
Pradeep Research Group
Indian Institute of Technology Madras
Chennai 600 036, India

(In case security permission is requested, please allow; you need to do it only once.)
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Ph.D. Students

- A. Anil Kumar
- A. Suganya
- Amoghavarsha R. Kini
- Amrita Chakraborty
- Anagha Jose
- Ankit Nagar*
- Arijit Jana
- Bijesh Malla
- Gaurav Vishwakarma
- Jayoti Roy
- M. P. Kannan*
- Madhuri Jash
- Md Rabiul Islam
- Mohd. Azhardin Ganayee
- Pallab Basuri
- Paulami Bose
- S. Jenifer*
- Sandeep Bose
- Sooraj B. S.
- B. K. Spoorthi
- Srikrishnarka Pillalamarri*
- Sritama Mukherjee*
- Subrata Duary
- Sudhakar Chennu
- Sugi Shivan
- Sujan Manna
- Swetashree Acharya
- Tanmayaa Nayak
- Tanvi Gupte*
- Vishal Kumar*
- Vivek Yadav

* Interdisciplinary/Joint students
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### Postdoctoral/Research Associates
- Dr. Abhijit Nag
- Dr. Angshuman Ray Chowdhuri
- Dr. Biswajit Mondal
- Dr. Esma Khatun
- Dr. Ganesan P.
- Dr. Kartheek Joshua
- Dr. Sourav Kanti Jana
- Dr. Tripti Ahuja

### Administrative Officer
- K. Priya

### Project Technicians
- Asish Kurian
- Devaraj. K
- E. Sundarraj

### M.S. Students
- Ananthu Mahendranath
- Ramesh Kumar
- Deeksha
- Raga Madhuri
- Sanjiiit Gayen
- Soumya Samanta
- Subhadip Das

### Acknowledgements

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$^s$Institute postdoctoral fellows
Glimpses of 2020

Prof. Pradeep with Prof. Ajay Sood, FRS during his visit to IITM and ICCW.

Prof. Pradeep with eminent scientists during the International Conference on Nano Science and Technology- 2020 (ICONSAT-2020) organized by S. N. Bose National Centre for Basic Sciences, Kolkata during March 5 -7, 2020.

Awards and Honors

Prof. T. Pradeep has been chosen as one of the winners of Nikkei Asia Prizes 2020. First presented in 1996, and thus in the 25th edition, “the Prizes shine a spotlight on individuals who have contributed to the region’s sustainable development and to the creation of a better future in Asia.”

Nation conferred the Padma Shri (the fourth highest civilian award in India) award on Prof. Pradeep.

https://www.youtube.com/watch?v=18FgoiQcm84&feature=youtu.be

Nikkei Asia Prizes, which are awarded each year, are designed to recognize outstanding achievements that contribute to the region’s sustainable development and to the creation of a better future in Asia.
Publications

Journal Publications*


8. Atomically precise noble metal cluster-assembled superstructures in water: Luminescence enhancement and sensing, Abhijit Nag, Papri Chakraborty, Athira Thacharon, Ganesan

Prof. T. Pradeep has been selected for the Chemical Research Society of India (CRSI) silver medal 2021, along with Professor Jiten Bera of IIT Kanpur.
1. Smartphone-based fluoride-specific sensor for rapid and affordable colorimetric detection and precise quantification at sub-ppm levels for field applications, Sritama Mukherjee, Manav Shah, Kamalesh Chaudhari, Arijit Jana, Chennu Sudhakar, Pillalamarri Srikrishnarka, Md Rabiul Islam, Ligy Philip and Thalappil Pradeep, ACS Omega, 5 (2020) 25253–25263 (DOI: 10.1021/acsomega.0c03465).


4. [Ag$_{15}$H$_{13}${(DPPH)$_{5}$}]$^{2+}$ and [Ag$_{27}$H$_{22}${(DPPB)$_{7}$}]$^{3+}$: Two new hydride and phosphine co-protected clusters and their fragmentation leading to naked clusters, Ag$_{13}^{+}$ and Ag$_{25}^{+}$, Madhuri Jash, Esma Khatun, Papri Chakraborty, Chennu Sudhakar and Thalappil Pradeep, J. Phys. Chem. C, 124(2020) 20569–20577 (DOI: 10.1021/acs.jpcc.0c05867).


12. Enhanced capture of particulate matter by molecularly charged electrospun nanofibers, Pillalamarri Srikrishnarka, Vishal Kumar, Tripti Ahuja, Vidhya Subramanian, Arun Karthick Selvam, Paulami Bose, Shantha Kumar Jenifer, Ananthu Mahendranath, Mohd Azhardin

Ankit Nagar and Thalappil Pradeep, ACS Nano, 2020 (Review Article). Cover page


*Some of these papers will appear in 2021.*

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**Editors of 2020**


2. Expectations for Manuscripts in ACS Sustainable Chemistry & Engineering: Scope Summary and Call for Creativity, David T. Allen, D. Julie Carrier, Jingwen Chen, Nicholas Gathergood, Jinlong
Interview with Prof. T. Pradeep in Asianet (In Malayalam)


Popular Science


Patent Applications

Indian Patents (Granted)


3. An enhanced carbon dioxide sorbent nanofiber membrane and a device thereof, T. Pradeep, Anangha Yatheendran, Ramesh Kumar and Arun Karthik, 201841031076, August 20, 2018, granted as patent no. 323314 on August 4, 2020.

4. Cellulose nanocrystal templated iron oxyhydroxide based adsorbent for arsenic removal from water and a device thereof, T. Pradeep, Avijit Baidya, Bibhuti Bhusan Rath and A. Anil Kumar, 201641027660, filed on August 12, 2016, granted as patent no 343818, August 10, 2020.


8. Chitosan reinforced mixed oxide nanocomposite for fluoride removal from water and a device thereof, T. Pradeep; Anil Kumar Avula; Bibhuti Bhusan Rath, filed as application number 201641045048, December 30, 2016, granted as patent no. 354374 on December 23, 2020.


\textbf{Indian Patents (Applied)}


2. A smartphone based fluoride-specific sensor for rapid and affordable colorimetric detection and precise quantification at sub-ppm levels for field applications, Thalappil Pradeep, Sritama Mukerjee, Manav Shah, and Kamaleesh Chaudhari, 202041026054, June 20, 2020.


\textbf{PCT Patents (Applied)}


\textbf{Degree Holders}

\textbf{PhD Graduates}

  ‘Clathrate hydrates in ultrahigh vacuum under cryogenic conditions’.

‘An investigation of the chemical properties of luminescent protein protected atomically precise noble metal clusters’.


‘Exploring chemical and structural diversity in atomically precise nanoclusters’.


‘Exploring the chemical and physical properties of 2D MoS2 for clean water’.

Tripti Ahuja, Department of Chemistry, IIT Madras, 2020.

‘Towards vibrational tomography of ligand protected nanoparticles’.


‘An investigation of atomically precise mono and multimetallic nanoclusters’.


‘Association between agrochemicals and non-communicable diseases in rural India: A case study on prevalence of diabetes and atherosclerosis’.

M.Sc Graduates


‘Transformation of nanodiamond particles to carbon onions by ambient electrospray deposition’.


‘Urea removal using thin-film nanocomposite reverse osmosis membrane’.


‘Exploring intercluster reactions and chemistry of copper nanoclusters’.


‘Formation of formaldehyde clathrate hydrates in interstellar conditions’.


‘Luminescent layered hybrid collagen-based material for synthetic skin’.

Parvathy M U*, University of Calicut, Kerala, 2020.

‘Atomically precise silver nanoclusters: surface protection by isomeric carboranethiols’.


‘Reactivity of silver clusters with gold nanotriangles’.


‘Size and shape-dependent atomic exchange in reactions of nanoclusters with nanoparticles’.

B.Tech Graduate


‘Selective enzyme-conjugated luminescent nanoclusters as organophosphate pesticide biosensors’.

* Graduates from other institutions.
Lectures Delivered

Offline Lectures

3. Atomically precise nanoparticles, Biodesign Institute, Arizona State University, Tempe, February 7, 2020.
5. Atom exchange in nanoparticles, Department of Chemistry, Purdue University, February 17, 2020.
6. Affordable clean water using advanced materials, Brick Nanotechnology Centre, Purdue University, February 18, 2020.
8. Nanoparticles are molecules, ICONSAT Kolkata, March 5, 2020.

At Biodesign Institute, Arizona State University

Online Lectures (Virtual)

1. Nanoparticles are molecules, ACS Virtual Talk: Science Lecture Series, April 9, 2020.

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**Students’ Activities**

**International Conferences**

1. ‘Confining an Ag$_{10}$ Core in an Ag$_{12}$ Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization’ by Esma Khatun at the Atomically Precise Nanochemistry Gordon Research Conference, Hotel Galvez, Galveston, TX United States, February 09-14, 2020.
3. Ananthu Mahendranath attended 2020 CEC Annual Workshop on Electrochemistry, organized by the Center for Electrochemistry at The University of Texas at Austin, from February 22-23, Austin, Texas, USA.

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**National Conferences**

5. ‘Confining an Ag$_{10}$ Core in an Ag$_{12}$ Shell: A Four-Electron Superatom with Enhanced Photoluminescence upon Crystallization’ by Esma Khatun at the Chemistry in House Symposium, IIT Madras, Chennai, December 03–04, 2020.
6. ‘Gas-phase ion chemistry of titanium oxofullerene anions, [H$_x$Ti$_{42}$O$_{60}$L$_y$]$^-$ [L= (OCH$_3$)$_{42}$(HOCH$_3$)$_{10}$(H$_2$O)$_y$, x = 7,12; y = 3,2; n = 1, 2]’ by Jayoti Roy at the Chemistry in House Symposium, IIT Madras, Chennai, December 03–04, 2020.


Students’ Recognitions


2. Srikrishnarka Pillalamarri has received a best poster award for ‘Highly-scalable, Affordable, Conducting Cloth as Wearable Breath Humidity Sensor’ presented at CiHS-2020 held by the Department of Chemistry, Indian Institute of Technology Madras during December 03–04, 2020.

3. Dr. Abhijit Nag has received the Prof. Langmuir Prize for the best Ph.D. thesis in Physical and Theoretical Chemistry for the year 2020.

4. Dr. Papri Chakraborty has received the prestigious Humboldt Fellowship for the year 2020-2021.

5. Dr. Udayabhaskararao Thumu has received the prestigious Chinese national talent award (2020), Overseas High-level Talent Introduction Program (16th batch). His proposal with National Natural Science Foundation of China (NSFC) on project entitled: A bottom-up nanofabrication approach for record-setting 10 nm-plasmonic cavity at the single quantum emitter limit (Grant No. 22050410280) got approved during the pandemic.

Alumni News

- Dr. Manju C. K. has joined as a postdoc at the Ohio State University, Department of Chemistry and Biochemistry, Newman&Wolf from lab, 100 W 18th Ave, Columbus, OH, 43210, USA.

- Dr. Papri Chakraborty has received the Humboldt Research Fellowship for 2020-21 at Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

- Dr. Debasmita Ghosh has joined as a postdoc at the IECB, University of Bordeaux, Institut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607 Pessac, France.
• **Dr. Wakeel Dar** has joined as Water Treatment Specialist, ICCW, 2nd floor B-Block, IITM Research Park, Chennai, India.

• **Dr. Ganapati Natarajan** has joined as Principal Scientist, ICCW, 2nd floor B-Block, IITM Research Park, Chennai, India.

• **Dr. Radha Gobinda Bhuin** has got appointed as Senior Research Officer (SRO), Indian Oil Corporation Limited (IOCL), R&D Centre, India.

• **Dr. Jyotirmoy Ghosh** has joined as a postdoc at Purdue University, West Lafayette, IN, USA. Aston Labs, Prof. R. Graham Cooks Research Group, Department of Chemistry, Purdue University.

• **Dr. Shridevi Bhat** has joined as a postdoc at the Stony Brook University, Department of Microbiology and Immunology, New York.

• **Ms. Deeksha** has joined as a PhD student at the school of Molecular Sciences, Arizona State University, USA.

• **Mr. Soumya Samanta** has joined IACS, Kolkata, India.

• **Ms. Pooja Ajayan** has joined as a PhD student in Chemistry, University of California, Riverside under the guidance of Prof. Ming Lee Tang.

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### Research Grants

**Approved this year**

1. National facility of cryo-electron microscopy: Remotely operable, 24x7 for academia and industry, SERB, Rs. 28.6 crores (principal investigator)
2. Sustainable ion exchange resin-based technology for rare earth extraction - MOMI Rs.52.51 lakhs (principal investigator)
3. Carborane - protected metal nanoclusters: A new family of materials with atomic precision - DST/Czech 37 lakhs (principal investigator)
4. DST-JSPS joint workshop on cluster science by interdisciplinary approach: Emerging materials and phenomena - DST-JSPS (conference proposal, principal investigator)
5. Atomically precise naked cluster assemblies from ligand-stabilized clusters: New materials for catalysis - DST-DFG - 79 lakhs (principal investigator)

**Ongoing**

6. 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)
7. Chemical transformations of clathrate hydrates under ultra-high vacuum, DST, Rs. 76.5 lakhs (principal investigator)
8. 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)
9. VAJRA project with Pulickel M. Ajayan, Rice University, Rs. 9.75 lakhs
10. SUTRAM for EASY water, DST, Rs. 890 lakhs (co-principal investigator with Prof. Ligy Philip) as (principal investigator)
11. Affordable clean water in arsenic affected areas, Millennium Alliance, 2018-2020, Rs. 50 lakhs (principal investigator along with Ramesh kumar)
12. 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).
13. Dust free glass, Saint-Gobain Research India Ltd. Rs. 36 lakhs (principal investigator with Prof. R. Nagarajan)
Consultancy

1. Steel – Rubber adhesion improvement – Phase 2, MRF Ltd., 2019–2021, Rs. 1.2 Cr (principal investigator)

Implementation Projects

2. Providing, fixing and maintenance of nano material based household water purifiers for providing in arsenic affected habitations of Punjab, Government of Punjab, Rs. 48.5 crores (principal investigator), undertaken by ICCW.
3. House-hold arsenic removal units for Government of Punjab, Rs. 4.8 crores (principal investigator), undertaken by ICCW.

Visits

- 18th Meeting of Project Evaluation and Review Committee (PERC) of Standing Scientific Advisory Group [SSAG] at Jawaharlal Nehru Aluminium Research Development Centre (JNARDDC), Amravati Road, Wadi, Nagpur, October 24, 2020.
- Visit to Arizona State University, Gordon Conference, Rice University, and Purdue University, USA, February 05–19, 2020.
- Meeting with Principle Secretary, Smt. Jaspreet Talwar, IAS, Water Supply & Sanitation Department, in her office Room No.720, 7th Floor, Mini Secretariat, Sector-9, Chandigarh, Discussions regarding the arsenic project, February 27, 2020.

Visitors to the Lab Before the Lockdown

3. Dr. Thomas Colacot - Millipore Sigma (a Business of Merck KGaA, Darmstadt, Germany), 6000 N, Teutonia Avenue, Milwaukee, WI 53209, USA, January 24, 2020.
5. Dr. Swaminathan Venkataraman, Adjunct Professor, Physics Department, Penn State University, USA, January 27, 2020.

Services
• Member, India-Japan Council of the Department of Science and Technology, 2014-Vice President, Indian Society for Mass Spectrometry, 2014-
• Member, Executive Committee, Neutron Scattering Society of India, 2011-
• Member of the Council of Materials Research Society of India, 2011 –
• Member, Board of studies, Manipal University, 2012-
• Member, Program Advisory Committee of Inorganic and Physical Chemistry, DST, 2018-
• Member, Industry Relevant R &D Expert Committee, DST, 2018-
• Member, Governing Council, Technology Information, Forecasting & Assessment Council (TIFAC)
• Member, Research Advisory Council, Manipal Academy of Higher Education, Manipal Member, 2018-
• Research Advisory Board, Pandit Deendayal Petroleum University, 2019-
• Member, Research Advisory Committee, IIT Ropar, 2019-
• Co-opted Member, Program Advisory Committee of SERB-SUPRA, 2019-
• 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
• Member, Program Advisory Committee on Exponential Technologies, DST, 2020
• Member, Editorial Board of the journals, Chemistry of Materials, ACS Nano, Analytical Chemistry, Nanoscale, Particle, Surface Innovations, International Journal of Water and Wastewater Treatment, Nanoscale Advances, and Chemical Communications.
• Associate Editor of the journal, ACS Sustainable Chemistry & Engineering.

Incubation

• **Hydromaterials** has installed 698 community water treatment units in 2020, each supplying arsenic and iron free water to over 900,000 people. Altogether there are 961 units of this kind operational in the country, supplying clean water to 1.2 million people. This year’s highlight is the internet-of-things (IoT) enabled community units. Over 100 units of this kind will be completed soon, many are already functional. A picture of one such unit in Amritsar District of Punjab is shown on the right. There are other types of installations too.

Amrit technology has been approved by the Jal Shakti Ministry.

• **InnoDI** has expanded its reach, it has installed more than 150 units across 10 states serving clean water to over 100,000 people and saving over 100 million litres of water every year which otherwise would have gone down the drain. One of the recent installations at Ullal in Karnataka is shown on the left.
• **VayuJal Technologies** is developing a 2000 litres per day (LPD) atmospheric water harvesting unit now, which will be installed at Engineers India Limited, Gurugram, Haryana. We have now 30, 100, 400, and 1000 lpd versions of this product. Shown on the right is the view of the factory.

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

• **EyeNetAqua Pvt. Ltd.** has been established to commercialise sensors for clean water.

**All are co-owned by IIT Madras.**

• A new initiative of IIT Madras, the **International Centre for Clean Water** has made tremendous progress in all its activities. We have initiated research, implementation, outreach and incubation activities. An overview of these efforts is available at: [ICCW Annual report 2020](#). Key to these initiatives is the support of all our well-wishers, well-meaning individuals such as Ram and Nandini, pictured on the left, as well as institutions.

### Media Reports

A short documentary titled ‘Hawa se Paani’ published on YouTube.

Channel: HISTORY TV18

Date: 21st of April 2020.

Links to access these are given below:


An article published in The Hindu on 26th January 2020.

PADMA SHRI AWARDEES

Seven unique achievers bring laurels for State

N. R. Madhava Menon, father of modern Indian legal education, and spiritual Guru Sri Murugan Padmanabha

An article on The New India Express published on 26th January 2020.

Providing safe drinking water is his mission

EXPRESS NEWS SERVICE (07-01-2020)

OVER more than two decades, an IIT Madras professor T. Pradeep and his research group have systematically developed advanced yet affordable technologies to solve major water-related problems in the country. His efforts were recognised by Union government, which bestowed Padma Shri, under Science and Engineering category. Over 450 papers have been published and 115 patents have been filed or granted. In the last five years, five companies have been incubated, whose technologies are providing nearly 18 million people across India with clean drinking water.

Pradeep told Express “I am happy that my team’s work has been recognised. Developing affordable and safe drinking water solutions using nanomaterials, from bench-scale science to commercial products, creating a sustainable business model that is cost-effective and simultaneously was very satisfying. We have demonstrated that research and technology from the core of traditional scientific disciplines can find applications in relevant technology for solving problems that are relevant and feasible.”

Covid: Lockdown leaves research scholars in a lurch

PRADEEP T

While Covid is佔ying a toll on the global economy, it has also derailed the professional careers of research scholars across the globe. From PhDs to post-doctoral researchers, the lockdown has taken a toll on the professional lives of many in the academic world. With universities and research institutions forced to transition to online work, many of these scholars have found themselves in a lurch.

At IIT Madras, more than 400 PhD scholars had embarked on new research projects as they awaited their thesis defence, or were planning to defend that would have happened over the past two months. However, this has come to a halt, with many research scholars now waiting for the lockdown to ease up so they can resume their work.

Research scholars, who were looking forward to successful completion of their projects, now face a new challenge: to adjust to a new mode of work. Many of them have been working on projects that require lab work, and with laboratories closed, they are struggling to find ways to continue their research.

The lockdown has also affected the mental health of many research scholars, with a rise in stress and anxiety levels. Many have reported feeling isolated and unable to connect with their peers and mentors.

However, some scholars have found ways to adapt to the new normal. Many have turned to online platforms to continue their work, and have also been able to connect with other researchers across the globe.

But for many, the lockdown has meant a pause in their research, and a struggle to find ways to continue their work in the absence of lab facilities.

Plight of doctoral students during the pandemic

T. Pradeep

March 30, 2020 07:39 pm IST

Updated: March 30, 2020 07:37 pm IST

This crisis will most severely affect those who have just finished, or are finishing, their PhD degrees.


An article in Deccan Chronicle published on 7th July, 2020.

An article on Times of India published on 13th August 2020.
Publication Analyses

Sources:
A covalently integrated reduced graphene oxide-ion exchange resin electrode for efficient capacitive deionization

Md Rabiul Islam, Soujit Sen Gupta, Sourav Kanti Jana, Pillalamarri Srikrishnarka, Biswajit Mondal, Sudhakar Chennu, Tripti Ahuja, Amrita Chakraborty, and Thalappil Pradeep

Adv. Mater. Interfaces, 2020. (Just Accepted)

Abstract:
Capacitive deionization (CDI) is an emerging, cost-effective alternative for energy-efficient desalination technology. Efficient electrode materials based on individual reduced graphene oxide (rGO) nanosheets were produced by functionalizing them with polystyrene (rGO-PS) through an in-situ polymerization process involving rGO, styrene monomer, and divinylbenzene (DVB). The rGO-PS integrated composite nanostructures were subsequently functionalized with sulfonate and quaternary amine functionalities to achieve positively and negatively charged electro-adsorbent ion-exchange resins (EAIERs), respectively. These EAIERs ‘molecular constructs’ were used to fabricate CDI electrodes, and deionization was performed to remove various ions. These molecular constructs promoted faster charge transfer at the electrode-electrolyte interface and maintained the electrical conductivity of the active rGO. This led to a high electroadsorption capacity of 15.93 mg/g of Cl\textsuperscript- using NaCl solution with a conductivity of 802 µS in laboratory batch experiments, which is ~5 times higher than the adsorption capacity of rGO electrodes reported earlier (~2-3 mg/g) in comparable experimental conditions. No significant Faradaic redox reactions or chemical changes were observed on the electrode surface, which made these electrodes exhibit excellent electrochemical stability even after multiple adsorption/desorption cycles.

New Routes for Multi-component Atomically Precise Metal Nanoclusters

Esma Khatun and Thalappil Pradeep

ACS Omega, 2020 (Invited Perspective) (DOI: 10.1021/acsomega.0c04832)

Abstract:
Atomically precise metal nanoclusters (NCs), protected by a monolayer of ligands are regarded as potential building blocks for advanced technologies. They are considered as intermediates between the atomic/molecular regime and the bulk. Incorporation of foreign metals in NCs enhances several of their properties such as catalytic activity, luminescence and so on; hence, it is of high importance for tuning their properties and broadening the scope of applications. In most of the cases, enhancement in specific properties was observed upon alloying due to the synergistic effect. In the past several years, many alloy clusters have been synthesized which show a tremendous change in the
properties than their monometallic analogs. However, controlling the synthesis and tuning the structures of alloy NCs with atomic precision are major challenges. Various synthetic methodologies have been developed so far for the controlled synthesis of alloy NCs. In this perspective, we have highlighted those diverse synthetic routes to prepare alloys which include co-reduction, galvanic reduction, antagalvanic reduction, metal deposition, ligand exchange, intercluster reaction and reaction of NCs with bulk metals. Advancement in synthetic procedures will help in the preparation of alloy NCs with the desired structure and composition. Future perceptions concerning the progress of alloy nanocluster science are also provided.

**Reaction Between Ag\textsuperscript{17\#} and Acetylene Outside the Mass Spectrometer: Dehydrogenation in the Gas Phase**

Madhuri Jash, Rabin Rajan J. Methikkalam, Mohammad Bodiuazzaman, Ganesan Paramasivam and Thalappil Pradeep


**Abstract:**

We present the first example of acetylide protected silver clusters by a reaction between Ag\textsuperscript{17\#} and acetylene, conducted around atmospheric pressure. The products were obtained after dehydrogenation of acetylene in the gas phase. The observed reaction mechanism may be helpful to design new catalysts useful in organometallic chemistry.

Ag\textsubscript{15}H\textsubscript{13}(DPPH)\textsubscript{5}\textsuperscript{2\#} and [Ag\textsubscript{27}H\textsubscript{22}(DPPB)\textsubscript{7}]\textsuperscript{3\#}: Two New Hydride and Phosphine Co-Protected Clusters and Their Fragmentation Leading to Naked Clusters, Ag\textsubscript{13\#} and Ag\textsubscript{25\#}

Madhuri Jash, Esma Khatun, Papri Chakraborty, Chennu Sudhakar, and Thalappil Pradeep

*J. Phys. Chem. C* 2020, 124, 20569−20577 (DOI: 10.1021/acs.jpcc.0c05867)

**Abstract:**

Here, we report the synthesis of two new hydride and phosphine coprotected clusters [Ag\textsubscript{15}H\textsubscript{13}(DPPH)\textsubscript{5}]\textsuperscript{2\#} (DPPH = 1,6-bis(diphenylphosphino)-hexane) and [Ag\textsubscript{27}H\textsubscript{22}(DPPB)\textsubscript{7}]\textsuperscript{3\#} (DPPB = 1,4-bis(diphenylphosphino)butane). The cluster composition was confirmed by high-resolution electrospray ionization mass spectrometric (HRESI MS) studies and also by other supporting data. To the best of our knowledge, the newly synthesized [Ag\textsubscript{15}H\textsubscript{13}(DPPH)\textsubscript{5}]\textsuperscript{2\#} and [Ag\textsubscript{27}H\textsubscript{22}(DPPB)\textsubscript{7}]\textsuperscript{3\#} clusters are the smallest and the largest known hydride and phosphine coprotected silver clusters, respectively.
synthesized in the solution phase. Collision-induced dissociation (CID) was used to probe their fragmentation pattern in the gas phase, which also supported their compositions. During the CID experiment, naked clusters Ag_{13}^+ and Ag_{25}^+ got formed starting from the ligated Ag_{15} and Ag_{27} clusters, respectively, where the number of metal atoms remained nearly the same as in the parent clusters.

Collision energy-dependent fragmentation pathways of the formation of naked clusters have been explored in detail. We suggest that silver clusters protected by hydride and phosphine ligands may become useful precursors to make new naked clusters in the gas phase.

**Accelerated Microdroplet Synthesis of Benzimidazoles by Nucleophilic Addition to Protonated Carboxylic Acids**

**Pallab Basuri, L. Edwin Gonzalez, Nicolás M. Morato, Thalappil Pradeep and R. Graham Cooks**


**Themed collection: Celebrating 10 years of Chemical Science**

**Abstract:**

We report a metal-free novel route for the accelerated synthesis of benzimidazole and its derivatives in the ambient atmosphere. The synthetic procedure involves 1,2-aromatic diamines and alkyl or aryl carboxylic acids reacting in electrostatically charged microdroplets generated using a nano-electrospray (nESI) ion source. The reactions are accelerated by orders of magnitude in comparison to the bulk. No other acid, base or catalyst is used. Online analysis of the microdroplet accelerated reaction products is performed by mass spectrometry. We provide evidence for an acid catalyzed reaction mechanism based on identification of the intermediate arylamides. Their dehydration to give benzimidazoles occurs in a subsequent thermally enhanced step. It is suggested that the extraordinary acidity at the droplet surface allows the carboxylic acid to function as a C-centered electrophile. Comparisons of this methodology with data from thin film and bulk synthesis lead to the proposal of three key steps in the reaction: (i) formation of an unusual reagent (protonated carboxylic acid) because of the extraordinary conditions at the droplet interface, (ii) accelerated bimolecular reaction because of limited solvation at the interface and (iii) thermally assisted elimination of water. Eleven examples are shown as evidence of the scope of this chemistry. The accelerated synthesis has been scaled-up to establish the substituent-dependence and to isolate products for NMR characterization.

**Microdroplet Impact-Induced Spray Ionization Mass Spectrometry (MISI MS) for Online Reaction Monitoring and Bacteria Discrimination**

**Pallab Basuri, Subhashree Das, Shantha Kumar Jenifer, Sourav Kanti Jana, and Thalappil Pradeep**

*JASMS, 2020 (doi.org/10.1021/jasms.0c00365)*

**Abstract:**

Microdroplet impact-induced spray ionization (MISI) is demonstrated involving the impact of microdroplets produced from a paper and their impact on another, leading to the ionization of analytes deposited on the latter. This cascaded process is more advantageous in comparison to standard spray ionization as it performs reactions and ionization simultaneously in the absence of high voltage directly applied on the sample. In MISI, we apply direct current (DC)
potential only to the terminal paper, used as the primary ion source. Charge transfer due to microdroplet/ion deposition on the flowing analyte solution on the second surface generates secondary charged microdroplets from it carrying the analytes, which ionize and get detected by a mass spectrometer. In this way, up to three cascaded spray sources could be assembled in series. We show the detection of small molecules and proteins in such ionization events. MISI provides a method to understand chemical reactions by droplet impact. The C–C bond formation reactions catalyzed by palladium and alkali metal ion encapsulation using crown ether were studied as our model reactions. To demonstrate the application of our ion source in a bioanalytical context, we studied the noninvasive in situ discrimination of bacteria samples under ambient conditions.

Enhanced Capture of Particulate Matter by Molecularly Charged electrospun Nanofibers
Pillalamarri Srikrishnarka, Vishal Kumar, Tripti Ahuja, Vidhya Subramanian, Arun Karthick Selvam, Paulami Bose, Shantha Kumar Jenifer, Ananthu Mahendranath, Mohd Azhardin Ganayee, Ramamurthy Nagarajan, and Thalappil Pradeep
ACS Sustainable Chem. Eng. 2020, 8, 21, 7762–7773 (DOI: 10.1021/acssuschemeng.9b06853)

Abstract:
As the concentrations of these PMs have been steadily increasing in the Southeast Asian countries, a dire need for protection against these particles is warranted. Filtering out the polluted air using various filtration media, such as face masks and nasal filters, has been the standard method for minimizing exposure to PM. Here, we demonstrate the removal of PM and VOCs by utilizing electrospun nanofibers of polystyrene (PS) and polyacrylonitrile (PAN) with molecular charges imparted on them via chemical treatment. The chemically treated fibers were successful in capturing even particles measuring 300 nm, which are considered to be the most penetrable particles. We report a filtration efficiency of ~93% for removing such particles, which is ~3 ± 1.5% enhancement when compared to the untreated fibers. The fibers have been subjected to extreme haze conditions (~1413 μg m⁻³) of PM2.5 for a duration of 1 h, and the filtration efficiency was measured to be ~99.01%. These fibers also possess the capability to capture model VOCs such as aniline, toluene, tetrahydrofuran, and chloroform. When PAN, PS, and their chemically treated counterparts were tested for their antibacterial activity, these filter mats had bactericidal effect on Escherichia coli, Bacillus subtilis, and Enterococcus faecalis. A nasal plug hosting these filter mats has been designed, which can offer personal protection from PM. Enhanced removal of residual particles is extremely important, and this difficult task is made possible with our approach. The efficiency of our approach is due to the charged nature of PM, especially of the smaller size regime.

Evaluating the Impact of Tailored Water Wettability on Performance of CO₂ Capture
Adil Majeed Rather, Pillalamarri Srikrishnarka, Avijit Baidya, Arpita Shome, Thalappil Pradeep and Uttam Manna
ACS Appl. Energy Mater. 2020, 3, 11, 10541–10549 (DOI: 10.1021/acsaem.0c01603)
Abstract:

The growing emission of CO$_2$ is a severe cause of concern due to its adverse impact on the environment and climate change worldwide. In the past, various approaches, including synthesis of porous materials and amino modifications, were adopted for efficient and direct separation of CO$_2$ from flue gas. Recently, hydrophobicity has been introduced to protect some of the highly potent porous materials and membranes from high humidity and aqueous exposures. While these approaches remained successful in removing CO$_2$ from flue gas, the exact role of hydrophobicity towards CO$_2$ separation is not yet validated in the literature. In this current study, an amine-amplified chemically reactive coating on fibrous cotton has been unprecedentedly developed for facile tailoring of different water wettability through the 1,4-conjugate addition reaction under ambient conditions. Further, these amine-amplified interfaces having tailored water wettability were extended to investigate independently the role of: (a) amine amplification and (b) hydrophobicity on the performance of CO$_2$ separation at room temperature and atmospheric pressure. The increased hydrophobicity on the amine-amplified interface played an important role in improving the CO$_2$ uptake from 24 mmol/L (water contact angle (WCA) of 86°) to 63 mmol/L (WCA of 151°). However, superhydrophobic coating that lacked the amine amplification process displayed a poor (7 mmol/L) CO$_2$ separation performance. Thus, controlled amalgamation of amine amplification and bioinspired superhydrophobicity in fibrous cotton lead to a synergistic impact towards efficient CO$_2$ separation at ambient temperature and pressure, irrespective of the level of humidity present during the course of the experiments. Thus, this current study would allow to design a more potent CO$_2$ removal material by strategic association of porosity, amine modulation, and liquid wettability.

Atom Transfer Between Precision Nanoclusters and Polydispersed Nanoparticles: A Facile Route for Monodispersed Alloy Nanoparticles and Their Superstructures

Paulami Bose, Papri Chakraborty, Jyoti Sarita Mohanty, Nonappa, Angshuman Ray Chowdhuri, Esma Khatun, Tripti Ahuja, Ananthu Mahendranath and Thalappil Pradeep

Nanoscale, 12 (2020) 22116-22128 (DOI: 10.1039/D0NR04033A)

Abstract:

Reactions between atomically precise noble metal nanoclusters (NCs) have been studied widely in the recent past, but such processes between NCs and plasmonic nanoparticles (NPs) have not been explored earlier. For the first time, we demonstrate spontaneous reactions between an atomically precise NC, Au$_{25}$(PET)$_{18}$ (PET = 2-phenylethanethiol), and polydisperse silver NPs with an average diameter of 4 nm and protected with PET resulting in alloy NPs under ambient conditions. These reactions were specific to the nature of the protecting ligands as no reaction was observed between Au$_{25}$(SBB)$_{18}$ NC (SBB = 4-(tert-butyl)benzyl mercaptan) and the very same silver NPs. The mechanism involves an interparticle exchange of the metal and ligand species where the metal-ligand interface plays a vital role in controlling the reaction. The reaction proceeds through transient Au$_{25}$xAg$_x$(PET)$_n$ alloy cluster intermediates as observed in time-dependent electrospray.
ionization mass spectrometry (ESI MS). High-resolution transmission electron microscopic (HRTEM) analysis of the resulting dispersion showed the transformation of polydispersed silver NPs into highly monodispersed gold-silver alloy NPs which assembled to form 2-dimensional superlattices. Using NPs of other average sizes (3 and 8 nm), we demonstrated that size plays an important role in the reactivity as observed in ESI MS and HRTEM.

Dithiol-Induced Contraction in Ag\textsubscript{14} Clusters and Its Manifestation in Electronic Structures

Mohammad Bodiuazzaman, Esma Khatun, Korath Shivan Sugi, Ganesan Paramasivam, Wakeel Ahmed Dar, Sudhadevi Antharjanam, and Thalappil Pradeep

*J. Phys. Chem. C, 124 (2020) 23426–23432 (DOI: 10.1021/acs.jpcc.0c07140)*

**Abstract:**

We report a dithiol-protected silver cluster, Ag\textsubscript{14}(BDT)\textsubscript{6}(PPh\textsubscript{3})\textsubscript{8} (BDT = 1,2-benzene dithiol), abbreviated as Ag\textsubscript{14}DT, which exhibits distinctly different optical properties than the analogous monothiol-protected Ag\textsubscript{14}(SC\textsubscript{6}H\textsubscript{5}F\textsubscript{2})\textsubscript{12}(PPh\textsubscript{3})\textsubscript{8}, abbreviated as Ag\textsubscript{14}MT. Replacement of monothiol by dithiol, keeping the composition constant, has not been possible so far. The inner cores of both Ag\textsubscript{14}DT and Ag\textsubscript{14}MT are composed of octahedral Ag\textsubscript{6}, but because of the presence of dithiol, the outer cubic Ag\textsubscript{8} shell became distorted in the former. Consequently, Ag\textsubscript{14}DT showed a unique absorption in the near-infrared (NIR) region, which is mainly due to transitions derived from ligands. It exhibits dual visible/NIR emission, at around 680 and 997 nm. The cluster with NIR absorption and emission open up a possibility for their application in solar thermal conversion and medical imaging. NIR luminescence in the range of 1000 nm in ultrasmall clusters is very new.

Co-crystals of Atomically Precise Noble Metal Nanocluster

Mohammad Bodiuazzaman, Wakeel Ahmed Dar and Thalappil Pradeep

*Small, (2020), 2003981 (DOI: 10.1002/smll.202003981) (Article ASAP)*

**Abstract:**

Co-crystallization is a phenomenon involving the assembly of two or more different chemical entities in a lattice, occurring typically through supramolecular interactions. It encompasses the study of multi-component crystalline solids as well as their design principles. In the last decade, co-crystals have become popular as a potential new solid form in pharmaceuticals. However, the study of co-crystals in nanomaterials is extremely limited. In this Concept, we present recent advancements in the co-crystallization of atomically precise noble metal cluster systems and their potential directions for future. In the beginning, we briefly introduce atomically precise clusters, their crystals, and importance of thiolate-protected nanoclusters. In the subsequent sections, we explain different strategies to create co-assembly of thiolate-protected noble metal nanoclusters. In the subsequent sections, we explain different strategies to create co-assembly of thiolate-protected noble metal nanoclusters. First approach introduced in this regard is the simultaneous synthesis, and co-crystallization of two clusters having similar structures, such as the same shell but different metal cores, as in a unique pair of clusters found recently, namely Ag\textsubscript{40} and Ag\textsubscript{46}. In
Another category, there is the same core, namely Ag\textsubscript{116} with different shells, as in a mixture of Ag\textsubscript{210} and Ag\textsubscript{211} nanoclusters. Next, we present an intercluster reaction to create mixed solids through selective crystallization of the reaction products. The co-existence of competing effects, magic sizes, and magic electron shells in a co-assembly of alloy nanoclusters is discussed next. Finally, an assembly strategy for metal nanoclusters using electrostatic interactions is described. We conclude this Concept with a future perspective on the emerging possibilities of mixed solids of atomically precise clusters of noble metals. Advancements in this field will certainly help the development of novel materials with potential optical, electrical, magnetic, and mechanical properties.

**Atomically Precise Noble Metal Cluster-Assembled Superstructures in Water: Luminescence Enhancement and Sensing**

Abhijit Nag, Papri Chakraborty, Athira Thacharon, Ganesan Paramasivam, Biswajit Mondal, Mohammad Bodiuazzaman and Thalappil Pradeep

*J. Phys. Chem. C, 124 (2020) 23426–23432 (DOI: 10.1021/acs.jpcc.0c07140)*

**Abstract:**

We present an example of host-guest complexes of atomically precise noble metal nanoparticles with cucurbit[7]uril (CB) in water, specifically concentrating on Ag\textsubscript{29}(LA)\textsubscript{12} (where LA is α-lipoic acid), a well-known red luminescent silver cluster. Such host-guest interactions resulted in enhanced luminescence of about 1.25 times for the modified system, compared to the parent cluster. We extended our study to cyclodextrins (CDs), where about 1.5 times enhanced luminescence was estimated compared to the parent cluster. The formation of supramolecular complexes was confirmed using high-resolution electrospray ionization mass spectrometry (HRESI MS) and nuclear magnetic resonance spectroscopy. Molecular docking and density functional theory calculations supported our experimental results and showed that while CB formed inclusion complexes by encapsulation of one of the LA ligands of the cluster, CD formed supramolecular adducts by interaction with the cavity built by the ligands on the cluster surface. The complexation was favored by geometrical compatibility. Consequently, these superstructures are labeled as Ag\textsubscript{29}LA\textsubscript{12}∩CB\textsubscript{n} and Ag\textsubscript{29}LA\textsubscript{12}@CD\textsubscript{n} (n = 1–3), where ∩ and @ indicate the inclusion complex and supramolecular adduct, respectively. Solution-phase Ag\textsubscript{29}LA\textsubscript{12}@CD\textsubscript{n} complexes were employed to detect dopamine (10 nM). Luminescent Ag\textsubscript{29}LA\textsubscript{12}@CD\textsubscript{n} and Ag\textsubscript{29}LA\textsubscript{12}∩CB\textsubscript{n} complexes in water could be potential candidates for organic pollutant sensing and biomedical applications.

**A Smartphone-Based Fluoride-Specific Sensor for Rapid and Affordable Colorimetric Detection and Precise Quantification at Sub-ppm Levels for Field Applications**
Abstract:

Higher levels of fluoride (F-) in groundwater constitute a severe problem that affects more than 200 million people spread over 25 countries. It is not only essential to detect but also accurately quantify aqueous F- to ensure safety. Need of the hour is to develop smart water quality testing systems that would be effective in location-based real-time water quality data collection, devoid of professional expertise for handling. We report a cheap, handheld, portable mobile device for colorimetric detection and rapid estimation of F-in water by the application of the synthesized core-shell nanoparticles (near-cubic ceria@zirconia nanocages) and a chemoresponsive dye (xylenol orange). The nanomaterial has been characterized thoroughly and the mechanism of sensing has been studied in detail. The sensor system is highly selective towards F- and shows unprecedented sensitivity in the range of 0.1 to 5 ppm of F-, in field water samples, which is the transition regime where remedial measures may be needed. It addresses multiple issues expressed by indicator based metal complexes used to determine F- previously. Consistency in the performance of the sensing material has been tested with synthetic F- standards, water samples from F- affected regions, and dental care products like toothpastes and mouthwash using a smartphone attachment and by naked eye. The sensor performs better than prior reports on aqueous F- sensing.

Dual Emitting Ag$_{35}$ Nanocluster Protected by 2-Pyrene Imine Thiol


Abstract:

In this communication, we present the synthesis of 2-pyrene imine thiol (2-PIT)-protected Ag$_{35}$ nanoclusters using a ligand exchange-induced structural transformation reaction. The formation of the nanocluster and its composition were confirmed through several spectroscopic and electron microscopic studies. UV-vis absorption spectrum showed a set of characteristic features for the nanocluster. This nanocluster showed blue emission under UV light due to pyrene to metal core charge-transfer, and a NIR emission due to charge-transfer within the metal core. This is the first report of dual emitting pyrene protected atomically precise silver nanocluster.
Ligand structure and charge state-dependent separation of monolayer protected Au25 clusters using non-aqueous reversed-phase HPLC

Korath Shivan Sugi, Shridevi Bhat, Abhijit Nag, Ganesan Paramasivam, Ananthu Mahendranath, and Thalappil Pradeep

Analyst, 145 (2020) 1337-1345 (DOI: 10.1039/c9an02043h)

Abstract:

The synthesis of atomically precise noble metal clusters using various protocols often results in a mixture of clusters with different cores. Hence, it is important to isolate such clusters in their pure form in terms of composition especially for crystallization. High-performance liquid chromatography (HPLC) is a powerful tool to achieve this. The interaction of ligands with column functionalities determine the extent of separation and their stability under conditions used. We demonstrate a systematic flow rate dependent study of three different aliphatic ligand protected Au25 clusters, with three commercially available alkyl and aryl functionalized reversed-phase HPLC columns, as they represent the variations encountered commonly. Molecular docking simulations were carried out to understand the interactions between the stationary phase and the cluster surface. These investigations enabled the selection of an appropriate column for better separation of structurally different ligand protected clusters. High-resolution separation of anionic and neutral Au25 clusters was achieved with a selectivity (α) of 1.2 by tuning the chromatographic conditions. This study would provide new insights in developing better methods for the efficient separation of monolayer protected clusters.

Manifestation of Structural Differences of Atomically Precise Cluster-Assembled Solids in Their Mechanical Properties

Korath Shivan Sugi, Payel Bandyopadhyay, Mohammad Bodiuzzaman, Abhijit Nag, Manjapoyil Hridya, Wakeel Ahmed Dar, Pijush Ghosh, and Thalappil Pradeep

Chem. Mater., 32 (2020) 7973–7984 (DOI: 10.1021/acs.chemmater.0c02905)

Abstract:

Cluster-assembled solids (CASs) formed by the self-assembly of monodispersed atomically precise monolayer-protected noble metal clusters are attractive due to their collective properties. The physical stability and mechanical response of these materials remain largely unexplored. We have investigated the mechanical response of single crystals of atomically precise dithiol-protected Ag29 polymorphs, monothiol-protected Ag46, and a cocrystal of the latter with Ag40 (formulas of the clusters have been simplified merely with the number of metal atoms). The Ag29 polymorphs crystallize in cubic and trigonal lattices (Ag29 C and Ag29 T, respectively), and Ag46 and its cocrystal with Ag40 crystallize in trigonal and monoclinic lattices (Ag46 T and Ag40/46 M, respectively). The time and loading-rate-dependent mechanical properties of the CASs are elucidated by measuring nanoindentation creep and stress relaxation. The obtained Young’s modulus (E) values of the CASs were similar to those of zeolitic imidazolate frameworks (ZIFs) and show the trend Ag29 T > Ag29 C > Ag40/46 M > Ag46 T. We have also studied the viscoelastic properties of all of the four CASs and found that the value of tan δ/damping factor of monothiol-protected Ag46 T
was higher than that of other CASs. The unusual mechanical response of CASs was attributed to the supramolecular interactions at the surface of nanoclusters. This observation implies that the stiffness and damping characteristics of the materials can be modulated by ligand and surface engineering. These studies suggest the possibility of distinguishing between the crystal structures using mechanical properties. This work provides an understanding that is critical for designing nanocluster devices capable of withstanding mechanical deformations.

Nonstoichiometric Copper Sulfide Nanostructures at the Brass–Rubber Interface: Implications for Rubber Vulcanization Temperature in the Tire Industry

M. P. Kannan, Anirban Som, Tripti Ahuja, Vidhya Subramanian A. Sreekumaran Nair, and Thalappil Pradeep

ACS Appl. Nano Mater., 3 (2020) 7685–7694 (DOI: 10.1021/acsanm.0c01298)

Abstract:

Brass (which is an alloy of copper and zinc)-coated steel cords (BCSCs) in the form of belts are embedded in rubber compound in radial tires (beneath the tread) to give stability and strength to the tread region of the tires. The life of the tires also depends on the strength and durability of the bond between the BCSCs and rubber. During the vulcanization process with sulphur, a series of sulfide and oxide nanostructures of copper and zinc are formed at the brass-rubber. These nanostructures have a dendritic morphology that can reinforce rubber primarily through mechanical interlocking created through the flow of rubber chains into the dendritic cavities followed by formation of crosslinks between rubber chains during vulcanization. The strength and durability of the bonding depend on a number of parameters such as rubber compound formulation, vulcanization temperature (VT) and time, nanostructure thickness (height) and chemical composition of the nanostructures, etc. (the so-called adhesion interface). A few methods have been stated in literature for assessing the chemical composition and thickness of the adhesion interface. However, simple, reliable and newer methodologies are needed for a better understanding of the same. The present manuscript details a new approach called “brass mesh experiment” to assess the thickness of the adhesion interface formed under particular vulcanization conditions using microscopy. Raman imaging and spectroscopy were employed to determine the chemical composition of the interface with complementary data from X-ray photoelectron spectroscopy and X-ray diffraction. Using the methodologies, VT optimization was done for a tire compound formulation and this was verified by the generally accepted pull-out force method. We believe that the methodologies outlined in the can trigger further research for a better understanding of the adhesion interface in radial tires.

Probing Subtle Changes in Molecular Orientations Using Ambient Electrospray Deposition Raman Spectroscopy (AESD RS)
Abstract:

Herein, subtle changes in the molecular orientations of different thiols upon interaction with soft-landed silver nanoparticles (AgNPs) have been probed using the technique called ambient electrospray deposition Raman spectroscopy (AESD RS). The method collects real-time surface-enhanced Raman scattering (SERS) spectra of analytes as Raman-active AgNPs were electrodeposited on a substrate. We have used p-mercaptobenzoic acid (pMBA), benzenethiol (BT), and cyclohexanethiol (CHT) as proof-of-concept ligands for understanding variations in molecular orientations as a function of time, immediately after 30-40 s of electrospray of AgNPs. During timedependent SERS measurements, we observed that the carboxylate (COO-) group of p-MBA preferred a flat orientation on the NP surface upon interaction with the electrosprayed AgNPs, which later transformed into a tilted two-legged standing-up orientation. We also observed a concomitant change in the orientation of the phenyl ring, which transformed from tilted to a flat orientation with respect to the NP surface. We have found that the time of tilting depends on the concentration of the analyte used for analysis. Additional information on the orientation flipping of thiols was achieved by performing real-time SERS experiments on other thiol derivatives such as CHT and BT. In the case of BT, SERS intensity variations were similar to p-MBA, which were attributed to the changes in orientation. However, in the case of CHT, such SERS intensity variations were absent. Time-dependent SERS spectra of p-MBA, BT, and CHT suggested that the interaction between the π-cloud of the phenyl ring and AgNPs could be one of the triggering factors for such orientation flipping of thiols on NP surfaces.

Entrapping Atomically Precise Clusters in Cyclodextrin-Functionalized Aminoclay Sheets: Synthesis and Enhanced Luminescence

Mohd Azhardin Ganayee, C. K. Manju, Wakeel Ahmed Dar, Biswajit Mondal, and Thalappil Pradeep


Abstract:

In this article, a unique covalently-linked aminoclay substrate, grafted with β-cyclodextrin (AC-CD), was prepared to entrap luminescent silver nanocluster. Chemically synthesized aminoclay (AC) sheets grafted with β-cyclodextrins (β-CD) were used to develop a supramolecular entity. Here, we have grafted β-CD onto aminoclays using cyanuric chloride as a linker. AC-CD material was thoroughly characterized using fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM). The grafting ratio of β-CD onto AC-CD was thoroughly characterized using fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM).
was determined using the phenolphthalein inclusion protocol. The as-prepared functionalized clay (AC-CD) is an effective and attractive material for entrapping a luminescent silver chalcogenide cluster stabilized by 4-(t-butyl)benzyl mercaptan (Ag$_{56}$Se$_{13}$S$_{15}$@SBB$_{28}$ shortened as Ag$_2$Se@SBB). The cluster AC-CD (AC-CD∩Ag$_2$Se@SBB) supramolecular nanocomposite is based on specific host-guest interactions involving β-CD of AC-CD and SBB of silver cluster. Entrapment of the cluster into the β-CD cavity was verified using optical absorption, luminescence spectroscopy, XRD and TEM. The entrapment results in the enhanced luminescence and stability of the cluster. Such a dispersible nanocomposite system exhibiting intense luminescence will be useful in creating novel materials for various applications such as sensors, optoelectronic devices, etc.

**Clean Water through Nanotechnology: Needs, Gaps, and Fulfillment**

Ankit Nagar and Thalappil Pradeep

*ACS Nano, 14 (2020) 6420–6435 (DOI: 10.1021/acsnano.9b01730)*

**Abstract:**

Sustainable nanotechnology has made substantial contributions in providing contaminant-free water to humanity. In this review, we present the compelling need for providing access to clean water through nanotechnology-enabled solutions and the large disparities in ensuring their implementation. We also discuss the current nanotechnology frontiers in diverse areas of the clean water space with an emphasis on applications in the field and provide suggestions for future research. Extending the vision of sustainable and affordable clean water to environment in general, we note that cities can live and breathe well by adopting such technologies. By understanding the global environmental challenges and exploring remedies from emerging nanotechnologies, sustainability in clean water can be realized. We suggest specific pointers and quantify the impact of such technologies.

**Iron Assisted Formation of CO$_2$ over Condensed CO and Its Relevance to Interstellar Chemistry**

Rabin Rajan J. Methikkalam,† Jyotirmoy Ghosh,† Radha Gobinda Bhuin, Soumabha Bag, Gopi Ragupathy, and Thalappil Pradeep (†equal contribution)


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Abstract:

Catalytic conversion of CO to CO$_2$ has been investigated in ultrahigh vacuum (UHV) under cryogenic conditions (10 K). This cryogenic oxidation is assisted by iron upon its co-deposition with CO on a substrate. The study shows that the interaction of Fe and CO results in a Fe-CO complex that reacts in the presence of excess CO at cryogenic conditions leading to CO$_2$. Here, the presence of CO on the surface is a prerequisite for the reaction to occur. Different control experiments confirm that the reaction takes place in the condensed phase and not in the gas phase. Surface sensitive reflection absorption infrared spectroscopy (RAIRS), temperature programmed desorption (TPD), and Cs$^+$ based low energy ion scattering are utilized for this study. The iron assisted formation of CO$_2$ may be proposed as another pathway relevant in interstellar ices, containing CO. This direct oxidation process, which occurs at extremely low temperatures and pressures, iron (the most abundant metal in the interstellar medium) may have astrochemical importance. It does not require any external energy in the form of photo-irradiation or thermal processing. Such reactions are highly relevant in cold dense molecular clouds where interactions between neutral species are more favoured.

Arsenic Toxicity: Carbonate’s Counteraction Revealed

Swathy Jakka Ravindran, Shantha Kumar Jenifer, Jayashree Balasubramanyam, Sourav Kanti Jana, Subramanian Krishnakumar, Sailaja Elchuri, Ligy Philip, and Thalappil Pradeep

ACS Sustainable Chem. Eng. 2020, 8, 13, 5067–5075 (DOI: 10.1021/acssuschemeng.9b06850)

Abstract:

Well-known purification technologies built for arsenic (As) removal from drinking water are not sustainable, either being unaffordable or inefficient in the elimination of traces of As. In our experiments, we observed that carbonate ion can counteract the effects of As exposure as it efficiently prevented As induced cytotoxicity on epithelial cell lines of the small intestine (IEC-6). The cotreatment of IEC-6 cells with 40 ppm of carbonates and As (≥3 ppm) showed substantial remissions in the As-induced cytotoxicity and increased the viability from 50% to 75%. The production of intracellular reactive oxygen species (ROS) and cellular acidification were also reduced in this process (pH increase from 5 to 6.5). Thus, the present study suggests that the cytoprotective effect of carbonate can involve multiple pathways, such as reduction of extracellular/intracellular acidosis, H$_2$O$_2$ decomposition, balancing mitochondrial potential, and immobilization of As. We show that As-contaminated drinking water enriched with carbonates up to 40 ppm has a reduced toxic effect on cells in comparison to that of an As-alone sample. Therefore, carbonates can act as an adjunct in addition to the prevailing approaches to tackle mass poisoning by As.

We believe that this study is initial evidence for developing an alternative method to tackle the prevailing mass environmental poisoning by As, using locally available, affordable, safe, and sustainable solutions.
Fullerene-Mediated Aggregation of $\text{M}_{25}(\text{SR})_{18}^-$ ($\text{M} = \text{Ag, Au}$) Nanoclusters

Papri Chakraborty, Abhijit Nag, Biswajit Mondal, Esma Khatun, Ganesan Paramasivam, and Thalappil Pradeep


Abstract:

We report fullerene ($\text{C}_{60}$ and $\text{C}_{70}$)-induced aggregation of atomically precise clusters, taking $\text{M}_{25}(\text{SR})_{18}^-$ ($\text{M} = \text{Ag, Au}$ and $\text{SR}$ is a thiolate ligand) clusters as an example. We show that dimers, trimers, tetramers, and even higher aggregates of the clusters can be created by supramolecular interaction with fullerenes. Adducts such as $\{\text{M}_{25}(\text{SR})_{18}\}^n(\text{C}_{60})^n−$ ($n = 1–5$), $\{\text{M}_{25}(\text{SR})_{18}\}^n(\text{C}_{60})^{n−1}$ ($n = 2–5$), and $\{\text{M}_{25}(\text{SR})_{18}\}^n(\text{C}_{60})^n$ ($n = 1, 2, 3, ... , etc.$) were formed, which were studied by electrospray ionization mass spectrometry. Similar adducts with $\text{C}_{70}$ were also observed. Structural insights were obtained from molecular docking and density functional theory calculations. Computational studies predicted the possibility of isomerism in some of these adducts. Fullerenes linked multiple clusters, causing aggregation. Fullerenes and clusters formed host–guest complexes in such assemblies. The possibilities of coassembly between the clusters and the fullerenes were also studied in the solid state. The nature of adducts observed in the case of $\text{M}_{25}(\text{SR})_{18}^-$ was completely different compared to the previously reported fullerene adducts of [$\text{Ag}_{29}(\text{BDT})_{12}^3$]− (where BDT is 1,3-benzene dithiol), in which multiple fullerenes were attached on the surface of a single cluster. Supramolecular aggregates formed in the case of $\text{M}_{25}(\text{SR})_{18}^-$ were independent of the nature of the metal atoms (Ag or Au). This implied that for an appropriate geometry of the cluster weak interactions with the ligands and ion-induced dipole interactions were more important in controlling the complexation compared to the metallophilic interactions. Exploring the interaction of atomically precise clusters with fullerenes is important, as the resulting adducts can show new properties such as isomerism, chirality, charge transfer, or enhanced optical properties.

Ultrafast Intersystem Crossing in Isolated Ag29(BDT)123- Probed by Time-Resolved Pump-Probe Photoelectron Spectroscopy

Aron P. Veenstra, Laurenz Monzel, Ananya Baksi, Joseph Czekner, Sergei Lebedkin, Erik K. Schneider, Thalappil Pradeep, Andreas-Neil Unterreiner, and Manfred M. Kappes


Abstract:

The photophysics of the isolated trianion $\text{Ag}_{29}^-\text{(BDT)}_{12}^3$− (BDT = benzenedithiolate), a ligand-protected cluster comprising BDT-based ligands, terminating a shell of silver thiolates and a core of silver atoms, was studied in the gas phase by femtosecond time-resolved, pump-probe photoelectron spectroscopy. UV excitation at 490 nm populates one or more singlet excited states with significant charge transfer (CT) character in which electron
density is shifted from shell to core. These CT states relax on an average time scale of several hundred femtoseconds by charge recombination to yield either the vibrationally excited singlet ground state (internal conversion) or a long-lived triplet (intersystem crossing). Our study is the first ultrafast spectroscopic probe of a ligand-protected coinage metal cluster in isolation. In the future, it will be interesting to study how cluster size, overall charge state, or heteroatom doping can be used to tune the corresponding relaxation dynamics in the absence of solvent.

Nonenzymatic Glucose Sensing Using Ni_{60}Nb_{40} Nanoglass

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Abstract:

Despite being researched for nearly five decades, chemical application of metallic glass is scarcely explored. Here we show electrochemical nonenzymatic glucose-sensing ability of nickel-niobium (Ni_{60}Nb_{40}) amorphous alloys in alkaline medium. Three different Ni_{60}Nb_{40} systems with the same elemental composition, but varying microstructures are created following different synthetic routes and tested for their glucosesensing performance. Among melt-spun ribbon, nanoglass, and amorphous crystalline nanocomposite materials, nanoglass showed the best performance in terms of high anodic current density, sensitivity (20 mA cm^{-2} mM^{-1}), limit of detection (100 nM glucose), stability, reproducibility, (above 5000 cycles), and sensing accuracy among nonenzymatic glucose sensors involving amorphous alloys. When annealed under vacuum, only the heat-treated nanoglass retained a similar electrochemical sensing property, while the other materials failed to yield desired results. In nanoglass, a network of glassy interfaces, compared to melt-spun ribbon, is plausibly responsible for the enhanced sensitivity.

Ferrofluid Microdroplet Splitting for Population-Based Microfluidics and Interfacial Tensiometry

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Abstract:

Ferrofluids exhibit a unique combination of liquid properties and strong magnetic response, which leads to a rich variety of interesting functional properties. Here, the magnetic-field-induced splitting of ferrofluid droplets immersed in an immiscible liquid is presented, and related fascinating dynamics and applications are discussed. A magnetic field created by a permanent magnet induces instability on a mother droplet, which divides into two daughter droplets in less than 0.1 s. During the splitting process, the droplet undergoes a Plateau–Rayleigh-like instability, which is investigated using high-speed imaging further increasing the field results in additional splitting events and self-assembly of microdroplet populations. The dynamics of the resulting satellite droplet formation is shown to depend on the roughness of the supporting surface, which can be magnetically actuated. The effects of magnetization and interfacial tension are systematically investigated by varying magnetic
nanoparticles and surfactant concentrations, and a variety of outcomes from labyrinthine patterns to discrete droplets are observed. As the splitting process depends on interfacial tension, the droplet splitting can be used as a measure for interfacial tension as low as 0.1 mN m⁻¹. Finally, a population-based digital microfluidics concept based on the self-assembled microdroplets is presented.

Phosphorylated Cellulose Nanofibers Exhibit Exceptional Capacity For Uranium Capture

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Abstract:

We investigate the adsorption of hexavalent uranium, U(VI), on phosphorylated cellulose nanofibers (PHO-CNFS) and compare the results with those for native and TEMPO oxidized nanocelluloses. Batch adsorption experiments in aqueous media show that PHO CNF is highly efficient in removing U(VI) in the pH range between 3 and 6. Gelling of nanofiber hydrogels is observed at U(VI) concentration of 500 mg/L. Structural changes in the nanofiber network (scanning and transmission electron microscopies) and the surface chemical composition (X-ray photoelectron spectroscopy) gave insights on the mechanism of adsorption. The results from batch adsorption experiments are fitted to Langmuir, Freundlich, and Sips isotherm models, which indicate a maximum adsorption capacity of 1550 mg/g, the highest value reported so far for any bioadsorbent. Compared to other metals (Zn, Mn, and Cu) and typical ions present in natural aqueous matrices the phosphorylated nanofibers are shown to be remarkably selective to U(VI). The results suggest a solution for the capture of uranium, which is of interest given its health and toxic impacts when present in aqueous matrices.

Association of co accumulation of arsenic and organophosphate insecticides with diabetes and atherosclerosis in a rural agricultural community: KMCH NNCD I study

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Abstract:

In last few decades, the prevalence of diabetes and vascular diseases has intensified concurrently with increased use of synthetic chemicals in agriculture. This study is aimed to evaluate the association of co accumulation of arsenic and organophosphate (OP) insecticides with diabetes and atherosclerosis prevalence in a rural Indian population. This study included observations from KMCH-NNCD-I (2015) cross-sectional study (n = 865) from an Indian farming village. The participants had assessment of clinical parameters including HbA1c and carotid intima–media thickness and urinary heavy metals. Serum OP residues were extracted and quantified by GC–MS. Statistical analyses were performed to unravel the co-association of arsenic and OPs on prevalence of diabetes and atherosclerosis. Results On multivariate regression analyses, total organophosphate level and arsenic accumulation showed association with diabetes and atherosclerosis. Higher odds ratio with significant trends were observed for the sub-quartiles formed by the combination of higher quartiles of arsenic and total organophosphates in association with diabetes and atherosclerosis. Conclusions We observed evidence of possible synergism between arsenic and OPs in association with prevalence of diabetes, pre-diabetes and atherosclerosis in
the study population. Our findings highlight the importance of understanding health effects of mixed exposures and raises vital questions on the role of these agrochemicals in the etiology of diabetes and vascular diseases.

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