electrospray ionization mass spectrometry

Arunan Suganya, Debal Deb and T. Pradeep*;

Rapid Commun. Mass Spectrom., 33 (2019) 727–736 (DOI: 10.1002/rcm.8397)

Abstract: Rationale: Documentation of the metabolite profiles of rice landraces is essential as most of them have been lost due to the conventional practices of cultivation. Therefore, application of mass spectrometry imaging (MSI) will be an appropriate analytical platform for molecular profiling, as it can provide a detailed understanding of the site-specific localization patterns of biomolecules, and the cues concerning metabolic pathways in organisms. Methods: Desorption electrospray ionization mass spectrometry (DESI-MS) is a relatively non-destructive analytical technique for surface sampling in natural conditions. Here, we report the spatial distribution of diverse molecules in the grains of different rice landraces of India using DESI-MSI. Molecules were identified by ESI-MS and tandem MS analysis of rice extracts. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were used for the



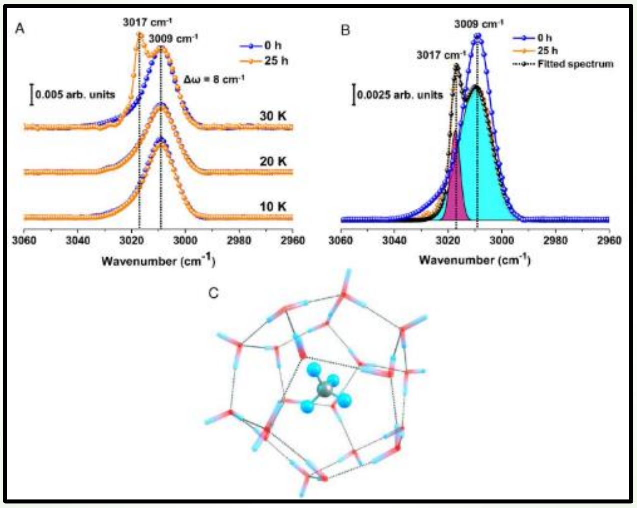
elemental mapping on the rice grains. Results: DESI-MSI showed a uniform distribution of choline (m/z 104.1), sucrose in the form of its sodium (m/z 365.1) and potassium (m/z 381.0) adducts, linoleic acid (m/z 279.2), 13-HODE-9-HODE (m/z 295.2), unidentified molecules with m/z 535.3, 559.5, and 561.5 and isoschaftoside (m/z 563.1) in the endosperm of rice grains. Gluconic acid (m/z 195.0) and signalling phospholipid intermediate molecules were localized in the embryo whereas oryzanol A (m/z 601.5) and oryzanol C (m/z 615.5) had a restricted localization in the bran region of the grain. SEM-EDS mapping showed the localization of potassium and phosphorus along the bran and embryo. Conclusions: DESI-MSI revealed the distribution of lipids and sugar molecules in the specific regions of the rice grains. Thus, molecules unique to some rice varieties were identified with this analytical platform. Mass spectrometry imaging of rice along with the elemental mapping by SEM-EDS will be of use in understanding the localization pattern of certain molecules in the context of metals present in the grain.

Clathrate hydrates in interstellar environment

Jyotirmoy Ghosh, Rabin Rajan J. Methikkalam, Radha Gobinda Bhuin, Gopi Ragupathy, Nilesh Choudhary, Rajnish Kumar, and T. Pradeep*

Proc. Natl. Acad. Sci. U.S.A., 116 (2019) 1526-1531 (DOI: 10.1073/pnas.1814293116)

Abstract: Proton Clathrate hydrates (CHs) are ubiquitous in earth under high pressure conditions, but their existence in the interstellar medium (ISM) remains unknown. Here, we report experimental observations of the formation of methane and carbon dioxide hydrates in an environment analogous to ISM. Thermal treatment of solid methane and carbon dioxide–water mixture in ultrahigh vacuum of the order of 10−10 mbar for extended periods led to the formation of CHs at 30 and 10 K, respectively. High molecular mobility and H bonding play important roles in the entrapment of gases in the in situ formed 512 CH cages. This finding implies that CHs can exist in extreme low-pressure environments present in the ISM. These hydrates in ISM, subjected to various chemical processes, may act as sources for relevant prebiotic molecules.



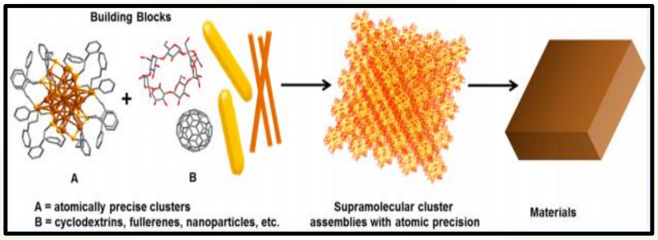
Approaching materials with atomic precision using supramolecular cluster assemblies

Papri Chakraborty, Abhijit Nag, Amrita Chakraborty and T. Pradeep*

Acc. Chem. Res., 52 (2019) 2–11 (DOI: 10.1021/acs.accounts.8b00369)

Abstract: Supramolecular chemistry is a major area of chemistry that utilizes weaker non-covalent interactions between molecules, including hydrogen bonding, van der Waals, electrostatic, π···π, and

C–H···π interactions. Such forces have been the basis of several molecular self-assemblies and host–guest complexes in organic, inorganic, and biological systems. Atomically precise nanoclusters (NCs) are materials of growing interest that display interesting structure–property correlations. The evolving science of such systems reaffirms their molecular behavior. This gives a possibility of exploring their supramolecular chemistry, leading to assemblies with similar or dissimilar cluster molecules. Such assemblies with compositional, structural, and conformational precision may ultimately result in cluster-assembled hybrid materials. In this Account, we present recent advancements on different possibilities of supramolecular interactions in atomically precise cluster systems that can occur at different length scales. We first present a brief discussion of the aspicule model of clusters, considering $Au_{25}(SR)_{18}$ as an example, that can explain various aspects of its atomic precision and distinguish the similar or dissimilar interacting sites in their structures. The supramolecular interaction of 4-tert-butylbenzyl mercaptan (BBSH)-protected $[Au_{25}(SBB)_{18}]^-$ NCs with cyclodextrins (CD) to form Au25SBB18∩CDn (n = 1–4) and that of $[Ag_{29}(BDT)_{12}]^{3-}$ with fullerenes to form $[Ag_{29}(BDT)_{12}(C_{60})_n]^{3-}$ (n = 1–9) (BDT = 1,3-benzenedithiolate) are discussed subsequently. The formation of these adducts was studied by electrospray ionization mass spectrometry (ESI MS), optical absorption and NMR spectroscopy. In the subsequent sections, we discuss how variation in intercluster interactions can lead to polymorphic crystals, which are observable in single-crystal X-ray diffraction. Taking $[Ag_{29}(BDT)_{12}(TPP)_4]^{3-}$ (TPP = triphenylphosphine) clusters as an example, we discuss how the different patterns of C–H···π and π···π interactions between the secondary ligands can alter the packing of the NCs into cubic and trigonal lattices. Finally, we



discuss how the supramolecular interactions of atomically precise clusters can result in their hybrid assemblies with plasmonic nanostructures. The interaction of p-mercaptobenzoic acid (p-MBA)-protected $Ag_{44}(p\text{-}MBA)_{30}$ NCs with tellurium nanowires (Te NWs) can form crossed-bilayer precision assemblies with a woven-fabric-like structure with an angle of 81° between the layers. Similar crossed-bilayer assemblies show an angle of 77° when $Au_{102}(pMBA)_{44}$ clusters are used to form the structure. Such assemblies were studied by transmission electron microscopy (TEM). Precision in these hybrid assemblies of Te NWs was highly controlled by the geometry of the ligands on the NC surface. Moreover, we also present how $Ag_{44}(p\text{-}MBA)_{30}$ clusters can encapsulate gold nanorods to form cage-like nanostructures. Such studies involved TEM, scanning transmission electron microscopy (STEM), and three-dimensional tomographic reconstructions of the nanostructures. The hydrogen bonding interactions of the –COOH groups of the p-MBA ligands were the major driving force in both of these cases. An important aspect that is central to the advancement of the area is the close interplay of molecular tools such as MS with structural tools such as TEM along with detailed computational modeling. We finally conclude this Account with a future perspective on the supramolecular chemistry of clusters. Advancements in this field will help in developing new materials with potential optical, electrical, and mechanical properties.

Acknowledgement

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