



2017



THEMATIC UNIT OF EXCELLENCE
DST UNIT OF NANOSCIENCE





Our materials characterisation laboratory

PREFACE



This brochure showcases the activities of our research group at IIT Madras during the past year.

It is intended to give a pictorial overview of our efforts. It presents the work highlighting the students involved along with the experimental infrastructure. Along with publications, several other related aspects such as patents, conference presentations, recognitions, visits, etc., are showcased. An important component of our work is business incubation and technology implementation. Some highlights of these are also presented.

Each page is about a paper. There is intense hard work behind each one of them. I thank my coworkers whose collective work made science possible. I also thank my collaborators and funding agencies for the success of the projects. Other aspects covered in the brochure are also equally intense in terms of work and dedication.

I am glad to see that many departments and research groups in our institute have started making such brochures showcasing their activities. A visible change in the research atmosphere is evident as a result of all of these activities.

This brochure combines the activities of the Thematic Unit of Excellence on Water Purification Using Nanotechnology and the DST Unit of Nanoscience, both of them are initiatives of Department of Science and Technology under the Nano Mission. Technology implementation was possible due to the support of Central and State Governments. Several companies and different arms of the Institute helped us. Our incubated companies took these tasks and executed them with perfection.

Everything became possible because the continued support of the Institute.

Let me thank each one of these individuals and institutions.

T. Pradeep

January 19, 2018
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Students sitting area of the Thematic Unit of Excellence

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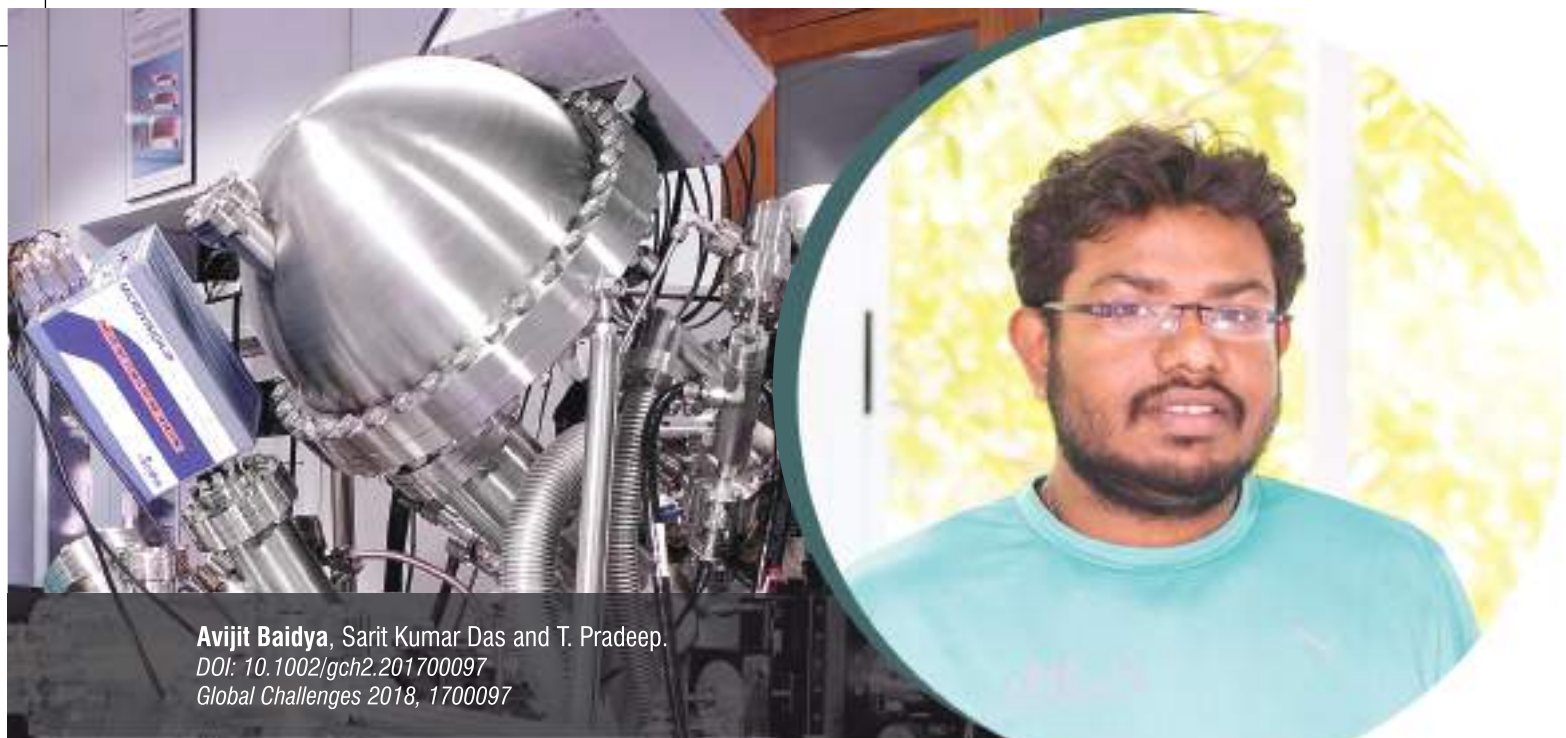
Front inner cover picture - Our materials characterisation laboratory

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Ice chemistry laboratory

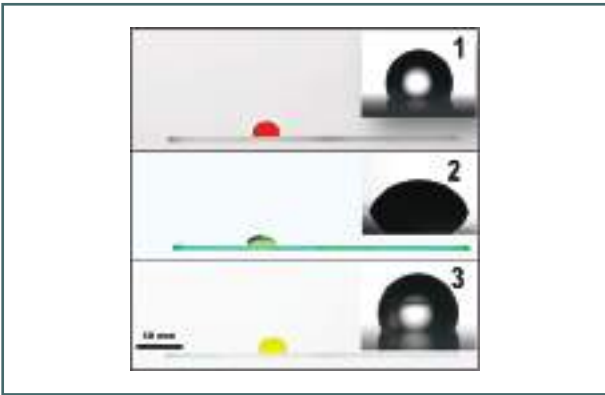


Avijit Baidya, Sarit Kumar Das and T. Pradeep.
DOI: 10.1002/gch2.201700097
Global Challenges 2018, 1700097

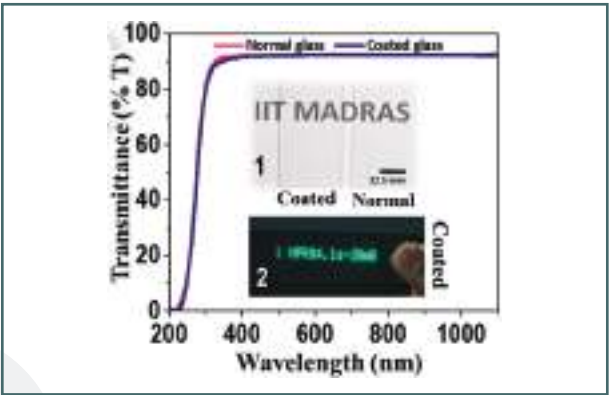
An aqueous composition for lubricant free, robust, slippery, transparent coatings on diverse substrates



Transparent durable coating materials that show excellent liquid repellency, both water and oil, have multiple applications in science and technology. In this perspective, herein, a simple aqueous chemical formulation is developed that provides a transparent slippery coating without any lubricating fluids, on various substrates extended over large areas. The coatings repel liquids having a range of polarity (solvents) as well as viscosity (oils and emulsions) and withstand mechanical strains. Exceptional optical transparency of 99% in the range of 350-900 nm, along with high stability even after cyclic temperature, frost, exposure to sunlight and corrosive liquids like aqua regia treatments make this material unique and widen its applicability in different fields. Besides, being a liquid, it can be coated on an array of substrates independent of their underlying topography, by various easily available techniques. Beside these interesting properties, the coating was demonstrated as a potential solution contributing to the remediation of one of the biggest global issues of tomorrow namely, affordable drinking water. Coated surface can capture 5L of water per day per m² at 27°C when exposed to an atmosphere of 63% relative humidity.



Photographs of the coated surface with different liquids; 1- Water, 2- Toluene, 3- Aqua regia. Inset, the static contact angle of the respective liquids.



Percentage transmission of coated glass in comparison to a normal glass. The coated surface showed 99% transmission when compared to the normal uncoated surface.



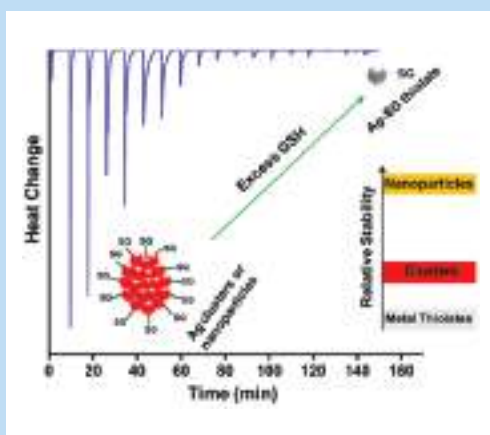
CO-AUTHORS



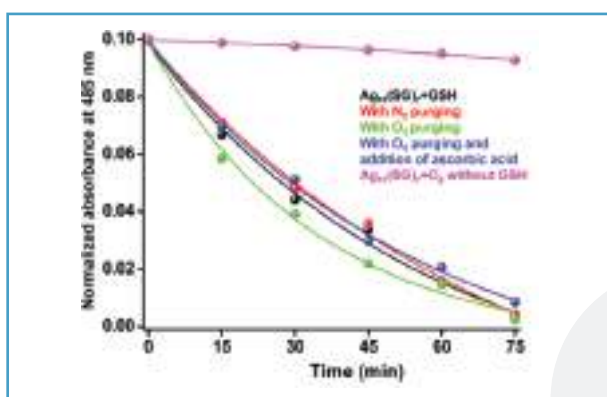
Ananya Baksi, M. S. Bootharaju, Pratap K. Chhotaray, Shridevi Bhat, Papri Chakraborty, Biswajit Mondal, Ramesh Gardas and T. Pradeep.
J. Phys. Chem. C. (2017), 121 (2017) 26483–26492
 (DOI: 10.1021/acs.jpcc.7b07557)



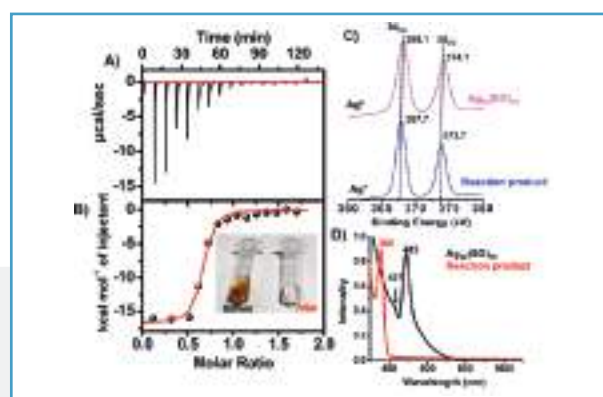
Reactivity of monolayer protected silver clusters toward excess ligand: A calorimetric study



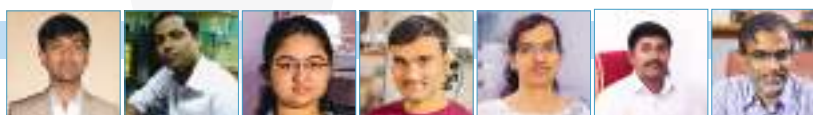
Reactivity of monolayer protected atomically precise clusters of noble metals is of significant research interest. To date very few experimental data are available on the reaction thermodynamics of such clusters. Here we report a calorimetric study of the reaction of glutathione (GSH) protected silver clusters in the presence of excess ligand, GSH, using isothermal titration calorimetry (ITC). We have studied $\text{Ag}_{11}(\text{SG})_7$ and $\text{Ag}_{32}(\text{SG})_{19}$ clusters and compared their reactivity with GSH protected silver nanoparticles (AgNPs) and silver ions. Clusters show intermediate reactivity toward excess ligand compared to nanoparticles and silver ions. Several control experiments were performed to understand the degradation mechanism of these silver clusters and nanoparticles. The effect of dissolved oxygen in the degradation process was studied in detail, and it was found that it did not have a significant role, although alternate pathways of degradation with the involvement of oxygen cannot be ruled out. Direct confirmation of the fact that functionalized metal clusters fall in-between NPs and atomic systems in their stability is obtained experimentally for the first time. Several other thermophysical parameters of these clusters were also determined, including density, speed of sound, isentropic compressibility, and coefficient of thermal expansion.



Degradation of $\text{Ag}_{11}(\text{SG})_7$ cluster at various conditions studied using UV–vis absorption spectroscopy. The absorbance values at 485 nm were normalized and plotted against time.



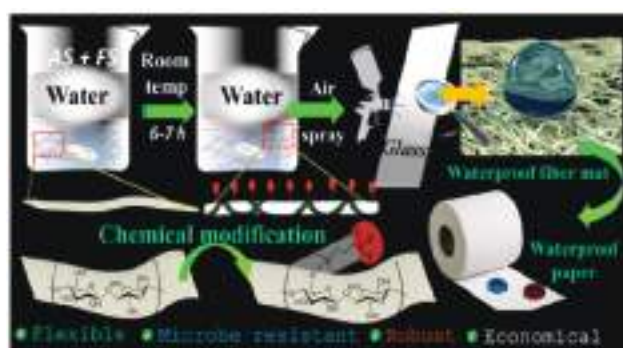
(A) Real-time isothermal titration calorimetric data of $\text{Ag}_{32}(\text{SG})_{19}$ (1 mM) vs GSH (10 mM) and (B) respective heat change data. The data were fitted with a one-site model, and the thermodynamic parameters obtained are listed in Table 1.





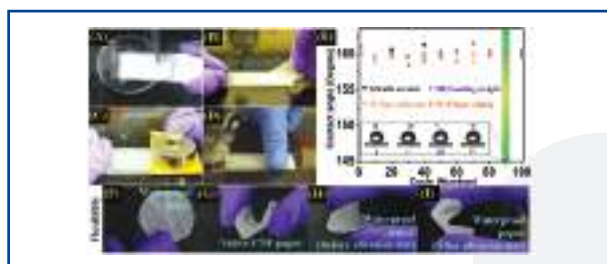
Avijit Baidya, Mohd Azhardin Ganayee, Swathy Jakka Ravindran, Kam (Michael) Tam, Sarit Kumar Das, Robin Ras and T. Pradeep.
ACS Nano, 11 (2017) 11091–11099 (DOI: 10.1021/acsnano.7b05170)

Organic solvent-free fabrication of durable and multifunctional superhydrophobic paper from waterborne fluorinated cellulose nanofiber building blocks

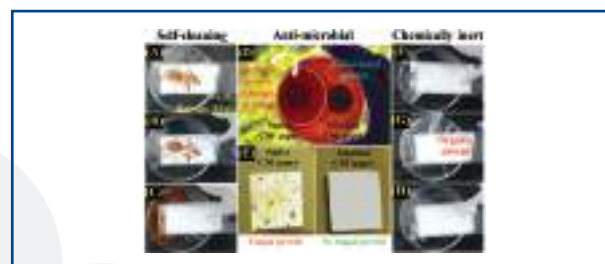


In the view of a great demand for paper-based technologies, non-wettable fibrous substrates with excellent durability have drawn much attention in recent years. In this context, the use of cellulose nanofibers (CNFs), the smallest unit of cellulosic substrates (5-20 nm wide and 500 nm to several microns in length), to design waterproof paper can be an economical and smart approach. In this study, an eco-friendly and facile methodology to develop a multifunctional waterproof paper via the fabrication of fluoroalkyl functionalized CNFs in the aqueous medium is presented. This strategy avoids the need for organic solvents, thereby minimising cost as well as reducing safety and environmental concerns. Besides, it widens the applicability of such materials as nanocellulose-based aqueous coatings on hard and soft substrates including paper, in large areas. Water droplets showed a contact angle of $160^\circ (\pm 2^\circ)$ over these surfaces

and rolled off easily. While native CNFs are extremely hydrophilic and can be dispersed in water easily, this waterborne fluorinated CNFs allow the fabrication of a superhydrophobic film that does not redisperse upon submersion in water. Incorporated chemical functionalities provide excellent durability towards mechano-chemical damages of relevance to daily use such as knife scratch, sand abrasion, spillage of organic solvents, etc. Mechanical flexibility of the chemically modified CNF composed paper remains intact despite its enhanced mechanical strength, without additives. Suprhydrophobicity induced excellent microbial resistance of the waterproof paper which expands its utility in various paper-based technologies. This includes waterproof electronics, currency, books, etc., where the integrity of the fibres, as demonstrated here, is a much-needed criterion.



Mechanical robustness of the modified CNF coated glass and its durability test. Flexibility of waterproof paper.



Inherent properties of the waterborne superhydrophobic CNF coating toward diverse applications.



CO-AUTHORS



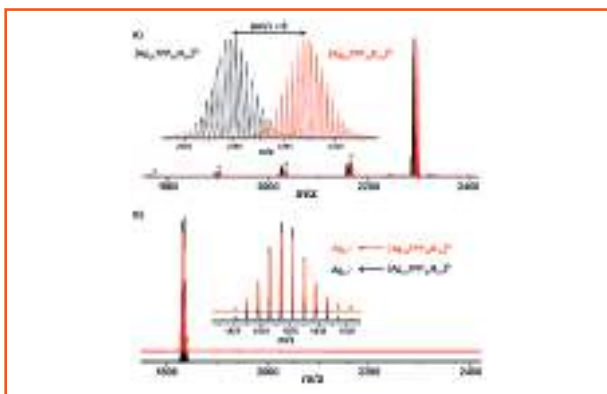
Atanu Ghosh, Mohammad Bodiuzzaman, Abhijit Nag, Madhuri Jash, Ananya Baksi and T. Pradeep.
ACS Nano, 11 (2017) 11145–11151
 (DOI:10.1021/acsnano.7b05406)

Sequential dihydrogen desorption from hydride protected atomically precise silver clusters and the formation of naked clusters in the gas phase

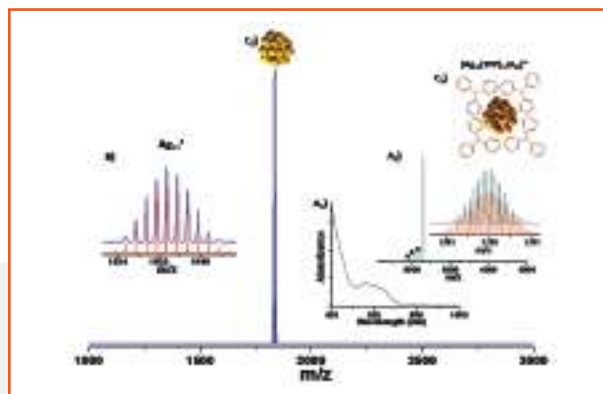
We report the formation of naked cluster ions of silver of specific nuclearities, uncontaminated by other cluster ions, derived from monolayer-protected clusters. The hydride and phosphine co-protected cluster, $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ (TPP, triphenylphosphine), upon activation produces the naked cluster ion, Ag_{17}^+ , exclusively. The number of metal atoms present in the naked cluster is almost the same as that in the parent material. Two more naked cluster ions, Ag_{21}^+ and Ag_{19}^+ , were also formed starting from two other protected clusters, $[\text{Ag}_{25}(\text{DPPE})_8\text{H}_{22}]^{3+}$ and $[\text{Ag}_{22}(\text{DPPE})_8\text{H}_{19}]^{3+}$, respectively (DPPE, 1,2-bis(diphenylphosphino)ethane). By systematic fragmentation, naked clusters of varying nuclei are produced from Ag_{17}^+ to Ag_1^+ selectively, with systematic absence of Ag_{10}^+ , Ag_6^+ , and Ag_4^+ . A seemingly odd number of cluster ions are preferred due to the stability of the closed electronic shells. Sequential desorption of dihydrogen occurs from the cluster ion, $\text{Ag}_{17}\text{H}_{14}^+$, during the formation of Ag_n^+ . A comparison of the pathways in the formation of similar naked cluster ions starting from two differently ligated clusters has been presented. This approach developed bridges the usually distinct fields of gas-



phase metal cluster chemistry and solution-phase metal cluster chemistry. We hope that our findings will enrich nanoscience and nanotechnology beyond the field of clusters.



(A) ESI MS spectra of the parent materials $[\text{Ag}_{18}(\text{TPP})_{10}\text{H}_{16}]^{2+}$ (black trace) and $[\text{Ag}_{18}(\text{TPP})_{10}\text{D}_{16}]^{2+}$ (red trace). (B) Naked Ag_{17}^+ cluster ions produced from the H (black trace) and D (red trace) protected parent clusters, respectively.



Mass spectrum of naked cluster ion (Ag_{17}^+) produced from cluster I. The absence of other peaks in the mass range of m/z 1000–3000 confirms that the product is uncontaminated by other cluster ions

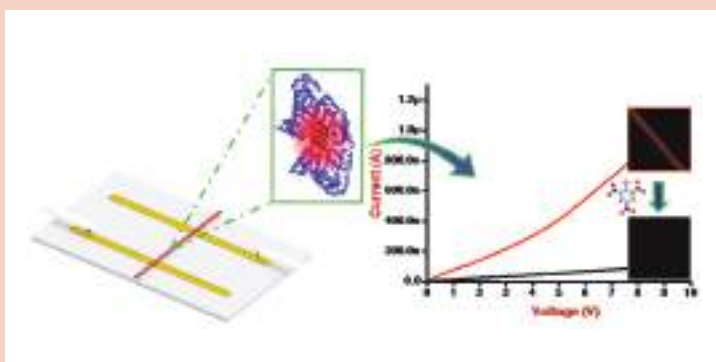




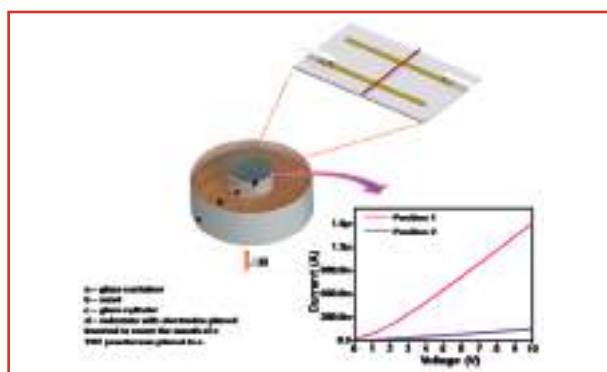
Vidhya Subramanian, Sanjoy Jena, Debasmita Ghosh, Madhuri Jash, Ananya Baksi, Debdutta Ray and T. Pradeep.
ACS Omega, 2 (2017) 7576–7583
 (DOI:10.1021/acsomega.7b01219)

Dual probe sensors using atomically precise noble metal clusters

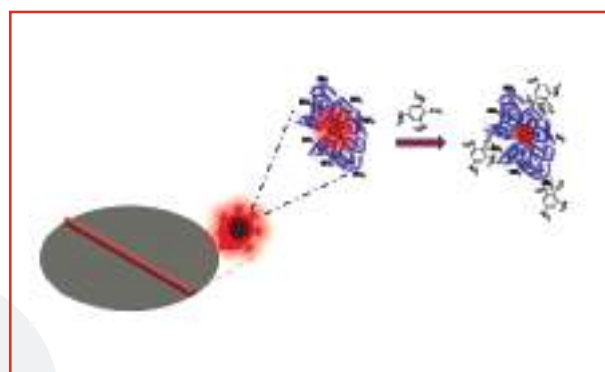
This paper adds a new direction to the functional capability of protein protected atomically precise gold clusters as sensors. Counting on the extensively researched intense luminescence of these clusters and considering the electron donating nature of select amino acids, we introduce a dual probe sensor



capable of sensing changes in luminescence and conductivity, utilizing bovine serum albumin protected atomically precise gold clusters hosted on nanofibers. To this end, we have also developed a hybrid nanofiber with a conducting core with a porous dielectric shell. We show that clusters in combination with nanofibers offer a highly selective and sensitive platform for the detection of trace quantities of trinitrotoluene, both in solution and in the vapor phase. In the solution phase, TNT can be detected down to 1 parts per trillion at room temperature while in vapor phase, 4.8×10^9 molecules of TNT can be sensed using a 1 mm fiber. Though the development in electrospinning techniques for fabricating nanofibers as sensors is quite substantial, a hybrid fiber with the dual properties of conductivity and luminescence has not been reported yet.



Schematic of set-up for vapour sensing experiments. Inset shows the fiber on the electrodes which is probed for I-V studies and the current variation with exposure to TNT.



Schematic representing the formation of Meisenheimer complex between the nitro groups of TNT and the free amino groups of BSA of the Au@BSA cluster immobilised on CNTs@SiO₂ fibers.



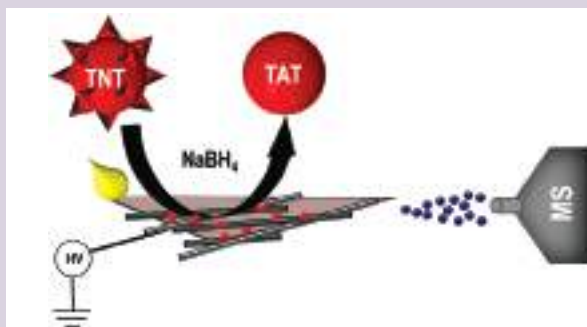
CO-AUTHORS



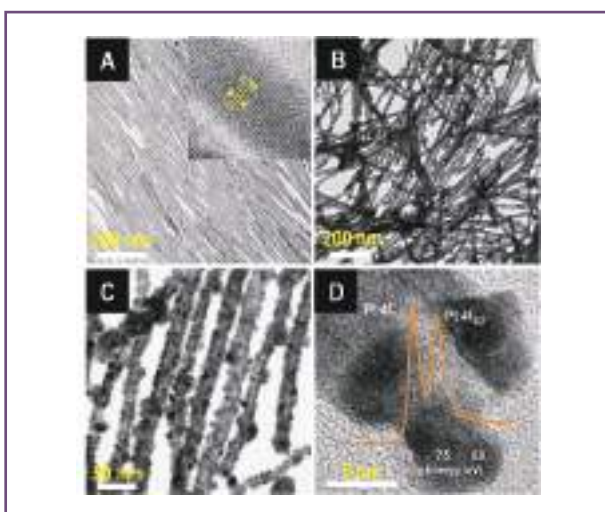
Depanjan Sarkar, Anirban Som and T. Pradeep.
Anal. Chem., 89 (2017) 11378–11382
 (DOI: 10.1021/acs.analchem.7b02288)



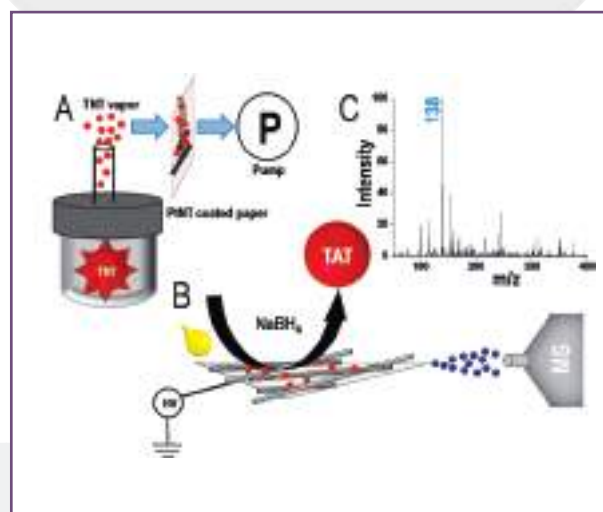
Catalytic paper spray ionization mass spectrometry with metal nanotubes and the detection of 2,4,6-trinitrotoluene (TNT)



Materials are making inroads into mass spectrometry, and an example is the use of advanced materials for enhanced ionization by transformation of a less-ionizable molecule to an easily ionizable one. Here we show the use of Pt nanoparticle-decorated nanotubes as highly active catalysts for the reduction of 2,4,6-trinitrotoluene to 2,4,6-triaminotoluene and subsequent easy detection of the product by in situ ambient ionization mass spectrometry.



A) TEM images of Te NWs, used as a sacrificial template, inset shows HRTEM image of the same showing Te lattices B) PtNTs after the washing (with saturated Na_2CO_3) process, showing uniform coating of PtNPs, C) higher magnification image of the same showing uniformly PtNP coated PtNTs, and D) higher magnification image showing the tubular structure.



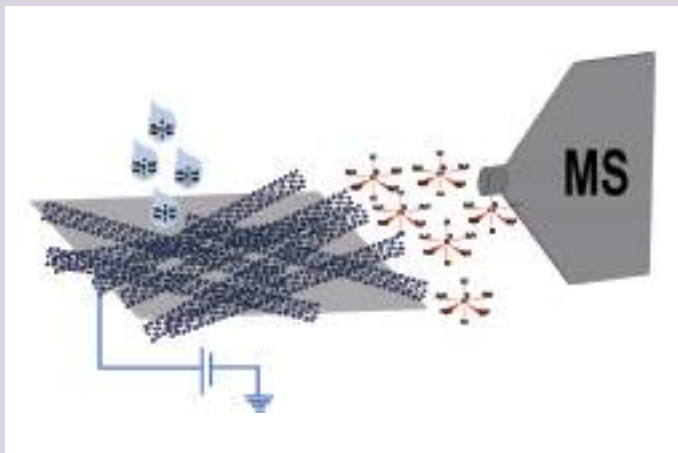
A) Schematic of the process for accumulation of TNT vapor on PtNT coated paper, B) schematic of a typical paper spray ionization process, showing after eluting the TNT adsorbed PtNT coated paper with NaBH_4 solution it transformed to triaminotoluene (TAT), and C) Typical mass spectrum showing peak of TAT at m/z 138.



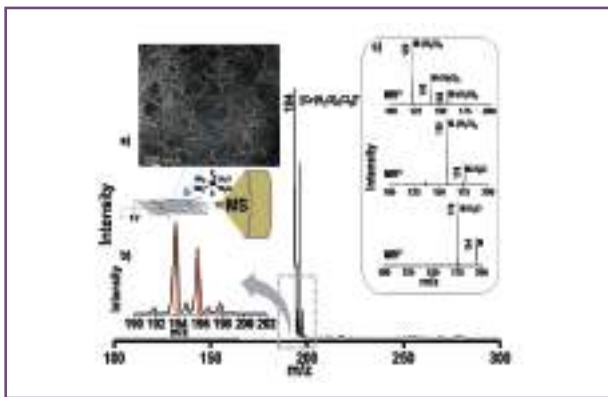


Rahul Narayanan and T. Pradeep.
Anal. Chem., 89 (2017) 10696–10701
 (DOI:10.1021/acs.analchem.7b01129)

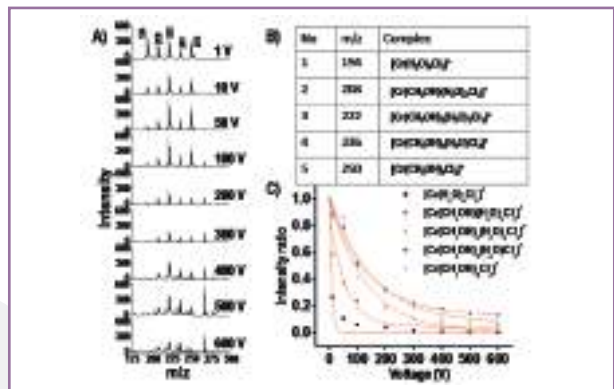
Probing coordination complexes by carbon nanotube-assisted low voltage paper spray ionization mass spectrometry



Fragile transition metal complex ions such as $[\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_2]^+$, difficult to be observed by gas-phase spectroscopy, are detected easily with carbon nanotube (CNT)-assisted low-voltage ambient ionization mass spectrometry. Observation of various substituted ions with D_2O and ROH ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \dots$) established the versatility of the technique in detecting diverse species. Ligand substitution occurring in solution was captured by the low-voltage technique. The extreme softness of the technique coupled with nanoscale ion sources enabled the creation of such species. Analysis was extended to other halides as well. The intensity of these fragile ions gradually disappeared at voltages beyond 500 V and are completely absent in standard high-voltage ionization. Detection of inorganic complexes further enhances the scope of low-voltage ionization.



Mass spectrum of $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$ in water at 1 V. The hexa-coordinated aquochloro chromium complex ion at m/z 194 is seen as the most prominent feature. Schematic of the process along with the FE SEM image of the CNT coated paper (a), experimental and simulated (sticks) mass spectra of the complex ion peak (b) and fragmentation patterns of the base peak at 194 by MS/MS methods (c) are shown in the inset.



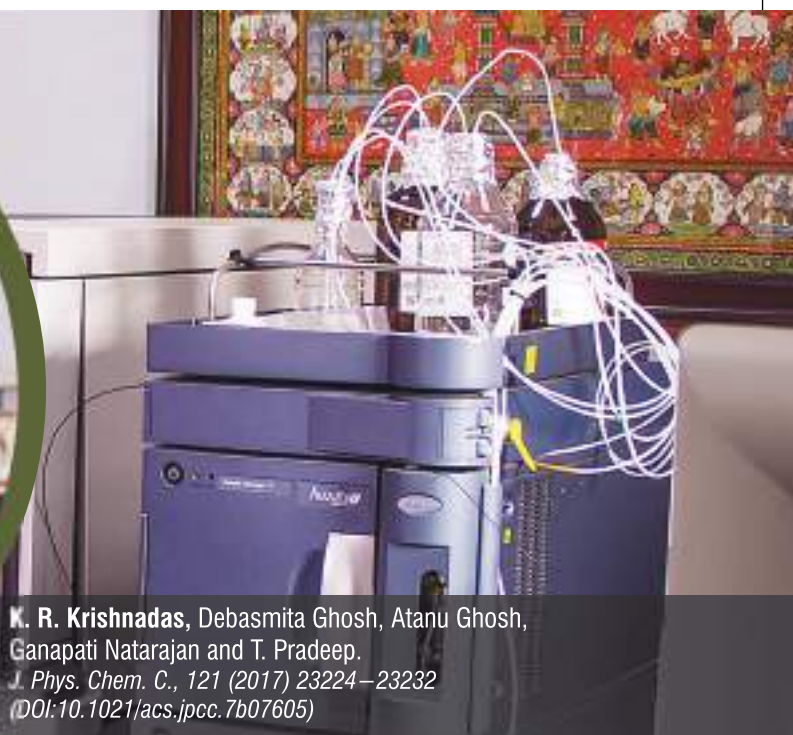
A) Mass spectra collected for methanol substituted Cr-complexes at various voltages, B) list of the complexes identified with their m/z values and C) variation of signal intensity ratio of each complex ion with respect to the voltage applied.



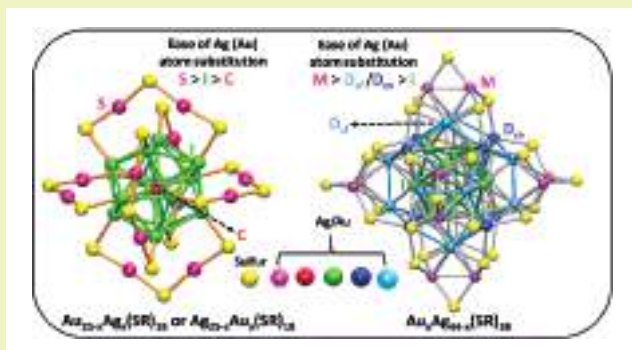
CO-AUTHORS



K. R. Krishnadas, Debasmita Ghosh, Atanu Ghosh,
Ganapati Natarajan and T. Pradeep.
J. Phys. Chem. C, 121 (2017) 23224–23232
(DOI:10.1021/acs.jpcc.7b07605)

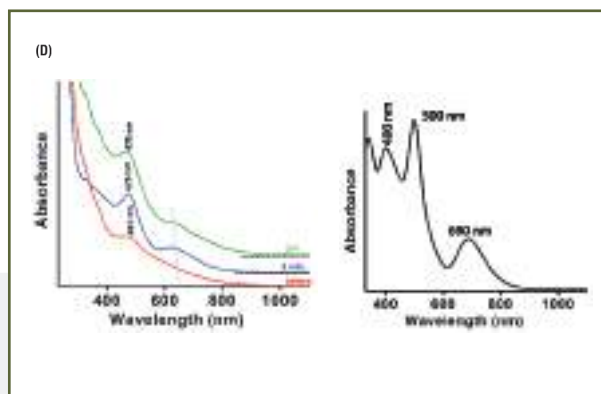
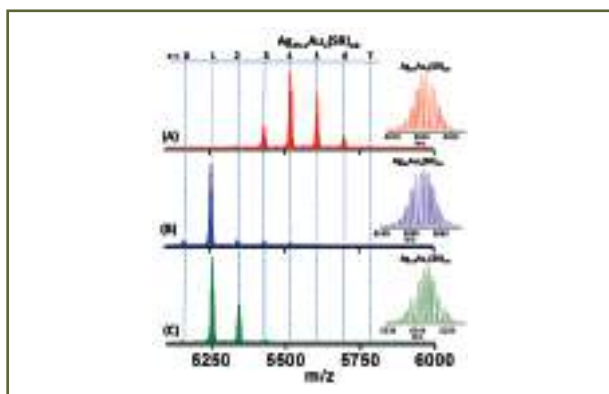


Structure-reactivity correlations in metal atom substitutions of monolayer protected noble metal alloy clusters



Structure-reactivity correlations in metal atom substitution reactions of three model monolayer protected alloy clusters, $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ (I), $\text{Au}_{25-x}\text{Ag}_x(\text{SR})_{18}$ (II) and $\text{Au}_{44-x}\text{Ag}_x(\text{SR})_{30}$ (III) where $(-\text{SR} = \text{alkyl/arylthiolate})$ are demonstrated. We show that the Au atoms of I and III, and Ag atoms of II can be substituted by their reactions with the parent clusters $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{44}(\text{SR})_{30}$ and $\text{Au}_{25}(\text{SR})_{18}$, respectively. Though these alloy clusters possess certain common structural features, they exhibit distinctly different reactivities in these substitution reactions. The Au of I and III, and Ag of II at the outermost sites, i.e., $\text{M}_2(\text{SR})_3$ staples of I and II and $\text{M}_2(\text{SR})_5$ mounts of III, were substituted more easily compared to those at the inner, icosahedral sites. Au atoms at the icosahedral shell of I were completely substituted while Ag atoms of II at similar positions were not labile for substitution. This shows that the icosahedral shell of II

is more rigid compared to that in I. We show that the Au atom in $\text{Ag}_{24}\text{Au}_1(\text{SR})_{18}$ cannot be substituted which indicates that this Au atom is located at the center of the icosahedral shell. Similarly, when $x \leq 12$, the Au atoms of III cannot be substituted, indicating that these atoms are located in the innermost icosahedral shell. In summary, our results demonstrate that metal atom substitution reactions correlates with the geometric structures of these clusters.

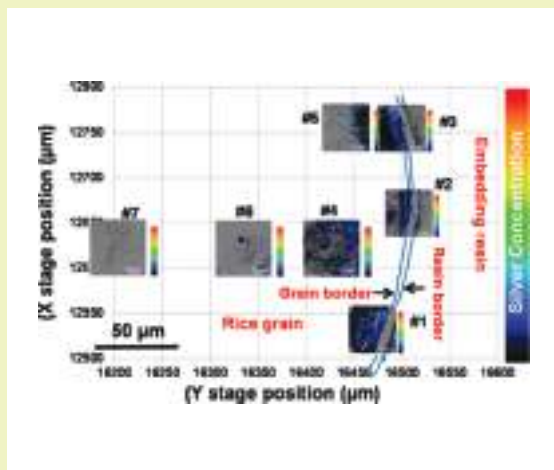


ESI mass spectra (A-C) and UV/Vis absorption spectra (D) of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ before and after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$. Traces A-C are the mass spectra of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ before, 2 minutes and 5 h after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$, respectively. All the features are with isotopic resolution, as illustrated in the respective insets. Red, green and blue traces in (D) are the UV/Vis absorption spectra of $\text{Ag}_{25-x}\text{Au}_x(\text{SR})_{18}$ before, 2 minutes and 5 h after the addition of $\text{Ag}_{25}(\text{DMBT})_{18}$, respectively. UV/Vis spectrum of pure $\text{Ag}_{25}(\text{DMBT})_{18}$ is shown as black trace in (D).





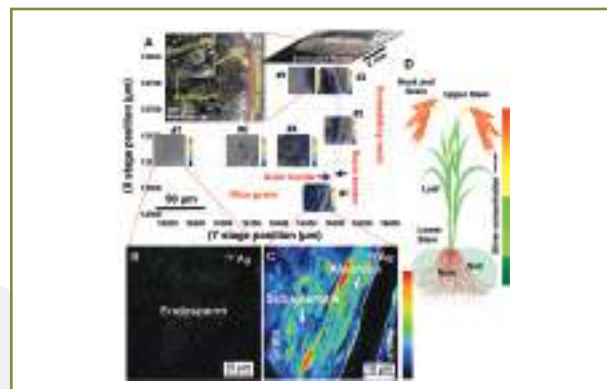
Unusual accumulation of silver in the aleurone layer of an Indian rice (*Oryza sativa*) landrace and sustainable extraction of the metal



Uptake of noble metals by cereal plants is not reported in literature. Our study of 505 native rice landraces showed that nine of them accumulate silver at a high concentration when grown in the same soil. Among these, a medicinal rice landrace from West Bengal, Garib-sal was found to accumulate silver at an especially high concentration in the grains. Cultivation of Garib-sal rice in three successive years in Basudha farm in the rice growing period of June – October confirmed that for the same concentration of silver in the soil (~ 0.15 mg/kg), Garib-sal accumulates it in the grains to the extent of ~ 15 mg/kg. Laboratory experiments also demonstrated that silver uptake by Garib-sal is significantly greater than for other varieties grown on the same soil, and that the metal accumulates mostly in the grain. To detect the location of deposition of silver in the grains, secondary ion mass spectrometry was performed. The images reveal that the silver is concentrated in the aleuronic layer of the rice bran. Its concentration decreases in the subaleurone and becomes negligible in the endosperm. Accumulation of silver does not alter the grain morphology and chemical characteristics. The metal may be extracted from the bran after milling of the rice, thereby causing no loss of the foodstuff.



Photographs of rice grains. Panicles of G02 rice grown in the lab in (A) normal soil; (B) silver enriched soil (sb: 50 mm); (a1 and a2) photograph of a few rice grains corresponding to A and B (sb: 8 mm); (b1 and b2) magnified photograph of decorticated grains corresponding to A and B (sb: 20 mm).



NanoSIMS imaging of a G02 rice grain. (A) Collection of nanoSIMS images from an embedded rice grain showing the distribution of ^{109}Ag at different positions of the grain. Grain border is marked and distinguished from the embedding resin.



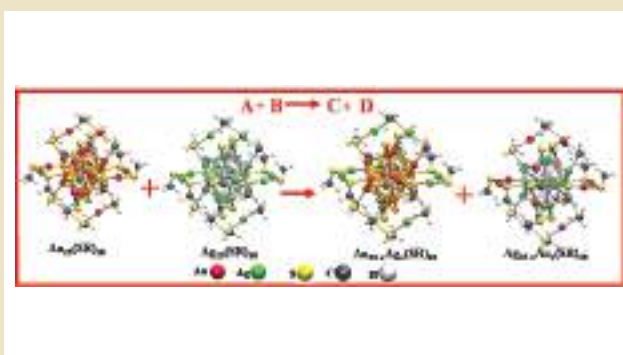
CO-AUTHORS



K. R. Krishnadas, Ananya Baksi, Atanu Ghosh,
Ganapati Natarajan, Anirban Som and T. Pradeep.
Acc. Chem. Res., 50 (2017) 1988–1996
(DOI:10.1021/acs.accounts.7b00224)

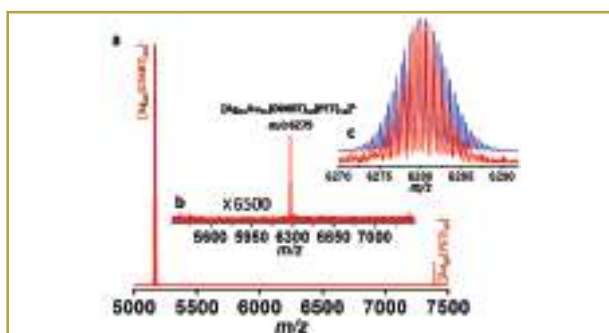


Interparticle reactions: An emerging direction in nanomaterials chemistry

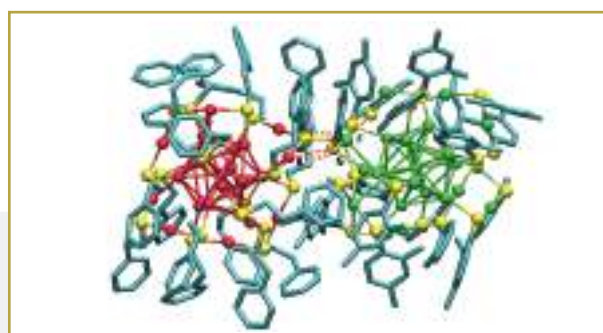


Nanoparticles exhibit a rich variety in terms of structure, composition and properties. However, reactions between them remain largely unexplored. In this Account, we discuss an emerging aspect of nanomaterials chemistry, namely, interparticle reactions in solution phase, similar to reactions between molecules, involving atomically precise noble metal clusters. A brief historical account of the developments, starting from the bare, gas phase clusters, which led to the synthesis of atomically precise monolayer protected clusters in solution, is presented at first. Then a reaction between two thiolate-protected, atomically precise noble metal clusters, $[\text{Au}_{25}(\text{PET})_{18}]^-$ and $[\text{Ag}_{44}(\text{FTP})_{30}]^{4+}$ (PET = 2-phenylethanethiol, FTP = 4-fluorothiophenol) is presented wherein these clusters spontaneously exchange metal atoms, ligands and metal-ligand fragments between them at ambient conditions. Next, a reaction of

$[\text{Au}_{25}(\text{PET})_{18}]^-$ with its structural analogue, $[\text{Ag}_{25}(\text{DMBT})_{18}]$ (DMBT = 2,4-dimethylbenzenethiol) is presented which shows that atom-exchange reactions happen with structures conserved. A reaction involving a dithiolate-protected cluster, $[\text{Ag}_{25}(\text{BDT})_{12}]^{3-}$ (BDT = 1,3-benzenedithiol) is also presented wherein metal atom exchange alone occurs, but with no ligand and fragment exchanges. A new proposed structural model of these clusters, namely, the Borromean ring model to understand the dynamics of the metal-ligand interfaces and to address the site-specificity and selectivity in these reactions. Reactions involving atomically precise noble metal clusters and one- and two-dimensional nanosystems are also presented. In summary, we present the emergence of a new branch of chemistry involving the reactions of atomically precise cluster systems which are prototypical nanoparticles.



Full range ESI MS of the mixture of $\text{Ag}_{25}(\text{DMBT})_{18}$ (I) and $\text{Au}_{25}(\text{PET})_{18}$ (II) at molar ratio (I:II) of 0.3:1.0 measured within 2 min after mixing (a), zoomed in region of panel a in the range between m/z 5270 and 7340 (b) and theoretical (blue) and experimental (red) isotope patterns of the adduct features (c).



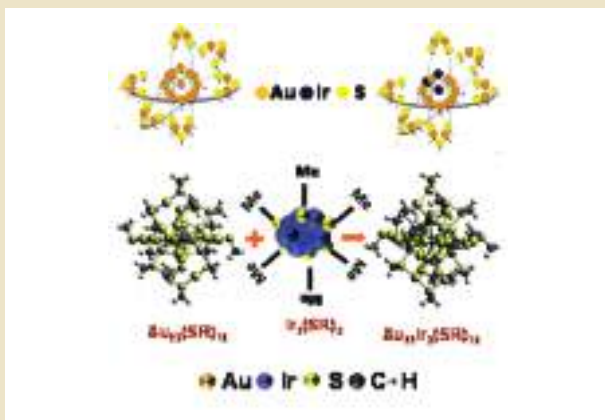
DFT-optimized geometry of $[\text{Ag}_{25}\text{Au}_{25}(\text{DMBT})_{18}(\text{PET})_{18}]^{2-}$ adduct obtained from DFT-optimization of the structure obtained from a force-field-based molecular docking simulation. The hydrogen atoms are omitted from the ligands for clarity.



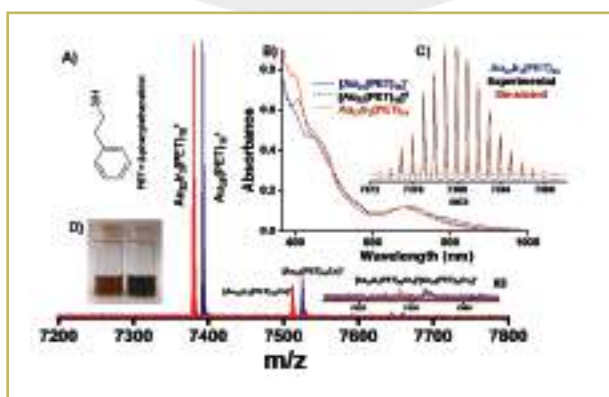


Shridevi Bhat, Ananya Baksi, Sathish Mudedla, Ganapati Natarajan, Venkatesan Subramanian and T. Pradeep
J. Phys. Chem. Lett., 8 (2017) 2787-2793
 (DOI: 10.1021/acs.jpclett.7b01052)

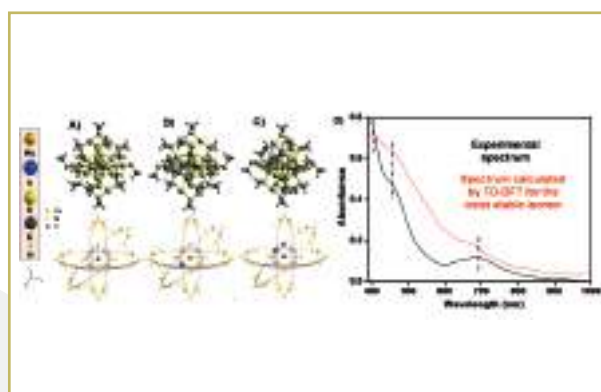
$\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$: An unusual alloy cluster through inter-cluster reaction



An inter-cluster reaction between $\text{Au}_{25}(\text{PET})_{18}$ and $\text{Ir}_9(\text{PET})_6$ producing the alloy cluster, $\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$ exclusively, is demonstrated where the ligand PET is 2-phenylethanethiol. Typical reactions of this kind between $\text{Au}_{25}(\text{PET})_{18}$ and $\text{Ag}_{25}(\text{SR})_{18}$ and other clusters reported previously, produce mixed cluster products. The cluster composition was confirmed by detailed high resolution electrospray ionization mass spectrometry (ESI MS) and other spectroscopic techniques. This is the first example of Ir metal incorporation in a monolayer protected noble metal cluster. The formation of a single product was confirmed by thin layer chromatography (TLC). Density functional theory (DFT) calculations suggest that the most favorable geometry of the $\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$ cluster is one wherein the three Ir atoms are arranged triangularly with one Ir atom at the icosahedral core and the other two on the icosahedral shell. Significant contraction of the metal core was observed due to strong Ir-Ir interactions.



A) ESI MS of $\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$ (red trace) and $\text{Au}_{25}(\text{PET})_{18}$ (blue trace) in positive ion mode. CSOAc was used as the ionization enhancer. B) UV/Vis absorption spectra of $\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$ (red trace) and $[\text{Au}_{25}(\text{PET})_{18}]^+$ (dotted black trace) in DCM. C) Simulated (red trace) and experimental (black trace) isotope distribution of $\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$. D) Photographs of $\text{Au}_{25}(\text{PET})_{18}$ (left) and $\text{Au}_{22}\text{Ir}_3(\text{PET})_{18}$ (right) solutions in DCM with comparable concentrations.



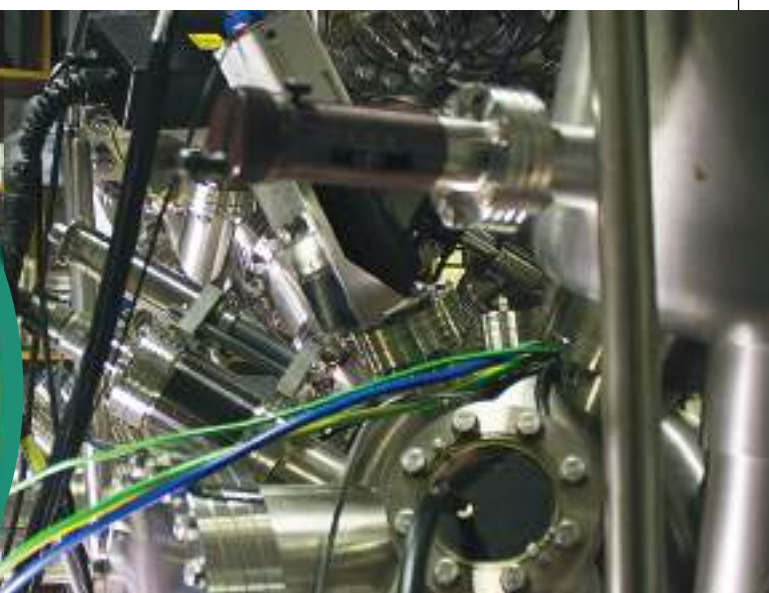
DFT optimized structures of lowest energy isomers of A) $\text{Au}_{24}\text{Ir}_3(\text{SMe})_{18}$, B) $\text{Au}_{22}\text{Ir}_3(\text{SMe})_{18}$, C) $\text{Au}_{22}\text{Ir}_3(\text{SMe})_{18}$. The aspicule representation of each structure is given below the structures. The positions of Ir are labeled prominently. Color code: Golden yellow – Au; bright yellow – S; blue – Ir; gray – C and white – H. D) The calculated UV/Vis absorption spectrum for the most stable isomer of $\text{Au}_{22}\text{Ir}_3(\text{SMe})_{18}$ (red trace) compared with the experimental spectrum (black trace).



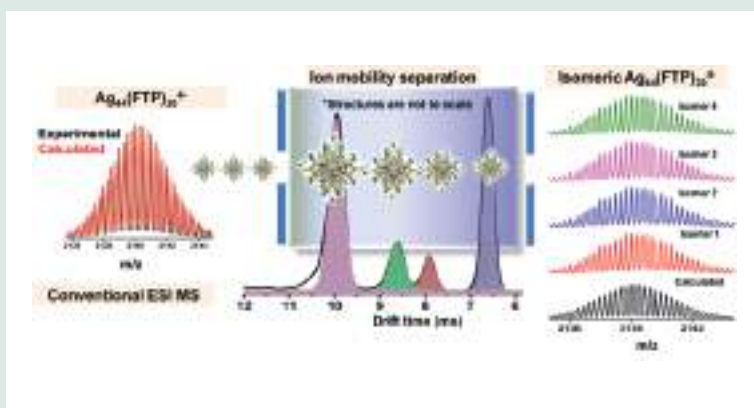
CO-AUTHORS



Ananya Bakshi, Atanu Ghosh, Sathish Mudedla, Papri Chakraborty, Shridevi Bhat, Biswajit Mondal, K. R. Krishnadas, Venkatesan Subramanian and T. Pradeep.
J. Phys. Chem. C, 121 (2017) 13421-13427 (DOI:10.1021/acs.jpcc.7b04559)

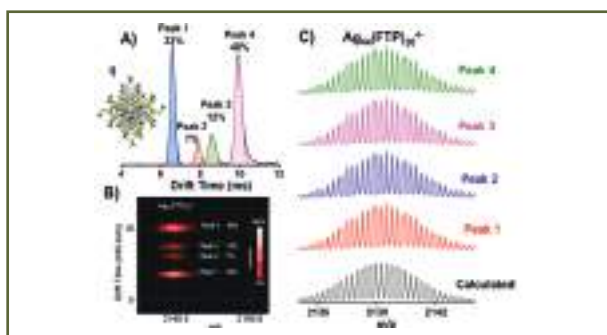


Isomerism in monolayer protected silver cluster ions: An ion mobility-mass spectrometry approach

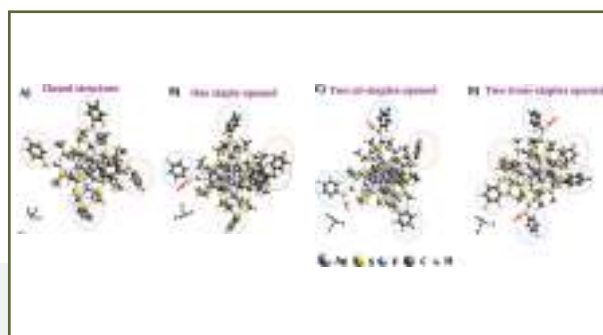


Experimental evidence for the existence of gas phase isomers in monolayer protected noble metal clusters is presented, taking $\text{Ag}_{44}(\text{SR})_{30}$ (SR = 4-fluorothiophenol, p-mercaptobenzoic acid) and $\text{Ag}_{29}(\text{BDT})_{12}$ (BDT: benzene dithiol) clusters as examples which do not show any isomeric structures in their crystals. Electrospray ionization coupled with ion mobility separation allowed for the identification of multiple isomers of $\text{Ag}_{44}\text{SR}_{30}$ cluster in its 3- and 4- charge states, their most abundant gas phase ions. $\text{Ag}_{29}(\text{BDT})_{12}$ showed isomerism in its common 3- charge state. Isomerism is likely to be due to different types of ligand orientations in the staples leading to changes in the overall size and shape of the cluster ions, which was further confirmed by density functional theory calculations

on $\text{Ag}_{44}(\text{FTP})_{30}^{4+}$. No isomers were seen in the ions of the well-known cluster, $\text{Au}_{25}\text{SR}_{18}$ (SR = phenylethanethiol, dodecanethiol, and butanethiol).



(A) Drift time profile of $\text{Ag}_{44}(\text{FTP})_{30}^{4+}$ (m/z 2140) showing four peaks due to distinct isomeric structures with relative abundances of 33, 7, 12, and 48%, respectively (calculated from peak area). Calculated structure of $\text{Ag}_{44}(\text{SMe})_{30}$ is shown in inset (i). (B) Four well-defined spots observed in m/z vs drift time plot. Each spot gave the same mass spectrum as shown in C, matched with the spectrum.



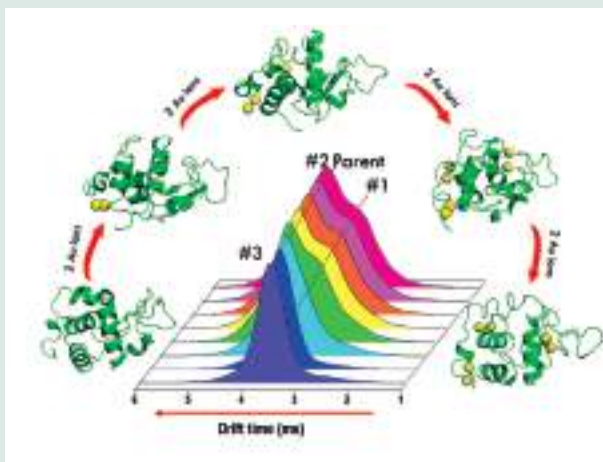
DFT optimized structures of different isomers of $[\text{Ag}_{44}(\text{SMe})_{24}(4\text{-FTP})_8]^{4+}$. Optimized geometries of (A) intact, (B) one staple opened (1), (C) two cis-staples opened, and (D) two trans-staples opened structures. Six axial ligands were optimized without any geometrical constraints. The other 24 positions were replaced with -SMe. Six 4-FTP ligands are circled. Opened positions are shown with arrows and are differently colored.



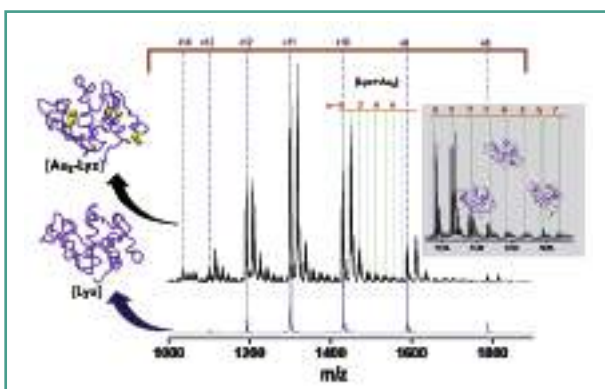


Debasmita Ghosh, Ananya Baksi, Sathish Mudedla, Abhijit Nag, Mohd Azhardin Ganayee, Venkatesan Subramanian and T. Pradeep.
J. Phys. Chem. C, 121 (2017) 13335-13344 (DOI: 10.1021/acs.jpcc.7b02436)

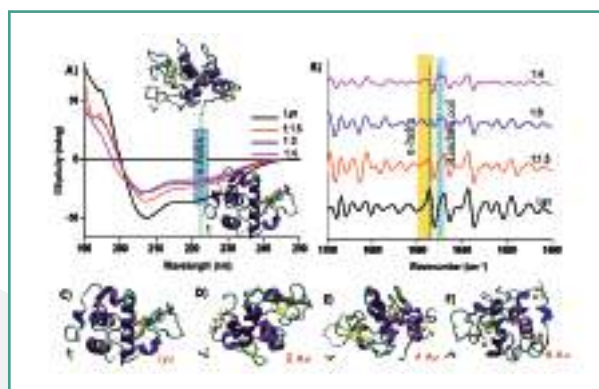
Gold-induced unfolding of lysozyme: Towards the formation of luminescent clusters



Ion mobility mass spectrometry studies on Au_n -Lyz adducts showed gradual unfolding of the protein structure during binding of Au^+ to the protein. The change of the charge state envelope in Au_n -Lyz from that of Lyz in ESI MS data confirmed the relaxation of the protein structure. This Au^+ binding occurs at cysteine sites through the breakage of disulfide bonds and this ruptures the H-bonded folded network structure of the protein leading to $\sim 30\%$ change in helicity. Nearly 15% loss in the total H-bonding occurred during the attachment of 8 Au to the protein as calculated by a molecular dynamics simulation. Different Au_n -Lyz structures were simulated which confirmed significant unfolding of the protein. The structural insights were used to understand similar unfolding in the solution state as seen via circular dichroism (CD) and Fourier transform infrared (FTIR) spectroscopy. This open structure is indeed necessary to accommodate a cluster core inside a protein cavity during luminescent cluster synthesis. These studies unambiguously establish noble metal binding-induced conformational changes of protein structures to accommodate the clusters.



Comparative ESI MS of Lyz (blue) and Au bound Lyz (black) in positive mode, showing 7 Au attachments to a protein molecule. Deconvoluted spectrum achieved from the charge state and m/z distribution also shows 7 Au attachments (inset). Schematics of protein and gold adducts are given.



(A) CD spectra of the Lyz and Au_n -Lyz complex at different Au: Lyz ratios like 1:1.5, 1:3 and 1:4. (B) Second derivative of FTIR spectra of Au attached Lyz in these ratios. (C), (D), (E), (F) are the simulated structures of the Lyz and Au_n -Lyz complexes of 2, 4 and 6 Au. Condensed phase results are well matched with the simulated ones



CO-AUTHORS



Wet laboratory of the Thematic Unit of Excellence

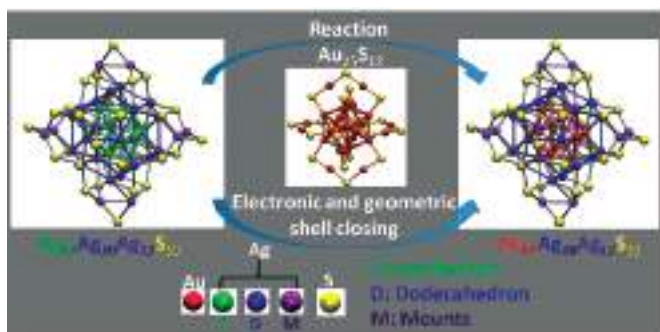


Prototype fabrication laboratory of the Thematic Unit of Excellence



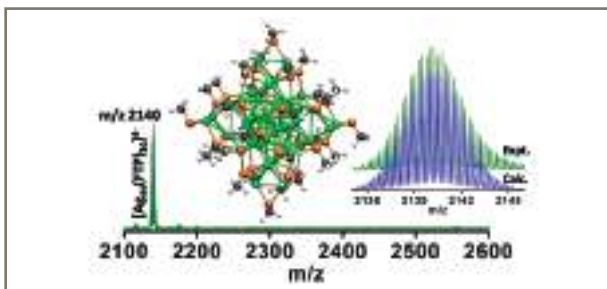
K. R. Krishnadas, Ananya Bakshi, Atanu Ghosh, Ganapati Natarajan and T. Pradeep.
ACS Nano, 11 (2017) 6015-6023
(DOI: 10.1021/acsnano.7b01912)

Manifestation of geometric and electronic shell structures of metal clusters in intercluster reactions

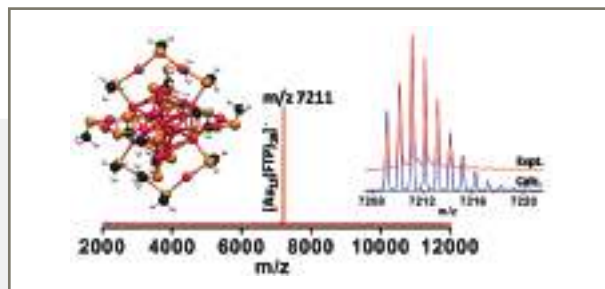


Monolayer protected clusters exhibit rich diversity in geometric and electronic structures. However, structure-reactivity relationships in these clusters are rarely explored. In this context, $[\text{Ag}_{44}(\text{SR})_{30}]^{4+}$, where $-\text{SR}$ is an alkyl/aryl thiolate, is an interesting system due to its geometrically and electronically closed shell structures and distinct charge states. We demonstrate that these structural features of $[\text{Ag}_{44}(\text{SR})_{30}]^{4+}$ are distinctly manifested in its solution state reaction with another cluster, $[\text{Au}_{25}(\text{SR})_{18}]^{-}$. Through this reaction an alloy cluster anion, $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ evolves spontaneously as revealed by high resolution electrospray ionization mass spectrometry. UV/Vis absorption spectroscopy and density functional theory calculations indicate that $[\text{Au}_{12}\text{Ag}_{32}(\text{SR})_{30}]^{4-}$ is formed

by the substitution of all of the Ag atoms in the innermost icosahedral shell of $[\text{Ag}_{44}(\text{SR})_{30}]^{4+}$ and the abundance is attributed to its higher stability due to closed geometric as well as electronic shell structure, similar to the reactant clusters. We further demonstrate that the substitution of metal atoms in the middle dodecahedral shell and the outermost mount sites are also possible, however such substitutions produce $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ alloy clusters with geometrically and electronically open shells. Depending on specific sites of substitution, an unexpected superatom - non-superatom transition occur in the distribution of $\text{Au}_x\text{Ag}_{44-x}(\text{SR})_{30}$ alloy clusters formed in this reaction. Our results present a unique example of a structure-reactivity relationship in the metal atom substitution chemistry of monolayer protected clusters wherein a systematic trend, reflecting the geometric and the electronic shell structures of the reactant as well as the product clusters, was observed.



ESI MS of $\text{Ag}_{44}(\text{FTP})_{30}$



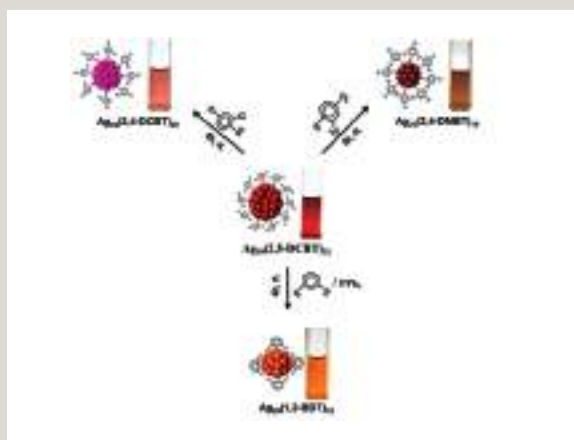
ESI MS $\text{Au}_{25}(\text{FTP})_{18}$





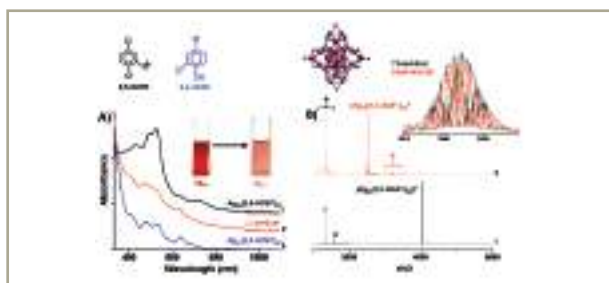
Esma Khatun, Atanu Ghosh, Debasmita Ghosh, Papri Chakraborty, Abhijit Nag, Biswajit Mondal, Sudhakar Chennu and T. Pradeep.
Nanoscale, 9 (2017) 8240-8248 (DOI: 10.1039/C7NR01670K)

$[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$: A new cluster and a precursor for three well-known clusters

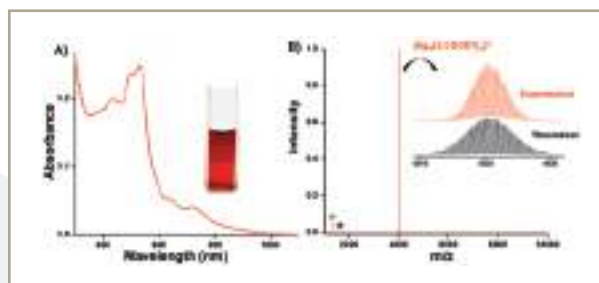


We report the synthesis of a new silver cluster, $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$ (**I**) (2,5-DCBT: 2,5-dichlorobenzenethiol), which acts as a precursor for the synthesis of three well-known silver clusters, $[\text{Ag}_{44}(\text{2,4-DCBT/4-FTP})_{30}]^{4-}$ (**II**) (4-FTP: 4-fluorothiophenol and 2,4-DCBT: 2,4-dichlorobenzenethiol), $[\text{Ag}_{25}(\text{2,4-DMBT})_{18}]^{-}$ (**III**) (2,4-DMBT: 2,4-dimethylbenzenethiol) and $[\text{Ag}_{25}(\text{1,3-BDT})_{12}(\text{PPh}_3)_4]^{3-}$ (**IV**) (1,3-BDT: 1,3-benzenedithiol and PPh_3 : triphenylphosphine). This newly synthesized silver cluster, **I**, is characterized using UV-vis absorption studies, high resolution electrospray ionization mass spectrometry (ESI MS) and other analytical tools. The optical absorption spectrum shows distinct features which are completely different from the previously reported silver clusters. We perform the rapid transformations of **I** to other well-known clusters **II**, **III** and **IV** by reaction with different thiols. The time-dependent UV-vis and ESI MS measurements reveal that **I** dissociates into distinct thiolate entities in the presence of thiols and the thiolates recombine to produce different clusters. The conversion mechanism is found to be quite different from the previous reports where it occurs through the initial formation of ligand exchanged products. Here, we also show the synthesis of a different cluster core, $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$ (**IIa**)

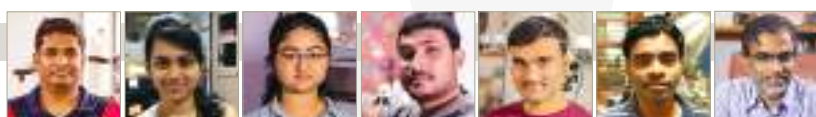
using 2,4-DCBT, a structural isomer of 2,5-DCBT under the same synthetic conditions used for **I**. This observation demonstrates the effect of isomeric thiols on controlling the size of silver clusters. The conversion of one cluster to several other clusters under ambient conditions and the effect of ligand structure in silver cluster synthesis give new insights into the cluster chemistry.



Comparison of the absorption spectra of **I** (black trace), 2,4-DCBT induced product (red trace) and pure **IIa** (blue trace). The spectrum of the **IIa** product has some thiolate impurities resulting in the exponential background. Spectra 1 and 2 are vertically shifted for clarity. (B) ESI MS of **I** (black) and 2,4-DCBT induced product (red). Red asterisk represents $[\text{Ag}_{44}(\text{2,4-DCBT})_{30}]^{4-}$ and its fragments.



(A) UV-vis absorption spectrum of the as-synthesized cluster which exhibits characteristic peaks around 430, 496, 529, 640 and 720 nm. Inset: Visible light photograph of the cluster solution in DCM. (B) Negative mode ESI MS of the as-synthesized cluster in the mass range of m/z 1000-10000. An intense peak at m/z 4020 corresponds to $[\text{Ag}_{59}(\text{2,5-DCBT})_{32}]^{3-}$.



CO-AUTHORS



Indranath Chakraborty and T. Pradeep.
Chem. Rev., 117 (2017) 8208-8271
 (DOI:10.1021/acs.chemrev.6b00769)



Atomically precise clusters of noble metals: Emerging link between atoms and nanoparticles

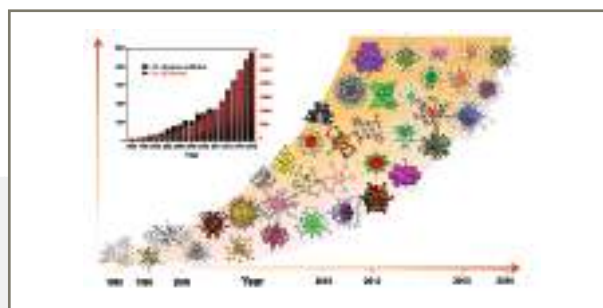


Atomically precise pieces of matter of nanometer dimensions composed of noble metals are new categories of materials with many unusual properties. Over 100 molecules of this kind with formulas such as $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$, and $\text{Au}_{102}(\text{SR})_{44}$ as well as $\text{Ag}_{25}(\text{SR})_{18}$, $\text{Ag}_{29}(\text{S}_2\text{R})_{12}$, and $\text{Ag}_{44}(\text{SR})_{30}$ (often with a few counterions to compensate charges) are known now. They can be made reproducibly with robust synthetic protocols, resulting in colored solutions, yielding powders or diffractable crystals. They are distinctly different from nanoparticles in their spectroscopic properties such as optical absorption and emission, showing well-defined features, just like molecules. They show isotopically resolved molecular ion peaks in mass spectra and provide diverse information when examined through multiple instrumental methods. Most important of these properties is luminescence, often in the visible–near-infrared window, useful in biological applications. Luminescence in the visible region, especially by clusters protected with proteins, with a large Stokes shift, has been used for various sensing applications, down to a few tens of molecules/ions, in air and water. Catalytic properties of clusters, especially oxidation of organic substrates, have been examined. Materials science of these systems presents numerous possibilities and is fast evolving. Computational insights have given reasons for

their stability and unusual properties. The molecular nature of these materials is unequivocally manifested in a few recent studies such as intercluster reactions forming precise clusters. These systems manifest properties of the core, of the ligand shell, as well as that of the integrated system. They are better described as protected molecules or *aspicules*, where *aspis* means shield and *cules* refers to molecules, implying that they are “shielded molecules”. In order to understand their diverse properties, a nomenclature has been introduced with which it is possible to draw their structures with positional labels on paper, with some training. Research in this area is captured here, based on the publications available up to December 2016.



Illustration of monolayer protected clusters, their chemical diversity, and different studies performed using them. Parts of the images are from the literature.



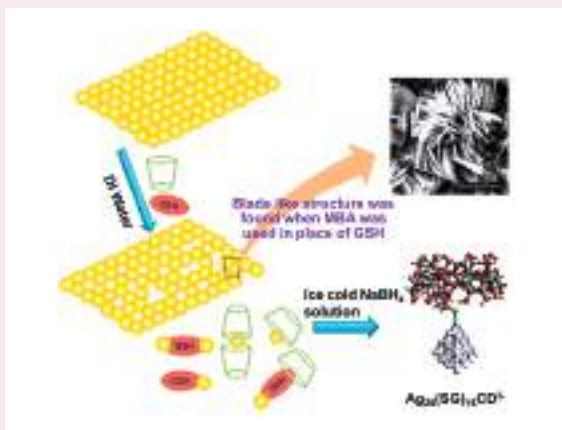
Evolution of clusters (of the type described here) with respect to time. Inset shows the number of papers published and citations in each year for metal nanoclusters (collected from Web of Science using “gold nanoclusters” or “silver nanoclusters” as keywords).





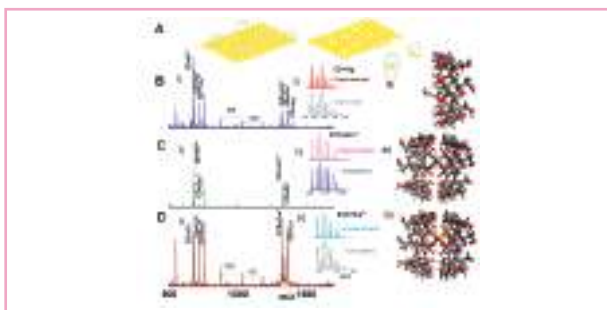
Abhijit Nag, Ananya Baksi, K. C. Krishnapriya, Soujit Sen Gupta, Biswajit Mondal, Papri Chakraborty and T. Pradeep.
Eur. J. Inorg. Chem., 2017 (2017) 3072-3079
 (DOI: 10.1002/ejic.201700182)

Synergistic effects in green extraction of noble metals and its consequences

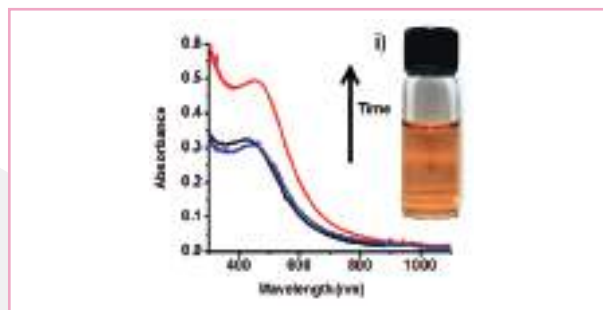


Extraction of silver into water occurs from its apparently inert metal surface by the simple carbohydrate glucose. Here we show that there are large synergistic effects in the extraction process, which results in ca. 45 times larger leaching with specific molecules, when used along with glucose. While glucose (1 g) alone can extract ca. 650 ppb of silver from the metal, 60 mg of it extracts ca. 30000 ppb in a combination with 200 mg of glutathione (GSH) under similar experimental conditions of 70 °C and an extraction time of 7 d, in deionized (DI) water (200 mL). This enhancement is similar when glucose is replaced with cyclodextrin (CD). This enhanced concentration of silver in solution enables the formation of the silver clusters protected with glutathione and cyclodextrin, $\text{Ag}_{20}(\text{SG})_{15}\text{CD}^3+$, in the presence of a reducing agent. A similar extraction for copper leads to excessive leaching, and typical concentrations are even higher than the solubility limit of the copper–glutathione complex. As a result, these complexes are precipitated. This synergistic extraction is observed for zinc and stainless steel as well. Enhanced extraction is a result of the formation of complexes of metals with glutathione and the consequent leaching of the complex into solution as well

as the stabilization of the complex by inclusion complexation with cyclodextrin. Enhanced leaching in the presence of glucose is mostly due to simultaneous complexation with glucose as well as glutathione. The science presented may be used for the green extraction of different metals and could be a new potential top-down approach for metal cluster synthesis. This may also be useful for green and sustained leaching of minerals into water to regulate its quality.



Schematic representation of silver extraction by γ -CD solution. Interaction of γ -CD with the metal surface is shown. B), C) & D) i) are the ESI MS of the solution from silver, brass and copper vessels, respectively.



Time-dependent UV-vis absorption spectra of the cluster in presence of γ -CD and GSH showing increased absorption at 457 nm, with time. For plasmonic silver nanoparticles, the shape and peak maxima are different. i) Photograph of the cluster solution.

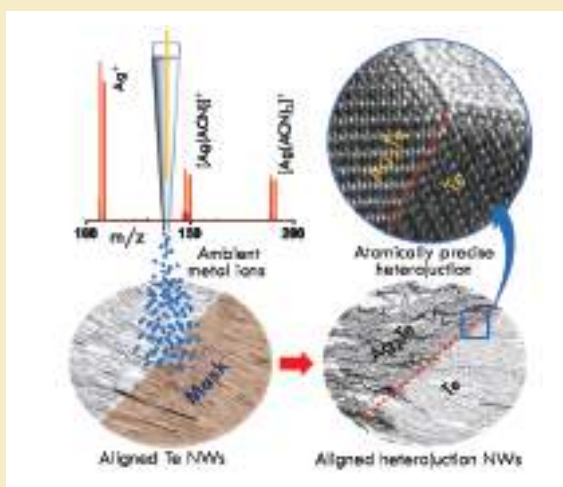


CO-AUTHORS

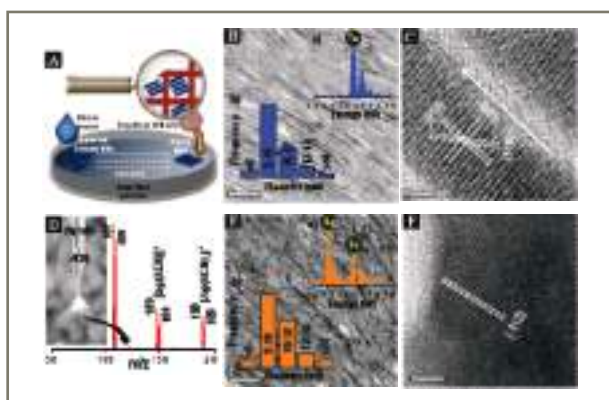


Anirban Som, Depanjan Sarkar, Sisira Kanhirathingal and T. Pradeep.
Part. Part. Syst. Charact., 34 (2017) 1700101
 (DOI: 10.1002/ppsc.201700101)

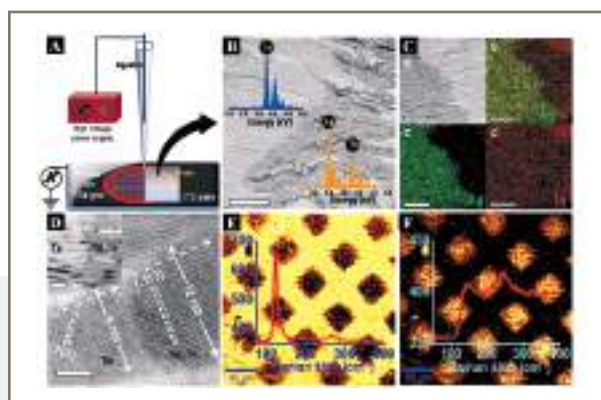
Atomically precise transformations and millimeter scale patterning of nanoscale assemblies by ambient electro spray deposition



Performance of semiconductor devices can be fine-tuned through chemical transformation of their nanostructured components. Such transformations are often undertaken in controlled conditions. Herein, we report the use of electrospray deposition of metal ions from solutions in air, to bring about chemical transformations across mm^2 -sized areas of nanostructures. We illustrate this with monolayer assemblies of ultrathin tellurium nanowires (NWs). The process did not require any reducing agent and can transform the NWs chemically, in the solid state itself, under ambient conditions. By using suitable masks, the beam of ions could be patterned to localize such transformation with nanometer precision to obtain aligned multiphase NWs, containing atomically precise phase boundaries. By controlling the time of exposure of the spray, scope of the process was further expanded to produce tellurium-metal telluride core-shell NWs. The method described here represents a crucial step for ambient processing of nanostructured components, useful for applications such as semiconductor device fabrication.



(A) Schematic of the process of the formation monolayer assembly of Te NWs. Slow drop-casting of a butanolic dispersion of Te NWs on static water surface leads to the formation of aligned NWs on the liquid which is transferred on TEM grids and examined. (B) Large area TEM image of aligned monolayer of Te NWs.



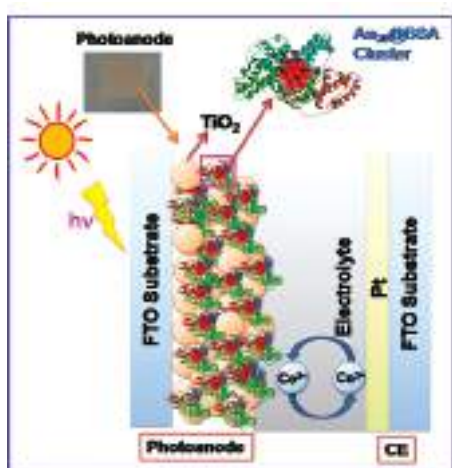
(A) Schematic illustration of the electrolytic spray deposition of Ag on aligned Te NWs taken on a TEM grid.



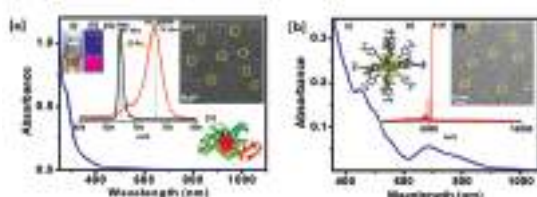


V. Jeseentharani, N. Pugazhenthiran, Ammu Mathew, Indranath Chakraborty, Ananya Baksi, Jyotirmoy Ghosh, Madhuri Jash, G.S. Anjusree, T. G. Deepak, A. Sreekumaran Nair and T. Pradeep. *ChemistrySelect*, 2 (2017) 1454-1463 (DOI: 10.1002/slct.201601730)

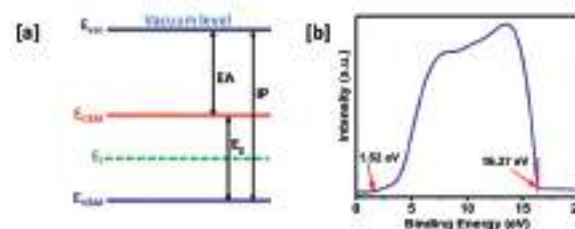
Atomically precise noble metal clusters harvest visible light to produce energy



Noble metal clusters protected by proteins and thiols ($\text{Au}_{30}@\text{BSA}$, $\text{Au}_{25}\text{SBB}_{18}$, and $\text{Ag}_{44}\text{MBA}_{30}$) have been used for photovoltaic studies. These metal clusters were used as sensitizers for the photoanodes fabricated using TiO_2 nanotubes (NTs) and the commercial $\text{P}_{25}\text{TiO}_2$ nanoparticles. A systematic I-V study revealed a conversion efficiency of 0.35 % for the $\text{Au}_{30}@\text{BSA}$ -sensitized solar cell made from TiO_2 NTs.



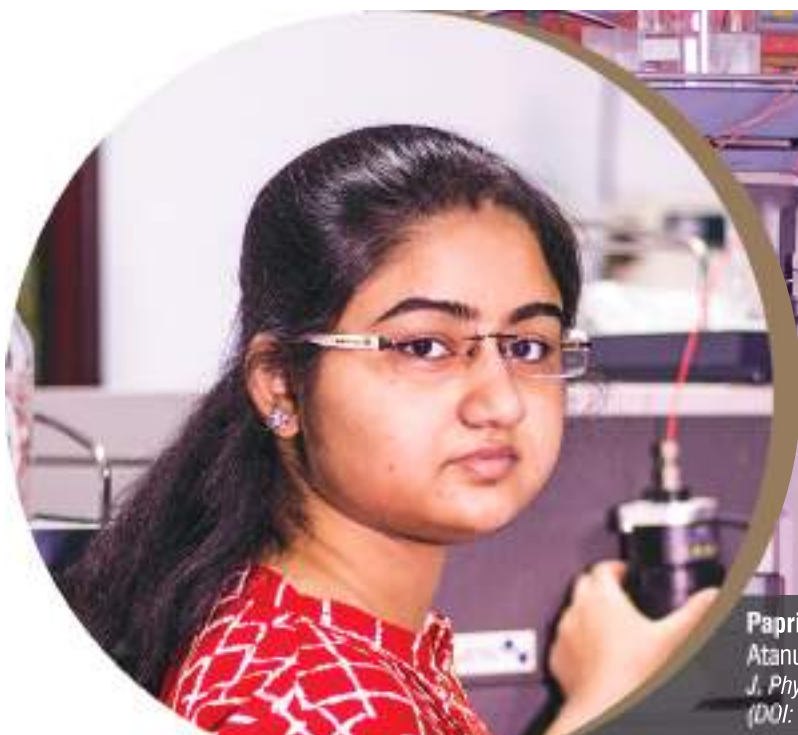
(a) UV-Vis absorption spectrum of $\text{Au}_{30}@\text{BSA}$ cluster in water. Insets show the photographs of clusters in water illuminated with visible. (b) UV-vis absorption spectra of $\text{Au}_{25}\text{SBB}_{18}$; inset shows the structure of $\text{Au}_{25}\text{SBB}_{18}$.



Energy levels diagram near the valence region [a] and typical He 1 UPS spectrum of Au_{30}BSA [b], $\text{Au}_{25}\text{SBB}_{18}$ (inset shows the point of maximum inflection) [c] and $\text{Ag}_{44}\text{MBA}_{30}$ [d].



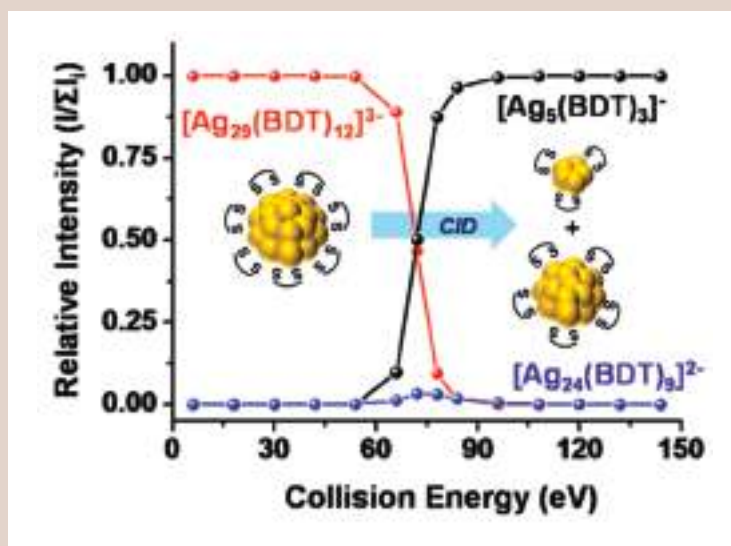
CO-AUTHORS



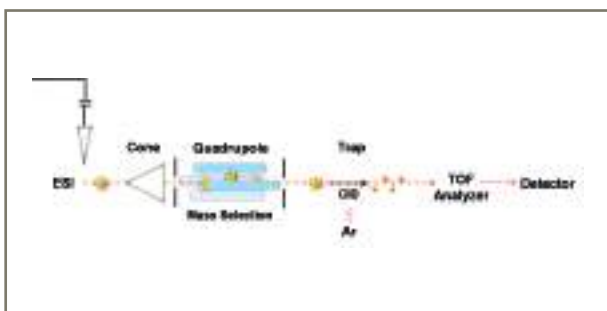
Papri Chakraborty, Ananya Baksi, Esma Khatun, Abhijit Nag, Atanu Ghosh and T. Pradeep.
J. Phys. Chem. C, 121 (2017) 10971-10981
 (DOI: 10.1021/acs.jpcc.6b12485)



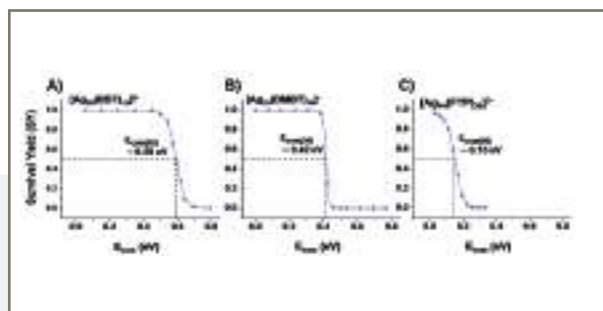
Dissociation of gas phase ions of atomically precise silver clusters reflects their solution phase stability



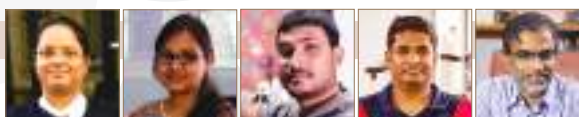
We report an attempt to probe into the energy demand of the fragmentation of atomically precise silver clusters using collision induced dissociation mass spectrometry. Energy resolved collisions of several gas phase ions of clusters, $\text{Ag}_{25}(\text{S}_2\text{R})_{12}^-$, $\text{Ag}_{25}(\text{SR})_{18}^-$, and $\text{Ag}_{44}(\text{SR})_{30}^-$, reveal distinct fragmentation kinetics involving charge separation. The fragmentation pattern of $[\text{Ag}_{25}(\text{SR})_{18}]^-$ is found to be different from its structural analog, $[\text{Au}_{25}(\text{SR})_{18}]^-$. Survival yield analysis has been used to establish a direct comparison between the stability of the ions of these clusters, which reveals that $[\text{Ag}_{25}(\text{S}_2\text{R})_{12}]^{3-}$ is the most stable cluster ion, followed by $[\text{Ag}_{25}(\text{SR})_{18}]^-$ and $[\text{Ag}_{44}(\text{SR})_{30}]^{4-}$. Gas phase stabilities reflect their solution phase stabilities, indicating that the molecular nature of the clusters is retained in the gas phase, too. We further report that fragmentation occurs in a stepwise fashion, conserving the closed shell electronic stability of the parent ion at each step. Such studies are important in understanding the electronic and geometric stability of cluster ions and their fragments.

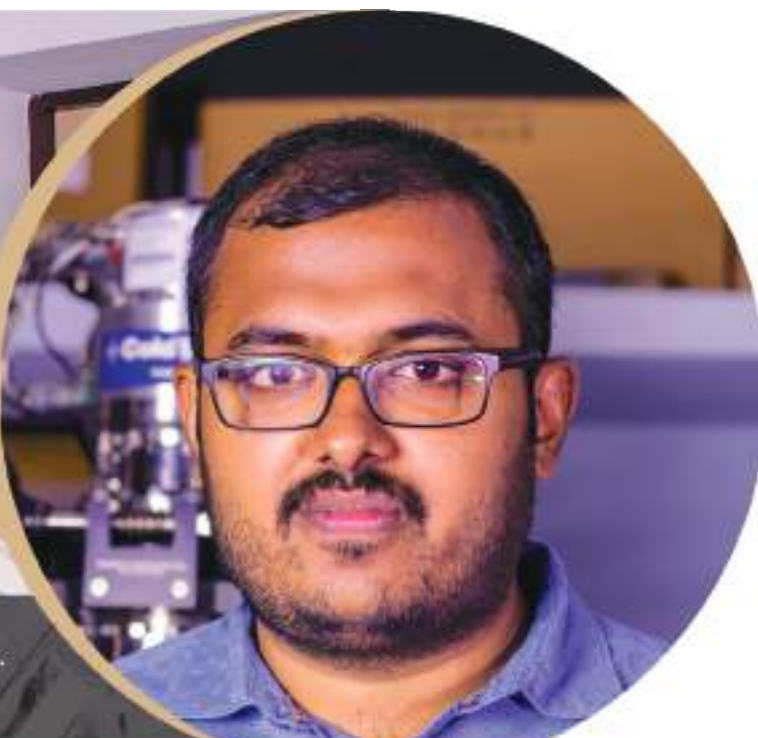


Schematic of the instrumental set-up for tandem mass spectrometric measurements where CID occurs in the trap after mass selection by the quadrupole. TOF refers to time of flight.



Survival yield curves plotted as a function of center-of-mass energy (E_{com}) for (A) $[\text{Ag}_{25}(\text{BDT})_{12}]^{3-}$, (B) $[\text{Ag}_{25}(\text{DMBT})_{18}]^-$, and (C) $[\text{Ag}_{44}(\text{FIP})_{30}]^{4-}$ cluster ions, respectively.





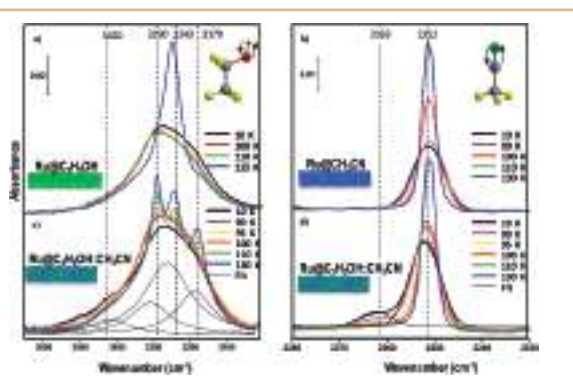
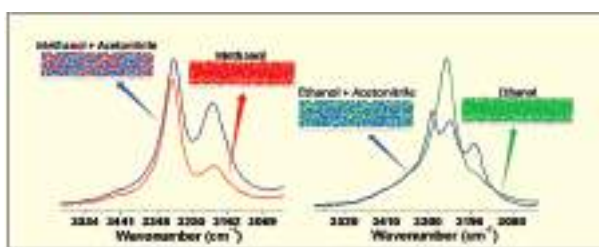
Rabin Rajan J. Methikkalam, Radha Gobinda Bhuin, Jyotirmoy Ghosh, Bhalamurugan Sivaraman and T. Pradeep. *J. Phys. Chem. C*, 121 (2017) 2822-2835 (DOI: 10.1021/acs.jpcc.6b11483)

Interaction of acetonitrile with alcohols at cryogenic temperatures

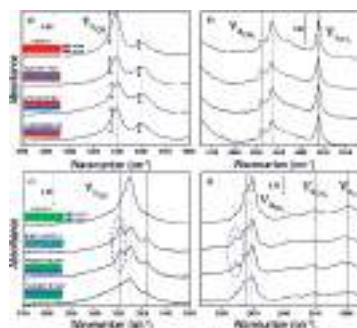
Temperature-dependent interaction of acetonitrile with methanol and ethanol, as codeposited and sequentially deposited films, was studied in the 10–130 K window, in ultra high vacuum. Films in the range of 50–100

monolayers were investigated using temperature-dependent reflection–absorption infrared spectroscopy (RAIRS), Cs^+ ion scattering mass spectrometry, and temperature-programmed desorption (TPD). Acetonitrile interacts with methanol and ethanol through intermolecular hydrogen bonding. When a codeposited system was annealed, acetonitrile underwent a phase segregation at 110 K, and large changes in the infrared spectrum were observed. The OH stretching of methanol gave two peaks characteristic of the change to the α -phase of methanol, while ethanol gave three peaks at the same temperature. The surface composition of the systems probed by 40 eV Cs^+ scattering showed that both the alcohols and the acetonitrile were of equal intensity below 110 K, while above 110 K the intensity of the latter went down substantially. We find that the presence of acetonitrile does not allow ethanol to undergo complete phase transition prior

to desorption, while methanol could do so. This behavior is explained on the basis of the size, extent of hydrogen bonding, and phase transition temperature, of the two alcohols. Additional peaks in the hydroxyl region observed in alcohols in the 110–130 K window may be used as a signature of the presence of acetonitrile mixed with alcohol, especially ethanol, and hence this may be used in observational studies of such molecular environments.



Temperature-dependent RAIRS of pure and codeposited mixtures of acetonitrile and ethanol.



Infrared spectra of methanol (a and b) and ethanol (c and d) at 130 K in O–H and C–H stretching regions, with the spectra of pure alcohols and alcohols codeposited and sequentially deposited with acetonitrile compared. Schematics within the figures show the systems compared.



CO-AUTHORS



Swathy Jakka Ravindran, Ramesh Kumar, Armitava Srimany, Ligy Philip and T. Pradeep.
Anal. Chem. (2017)
(DOI: 10.1021/acs.analchem.7b04236)

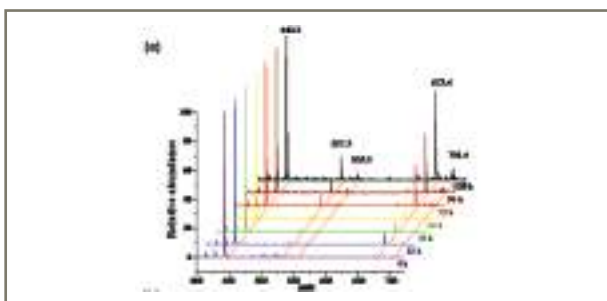


Early detection of biofouling on water purification membranes by ambient ionization mass spectrometry imaging

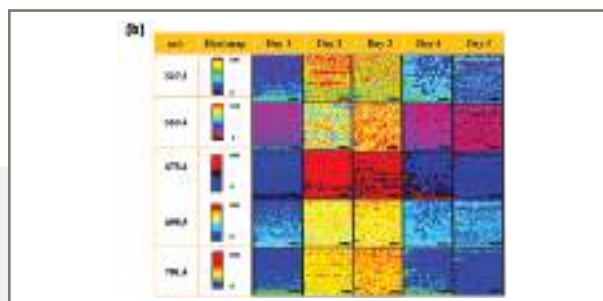


By direct analysis of water purification membranes using ambient ionization mass spectrometry, an attempt has been made to understand the molecular signatures of bacterial fouling. Membrane based purification methods are used extensively in water treatment and a major challenge for them is biofouling. The build-up of microbes and their polymeric matrix clog the membranes and reduce their efficiency. To understand the early stages of bacterial fouling on water purification membranes, we have used Desorption Electrospray Ionization Mass Spectrometry (DESI MS), where ion formation occurs in ambient conditions and the ionization event is surface sensitive. Biosurfactants at the air-water interface generated by microorganisms as a result of quorum sensing, influence the water-membrane interface and are important for the bacterial attachment. We show that these biosurfactants produced by bacteria can be indicator molecular species signifying initiation of biofilms on membrane surfaces, demonstrated by specific DESI MS signatures. In *Pseudomonas aeruginosa*, one of the best studied models for biofilm formation, this process is mediated by rhamnolipids forewarning bacterial fouling. Species dependent variation of such molecules can be used

for the precise identification of the microorganisms, as revealed by studies on *P. aeruginosa* (ATCC 25619). The production of biosurfactants is tightly regulated at the transcriptional level by the quorum-sensing (QS) response. Thus, evolution of these molecules across the membrane surface allows rapid screening of the biofilm community. We show that, the ambient ionization mass spectrometry can detect certain toxic heavy metals present in water, using surfactant-metal complexes as analytes. We believe that such studies conducted on membranes in various input water streams will help design suitable membrane processes specific to the input streams.



(a) Electrospray ionization mass spectra (ESI MS) corresponds to rhamnolipids of biofilms collected within 4 h, after 12, 24, 48, 72, 96 and 120 h (up to five days).



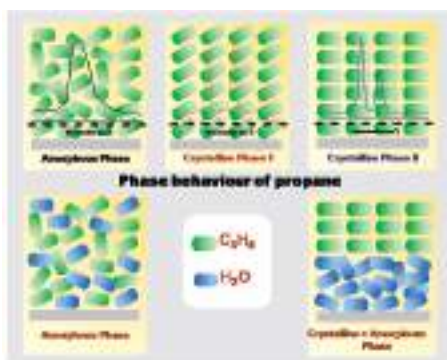
(b) Individual mass spectral image scan collected from the RO membrane cross flow test unit after 24, 48, 72, 96 and 120 h (up to 5 days). The scale bar corresponds to 5 mm and are same in all the images.



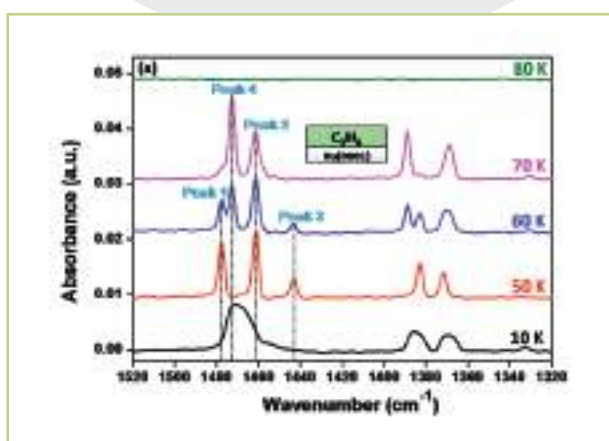


Jyotirmoy Ghosh, Annapoorani Kobuvayur Hariharan,
Radha Gobinda Bhui, Rabin Rajan Methikalam and
T. Pradeep.
Phys. Chem. Chem. Phys. (2017) (DOI: 10.1039/C7CP06467E)

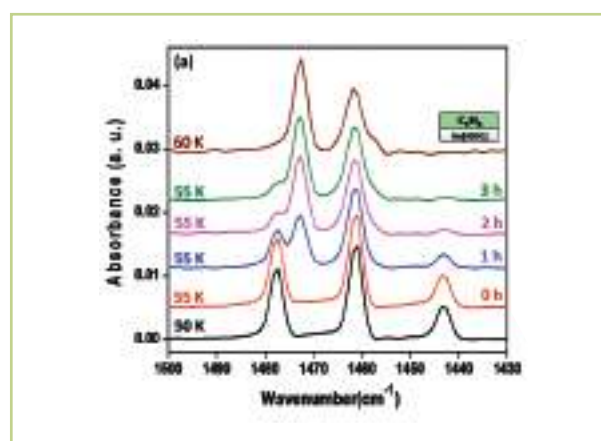
Propane and propane-water interactions: A study at cryogenic temperatures



The phase transition of solid propane and propane-water mixture under ultrahigh vacuum has been investigated using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption mass spectrometry (TPD-MS). Here, the investigation was divided into two sections: phase transition of pure propane and the interaction of propane with water. RAIR spectra of pure propane reveal an unknown crystalline phase at 50 K (phase I) which gradually converts to a known crystalline phase (phase II) at higher temperature. This conversion is associated with certain kinetics. Co-deposition of water and propane restricts the amorphous to crystalline phase transition while sequential deposition ($\text{H}_2\text{O}@C_3H_8$; propane over predeposited water) does not hinder it. For an alternative sequential deposition ($C_3H_8@H_2O$; water over predeposited propane), the phase transition is hindered due to diffusional mixing within the given experimental time which is attributed to the reason behind the restricted phase transition.



Temperature-dependent RAIR spectra of 150 MLs of solid propane deposited at 10 K on Ru(0001). Spectra corresponding to the (a) $-\text{CH}_3$ deformation region



Time-dependent RAIR spectra of 150 MLs of propane at 55 K. RAIR spectra in the (a) $-\text{CH}_3$ d-deformation region



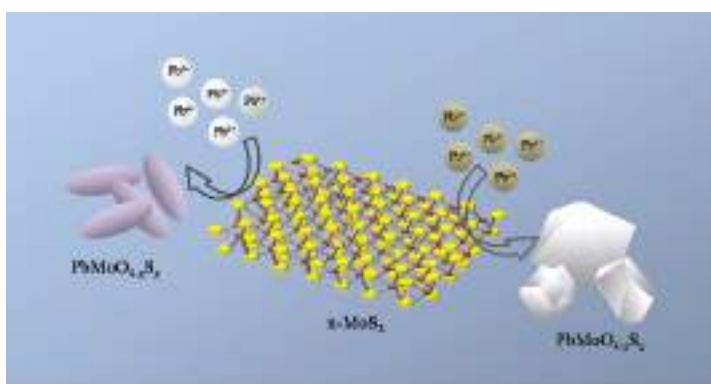
CO-AUTHORS



Biswajit Mondal, **Ananthu Mahendranath**, Anirban Som, Sandeep Bose, Tripti Ahuja, Avula Anil Kumar, Jyotirmoy Ghosh and T. Pradeep

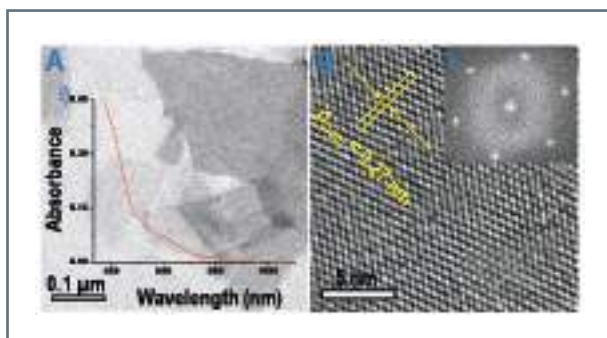
Nanoscale (2017) (DOI: 10.1039/C7NR07523E)

Rapid reaction of MoS₂ nanosheets with Pb²⁺ and Pb⁴⁺ ions in solution

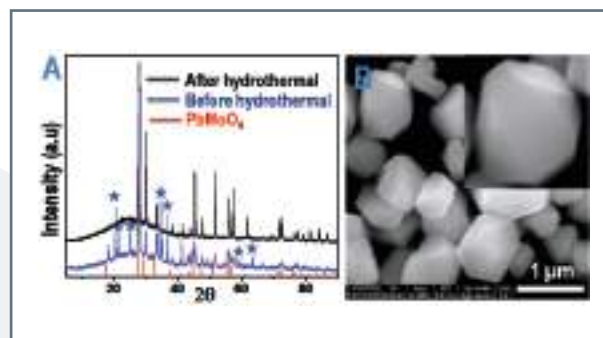


Understanding the chemical changes happening to nanostructures during a process is vital in selecting them for applications. Here, we investigated the difference in the reactivity of bulk and nanoscale forms of molybdenum disulfide (MoS₂) in solution, with lead ions (Pb²⁺ and Pb⁴⁺) as probes, at room temperature. While the bulk form did not show any reactivity in experimental timescale, the two-dimensional (2D) nanoscale form showed not only reactivity but also quite rapid kinetics that resulted in the formation of distinct products, principally PbMoO₄ with anion substitution, in a few seconds. Depending on the charge state of the cation, and pH of the reaction mixture, two different kinds of morphologies of the same reaction product were formed. Furthermore, we demonstrate that this unusual reactivity of the

MoS₂ nanosheets (NSs) was retained in its supported form and hence, such supported materials can be effective for the abstraction of toxic lead from water, with fast kinetics.



(A-C) Characterization of MoS₂ NSs. (A) TEM and (B) HRTEM image (corresponding FFT pattern is shown in the inset (i); lattice plane is marked) of NSs. Optical absorption spectrum is shown in the inset of (A, i).



Characterization of the reaction product of MoS₂ and Pb²⁺ ions. (A) Standard peaks of PbMoO₄ (red) is plotted along with the observed XRD pattern of before (blue) and after (black) the hydrothermal treatment of reaction product. (B) SEM image showing octopod morphology of PbMoO₄.





Analysis lab of the Thematic Unit of Excellence

STUDENTS' POSTER PRESENTATIONS



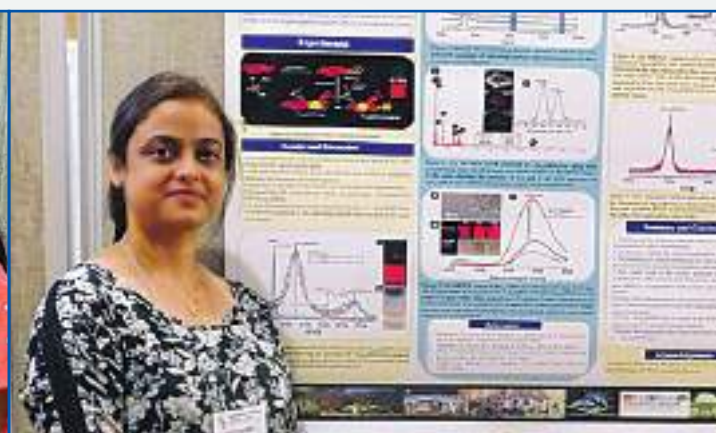
'Unusual reactivity of MoS₂ nanosheets' by **Biswajit Mondal** in 20th Chemical Research Society of India Symposium (CRSI), Guwahati University, February 3-5, 2017.



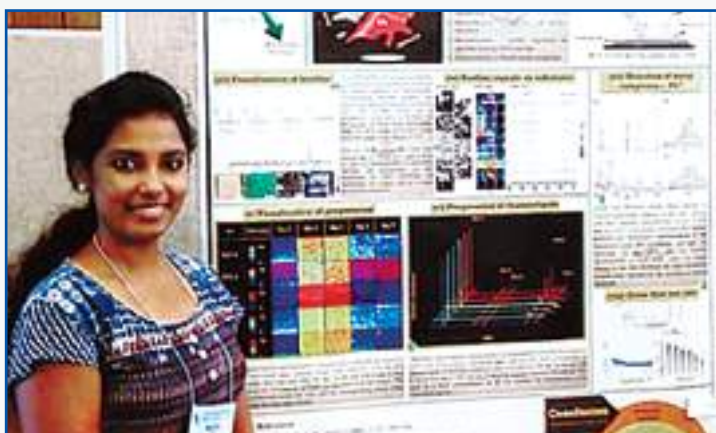
'Manifestation of Faceted Structures by Cluster Assemblies on Ultra-small Gold Nanorod' by **Amrita Chakraborty** in 20th Chemical Research Society of India Symposium (CRSI), Guwahati University, February 3-5, 2017.



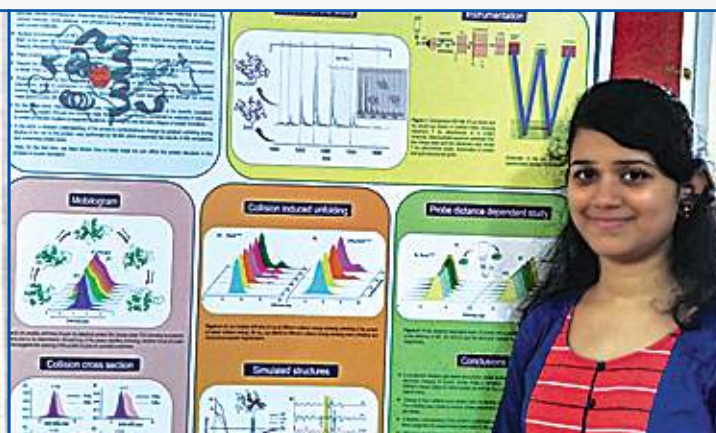
'Highly luminescent monolayer protected Ag₃₉Se₇S₁₅ clusters' by **C. K. Manju** in Gordon Research Conference held at Mount Holyoke College, South Hadley, MA, USA, July 9-14, 2017.



'Noble metal clusters protected with mixed proteins exhibits intense photoluminescence' by **Jyoti Sarita Mohanty** in Gordon Research Conference held at Mount Holyoke College, South Hadley, MA, USA, July 9-14, 2017.

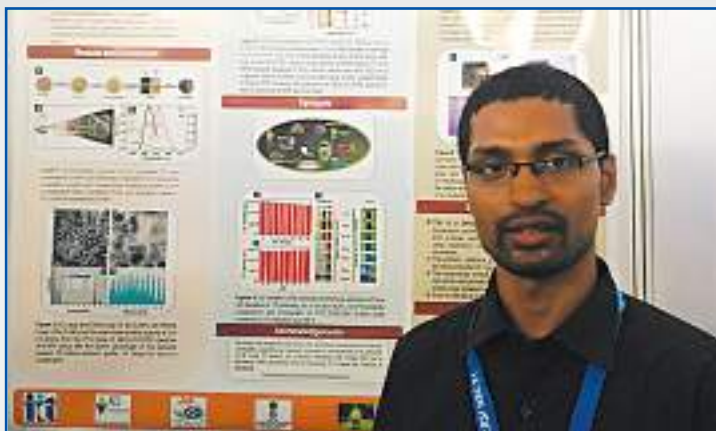


'Early detection of biofouling on water purification membranes by ambient ionization mass spectrometry Imaging' by **J. R. Swathy** in Gordon Research Conference on Applied and Environmental Microbiology held at Mount Holyoke College, South Hadley, MA, USA, July 15-23, 2017.

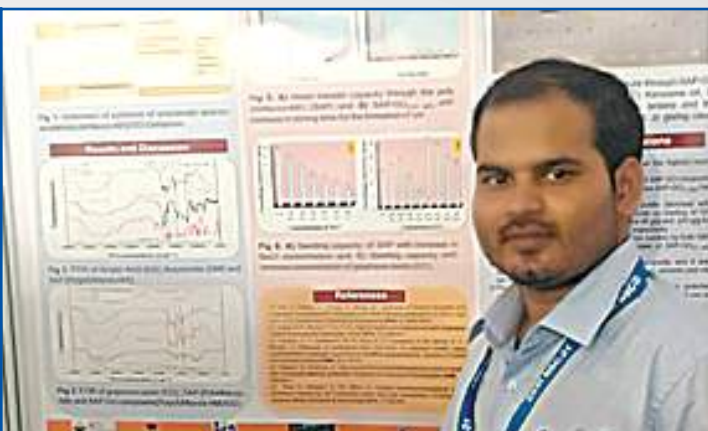


'Gold-induced unfolding of lysozyme; Towards the formation of luminescent clusters' by **Debasmita Ghosh** in Chemistry In-House Symposium (CiHS), held at IIT Madras, August 17, 2017.

STUDENTS' POSTER PRESENTATIONS



'Direct conversion of rice husk to silicon nanoparticles: Sustainable fluorophores for white light emission' by **Sandeep Bose** in 21st CRSI, IICT Hyderabad, July 16-18, 2017.



'Preparation of graphene grafted super absorbing polymer: Unusual behavior and its application' by **Rabiul Islam** in 21st CRSI, IICT Hyderabad, July 16-18, 2017.



'Naked clusters of noble metals in air from ligand protected clusters in solution' by **Madhuri Jash** in 20th CRSI, Guwahati University, February 3-5, 2017.



J. R. Swathy attended ACS Industrial Symposium 2017 on 'Global challenges and recent advances in biologics and biosimilars', held at Mumbai, December 14-15, 2017.

- 'Gold-induced unfolding of lysozyme: Toward the formation of luminescent clusters' by **Debasmita Ghosh** in 21st CRSI 2017, IICT Hyderabad, July 16-18, 2017.
- 'Systematic self-assembly of Ag_{44} clusters on reconstructed gold nanorod surface leading to octahedral nanocages' by **Amrita Chakraborty** in ISMPC17, Hotel Monte Verità, Ascona, Switzerland, August 13-16, 2017.
- 'Ionization of hydrocarbons by laser assisted paper spray ionization mass spectrometry (LAPSI MS)' by **Pallab Basuri** in CiHS held at IIT Madras, August 17, 2017.
- 'Organic solvent-free fabrication of durable and multifunctional superhydrophobic paper from waterborne fluorinated cellulose nanofiber building blocks' by **Avijit Baidya** in 9th Bengaluru India Nano held at The Lalit Ashok, Bengaluru, December 7-9, 2017.
- **Ananthu Mahendranath** attended HORIBA Optical School, jointly organized by Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore, and HORIBA Scientific Group, May 22-26, 2017.

STUDENTS' VISITS



In Unleash Lab, Denmark



At Alto University, Finland



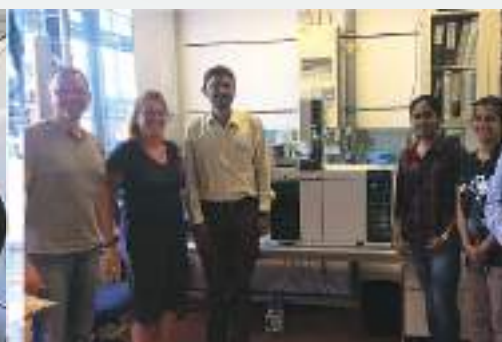
At University of Dhaka, Bangladesh



At Nadia District, West Bengal



Bio Nano Consulting, UK



With Prof. Andrea Schaefer, KIT

OTHER VISITORS



Keisuke Hirata, University of Tokyo, Japan



Dr. Kalyani Ramachandran, Biotechnology Industry Research Assistance Council (BIRAC)



Dr. Md. Zakir Sultan, Centre for Advanced Research in Sciences (CARS), University of Dhaka, Bangladesh

AWARDS & RECOGNITIONS



Biswajit Mondal, won a best poster award at 20th (CRSI), Guwahati University for the poster entitled "Unusual reactivity of MoS₂ nanosheets", February 2-5, 2017.



Pallab Basuri, won a best poster award at the CiHS 2017, Department of Chemistry, IIT Madras for the poster entitled "Ionization of hydrocarbons by laser assisted paper spray ionization mass spectrometry (LAPSI MS) held at" IIT Madras, August 17, 2017.



Ramesh Kumar won the Gandhian Young Technological Innovation (GYTI) award under "More from Less for Many" category, Rastrapati Bhavan, India, March 4-5, 2017. A project support of 1 Lakh rupees from BIRAC SRISTI was awarded.



Avijit Baidya, won a best poster award at the 9th Bengaluru India Nano, The Lalit Ashok, Bangaluru, for the poster entitled "Organic solvent-free fabrication of durable and multifunctional super hydrophobic paper from waterborne fluorinated cellulose nanofiber building blocks", December 7-9, 2017.



twas

Dr. K. R. Krishnadas received the "Prof. Langmuir award for one of the best PhD theses in physical chemistry" for the year 2017.

Avijit Baidya and team won the Silver prize under the theme "WATER" in Unleash Lab 2017, Denmark. The team Avijit Baidya (India), Lily Saporta Tagiuri (USA), Karlijn Arts (Netherlands) presented a proposal on 'Renewable water resource for future: Hidden water for all', August 13-21, 2017, Copenhagen, Denmark.

Dr. G. Velmurugan won the Young Scientist Award 2017 by the Association of Microbiologists of India for his contributions to Microbiology, which are of both fundamental and applied value.

Prof. T. Pradeep was awarded the Deepak Parekh Institute Professorship on April 12, 2017.

Prof. T. Pradeep, is the winner of The World Academy of Sciences (TWAS) prize in chemistry for the year 2018, "for his discovery of novel nanomaterials and development of products using such materials, leading to applications which support a clean environment, affordable clean water and ultrasensitive devices".

GRADUATION

Ph.D.

Atanu Gosh, Department of Chemistry, IIT Madras, 2017. Atomically precise noble metal clusters: Synthesis, transformation and applications.

Depanjan Sarkar, Department of Chemistry, IIT Madras, 2017. Ambient ions: investigations at the materials-mass spectrometry interface.

N. Rahul, Department of Chemistry, IIT Madras, 2017. Molecular Ionization at low voltage from one-dimensional nanostructures: Phenomena and applications.

M.Sc.

Mr. Abhijith Menon, Rapid phase segregation in acetonitrile-water system at cryogenic temperatures, 2017.

Ms. Pratyusha Das, Droplet synthesis of quantum dots, 2017.

Mr. Rohan Chowdhury, Ligand shell modification of noble metal clusters by functionalized fullerenes, 2017.

Ms. Sohini Mukherjee, Chitosan reinforced mixed metal oxide/hydroxide nanocomposite for arsenic and fluoride removal from water, 2017.

Mr. Arunava Saha, 2D-Nanoclay incorporated superabsorbent polymer composite having efficient water transfer ability, 2017.



International

- Dr. Rajeev Kumar joined as a Professor at the School of Natural and Computational Sciences, Wollega University Nekemte, Ethiopia.
- Dr. Rabin Rajan J Methikkalam joined as a Postdoctoral Researcher at the Institute of Chemistry, The Hebrew University of Jerusalem, Israel.
- Dr. Udayabhaskararao Thumu has been selected for the Marie Curie fellowship- NanoTRAIN for Growth II COFUND position and he has joined the Department of Micro and Nanofabrication International Iberian Nanotechnology Laboratory (INL) Braga, Portugal.
- Dr. M. Dhivakar joined as a Post-doctoral Fellow at the Department of Microbiology and Molecular Genetics, Institute for Medical Research Israel – Canada, The Hebrew University-Hadassah Medical School, Jerusalem, Israel.
- Dr. K. R. Krishnadas joined as a Post-Doctoral Research Fellow in the research group of Prof. Thomas Buerger at the Dept. of Physical Chemistry, University of Geneva, Switzerland.
- Dr. Naresh Kumar is now a Researcher co-investigator on the project, "Quantitative non-destructive nanoscale characterization of advanced materials" funded by The Engineering and Physical Sciences Research Council (EPSRC) and started in July 2017.
- Dr. Atanu Gosh joined as a Post-Doctoral Research Fellow at the King Abdullah University of Science and Technology (KAUST), Saudi Arabia.
- Dr. Indranath Chakraborty is now Junior Group Leader at the Parak Research Group, Centre for Hybrid Nanostructure (CHyN), University of Hamburg, Germany.
- Dr. Sajanalal R. Panikkanvalappil is now Research Scientist II at the Laser Dynamics Lab, School of Chemistry and Biochemistry, Georgia Institute of Technology.
- Dr. N. Pugazhenthiran joined as a Post-Doctoral Research Fellow (CONICYT-FONDECYT) at the Department of Mechanical Engineering, Faculty of Engineering, University of Concepción, Concepción, Chile.
- Dr. Habib Muhammad joined as a Senior Researcher at the Advanced Membranes and Porous Materials Center King Abdullah University of Science and Technology (KAUST), Saudi Arabia.
- Dr. Radha Gobinda Bhui joined as a Post-Doctoral Researcher at the group of Prof. Hans-Peter Steinrück, Friedrich-Alexander-Universität Erlangen-Nürnberg Lehrstuhl für Physikalische Chemie II, Germany.
- Dr. Anirban Som joined as a Post-Doctoral Researcher at the Molecular Materials group of Department of Applied Physics, Aalto University School of Science, Finland.

National

- Dr. E. S. Shibu received a Ramanujan Research Fellowship from SERB. He has joined the CECRI-Kararikudi, Tamil Nadu as a Ramanujan Scientist.
- Dr. S. Arun Karthick joined as an associate professor at the Department of Biomedical Engineering, SSN College of Engineering, Kalavakkam, Tamil Nadu.
- Dr. A. Sreekumaran Nair was promoted in 2017 to Senior Manager (II) level (R&D) at the Advanced Design and Materials Group, MRF Limited, R&D Centre/Corporate Technical, Chennai.
- Dr. Akshaya K. Samal has joined as an assistant professor at the Photo and Electrocatalysis Research Group, Centre for Nano and Materials Sciences (CNMS), Jain University Jakkasandra Post, Kanakpura Taluk, Bangalore.
- Dr. V. Suryanarayanan is now a Senior Scientist at the Electroorganic Division, CSIR-CECRI, Karaikudi.
- Dr. K. Karthik Kumar has joined as an assistant professor at the Department of Chemistry, The American College, Madurai.

AMRIT



New Installations



The home town of the Golden Temple – AMRITSAR - the ground water in certain areas in this fertile land is contaminated with the deadly arsenic.

In a World Bank assisted project, the DDWSS, Govt. of Punjab, has embarked on a scheme of setting up nanotechnology based water treatment plants in these areas.

A program to install these nano-technology based water treatment plants was taken up at 3 locations in Amritsar district, namely, GoreyNangal, BudhaTheh and Chak Kamal Khan. These purification plants are now

supplying purified water, which have been well received by the citizens. The levels of purification achieved, exceeds international norms.

This nanotechnology based water treatment plant accomplishes its work without the use of electricity, and is the only plant in the world that removes iron through adsorption, leading to very less waste generation and consequently near zero maintenance. The cost of providing clean water is the lowest in the world at just Rs. 23 per 1000 Liters; or 0.35 US dollars per 1000 liters.



PATENT APPLICATIONS

- 1 **Multilayer multifunctional nasal filter**; T. Pradeep, S. Arun Karthick, Pillalamarri Srikrishnarka, Vishal Kumar and Ramesh Kumar; *201741007433*, March 2, 2017.
- 2 **Method of making nanometer thin sheets of metals in air**; T. Pradeep, Depanjan Sarkar and Anirban Som; *201741036233*, October 12, 2017.
- 3 **Aqueous composition for durable and extremely efficient water repelling superhydrophobic materials**; T. Pradeep, Avijit Baidya, Azhar Ganayee and Jakka Ravindran Swathy; *201741036772*, October 17, 2017.
- 4 **Method of making nanoparticles of precise isotopic composition by rapid isotopic exchange**; T. Pradeep, Papri Chakraborti and Esma Khatun; *201741037148*, October 20, 2017.
- 5 **Method for creating nanopores in MoS₂ nanosheets by chemical drilling for disinfection of water under visible light**; T. Pradeep, Depanjan Sarkar, Anirban som, Biswajit Mondal and Jakka Ravindran Swathy; *201741037148*, October 20, 2017.
- 6 **A modified surface for condensation**; T. Pradeep, Ankit Nagar and Ramesh Kumar; *201741039127*, November 2, 1017.
- 7 **Method of field induced photoionization of molecules using low power pointer laser in laser assisted paper spray ionization mass spectrometry (LAPSI MS)**; T. Pradeep, Pallab Basuri, Depanjan Sarkar, Ganesan Paramasivam; *201741040383*, November 13, 2017.
- 8 **A method of identifying isomers of curcumin and preferential stabilisation of one of them**; T. Pradeep, Abhijit Nag, Papri Chakraborty, Ananya Baksi, Ganapati Natarajan; *201741040570*, November 14, 2017.
- 9 **Method of reduction of carbon dioxide on nickel nanobrushes formed by electrospray deposition**; T. Pradeep, Sandeep Bose, Depanjan Sarkar; *201741042540*, November 28, 2017.
- 10 **Removal of lead from waste water using nanoscale MoS₂**; T. Pradeep, Biswajit Mondal, Ananthu Mahendranath, Anirban Som, Sandeep Bose, Tripti Ahuja, Avula Anil Kumar and Jyotirmoy Ghosh; *201741044447*, December 11, 2017.
- 11 **Method for preparing luminescent silicon nanoparticles from rice husk using microwave irradiation**; T. Pradeep, Sandeep Bose, Mohd. Azhardin Ganayee, Biswajit Mondal and Sudhakar Chennu; *201741046491*, December 23, 2017.
- 12 **A method of detection of low concentration of analytes by superhydrophobic pre-concentration paper spray ionization mass spectrometry (SHPPSI MS)**; T. Pradeep, Pallab Basuri, Avijit Baidya, Tripti Ahuja; *201741047403*, December 30, 2017.
- 13 **A portable water filtration device for removing impurities from water using contaminant-specific purification cartridges**; T. Pradeep, Ramesh Kumar, Anupam Chandra; *201741047404*, December 30, 2017.
- 14 **An integrated CDI electrode**; T. Pradeep, Md Rabiul Islam, Soujit Sengupta, Srikrishnarka Pillalamarri; *201741047400*, December 30, 2017.

PCT Applications

- 1 **Patterned metallic nanobrushes for capture of atmospheric humidity**; *PCT/IN2017/050621*; December 28, 2017.
- 2 **Method for preparing cellulose microstructures-templated nanocomposites with enhanced arsenic removal capacity and a purifier thereof**; *PCT/IN2017/050627*; December 28, 2017.
- 3 **Chitosan reinforced mixed oxyhydroxide nanocomposite for fluoride and arsenic removal from water and a device thereof**; *PCT/IN2017/050620*; December 28, 2017.



Gravity-fed axial flow filter block for domestic water purifiers and the method of making the same; T. Pradeep, M. Udhaya Sankar, Anshup and Amrita Chaudhary; *2892/CHE/2010* filed on September 30, 2010; *Patent number 282257*, granted on March 31, 2017.

A sustained silver release composition for water purification; T. Pradeep, Anshup, Amrita Chaudhary, M. Udhaya Sankar and S. Gayathri; *947/CHE/2011* filed on March 25, 2011; *Patent number 286423*, granted on August 18, 2017.

Multilayer organic-templated-boehmite-nanoarchitecture for fluoride removal; T. Pradeep, A. Leelavathi, Amrita Chaudhary, M. Udhaya Sankar and Anshup; *4062/CHE/2011*, November 24, 2011; *Patent number 286929*, granted on August 31, 2017.

Domestic water purification unit; *Design Patent number 288810* dated 24/11/2016; granted on October 16, 2017.

RESEARCH PROJECTS AT HAND

Thematic project on frontiers of nanoscience and nanotechnology (TPF), DST, Rs. 541 lakhs.

Soft ionization ion mobility mass spectrometry of atomically precise clusters of noble metals, Rs. 608 lakhs.

Improve rubber to steel bonding in steel radial tyres through scientific understanding, MRF Ltd. Rs. 130 lakhs.

Dust free glass, Saint-Gobain Research India Ltd. Rs. 36 lakhs (with Prof. R. Nagarajan).

Development of a novel combined arsenic filtration/monitoring system for community-scale water supplies, India-UK project supported by GITA, total funds Rs. 130 lakhs (with InnoNano Research Pvt. Ltd.).

Arsenic free South 24 Parganas district, DST, Rs. 374.88 lakhs.

Cluster composite nanofibre membranes for rapid, ultra-trace detection of waterborne contaminants, Indo-German Science and Technology Forum, Total funds Rs. 191.324 lakhs (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 2017

Thematic Projects in Frontiers of Nano S&T on Water Purification using Nanotechnology, sanctioned for 3 years.

Extension of Thematic Unit of Excellence (TUE) on water purification using nanotechnology at IIT Madras, DST, for 2 years.

Development of capacitive deionization prototype for brackish water desalination using sustainable nanomaterials, DST, for 2 years.

LAB VISITORS



Prof. T. Pradeep is with Dr. Nonappa (2nd from right) from Aalto University, Amrita Chakraborty and Avijit Baidya (joint doctoral student of IITM and Aalto).



Prof. T. Pradeep and Prof. R. L. Whetten at TUE, May 13, 2017

Prof. T. Pradeep and Prof. Dick Zare at IITM Research Park, February 23, 2017



Prof. T. Pradeep and Prof. Paul S. Weiss, May 6, 2017



Dr. Andrea Schäfer (KIT), Sritama Mukherjee (IITM), Prof. T. Pradeep, Dr. Arun Karthick (IITM) and Sahana Seshachala (KIT).



Prof. T. Pradeep, Prof. Tapas Maji and K. S. Sugii, May 12, 2017



Team from Industrial waters, Finland in collaboration with Aalto University. From Left: Anil Kumar Avula (IITM), Swathy Ravindran (IITM), Riina Honkanen (IW), Anna Björkqvist (IW), Jukka Hassinen (Aalto), Janika Lehtonen Mukharjee (Aalto), Akashdeep Oberoi (IITM), Sritama (IITM), T. Ragul(IITM)



Prof T. Pradeep is with Prof. Haiwon Lee, Dr. Misoon Mah, Dr. Kristopher Ahlers, Dr. Sheena Winder, Ms. Audrey Gray, July 05, 2017



Prof. T. Pradeep is with Dr. Vikas Abrol and Dr. T.N.V.K.V. Prasad, January 09, 2017



LAB VISITORS

05/01/2017	Dr. K. Vijayamohan, Director, CSIR-CECRI, Tamil Nadu
06/01/2017	Mr. Srinivas Reddy, Blue Star, Tamil Nadu
06/01/2017	Mr. Suresh Oliver, GRIND Technology Pvt. Ltd., Chennai
09/01/2017	Dr. Vikas Abrol, Associate Professor, Sr. Scientist (Soil Science), SKUAST, Jammu
09/01/2017	Dr. T.N.V.K.V. Prasad, Senior Scientist, A.N.G. Ranga Agricultural University, Andhra Pradesh
10/01/2017	Prof. Ronojoy Adhikari, The Institute of Mathematical Sciences, CIT Campus, Tamil Nadu
13/01/2017	Dr. Rinaldo Poli, Laboratoire de Chimie de Coordination, France
20/01/2017	Dr. Pradip Subramanian, Growtech, Bengaluru
20/01/2017	Mr. Sundar Kamath, Clean Water for Villages, Karnataka
27/01/2017	Mr. Hari Pulakkat, Senior Editor of Economic Times, Bengaluru
28/01/2017	Prof. Anil Gupta, Indian Institute of Management, Ahmedabad
30/01/2017	Dr. Rahul Dutta, BITS, Pilani, Rajasthan
02/02/2017	Prof. Andrea Schaefer, KIT, Germany
08/02/2017	Dr. R. S. Suja Rose, Assistant Professor, Madurai Kamaraj University, Tamil Nadu
16/02/2017	Dr. Pradip Subramaniam, Grow Tech, Pune, Maharashtra
22/02/2017	Prof. Tuula Teeri, President, Aalto University, Finland
22/02/2017	Prof. Kimmo Kaski, Department of Computer Science, Aalto University, Finland
22/02/2017	Prof. Risto Ilmoniemä, Professor of Applied Physics, Aalto University, Finland
22/02/2017	Prof. Rojas Orlando, Department of Forest Products Technology & Chemical Engineering, Aalto University, Finland
22/02/2017	Professor Jan Deska, Department of Chemistry and Materials Science, Aalto University, Finland
22/02/2017	Dr. Jukka Hassinen, Post-Doctoral Researcher, Aalto University, Finland
22/02/2017	Dr. Mari Anna Suurmunne, Head of Aalto International Relations, Aalto University, Finland
23/02/2017	Prof. Richard N. Zare, Department of Chemistry, Stanford University, USA
06/03/2017	Prof. Sanjay Chaudhary, Associate Dean, Ahmedabad University
11/03/2017	Prof. Horst Hahn, KIT, Germany
21/03/2017	Dr. J. Raghava Rao, CLRI, Chennai
25/03/2017	Prof. Atsushi Takayuki Suzuki, Yokohama National University, Japan
28/03/2017	Dr. Vasundhara Singh, Department of Applied Sciences, PEC University of Technology, Chandigarh
17/04/2017	Dr. Nonappa, Aalto University, Finland
28/04/2017	Dr. P.V. Lalitha, Senior Scientific Officer, Indo-German Science and Technology Centre
05/05/2017	Prof. Paul S. Weiss, CNSI, UCLA, Los Angeles
08/05/2017	Prof. Robert Lloyd Whetten, Department of Physics and Astronomy, The University of Texas
13/05/2017	Prof. Tapas Maji, JNCASR, Bengaluru
19/05/2017	Mr. Deepak S Parekh, Chairman, HDFC Ltd, Mumbai
07/06/2017	Prof. G. U. Kulkarni, Director CeNS, Bengaluru
09/06/2017	Prof. V Anilkumar Amrutur, Vanderbilt Aerospace Design laboratory, Nashville, Tamil Nadu
16/06/2017	Mr. Siddaram Shabadi, Anarghya Innovations and Technology Pvt. Ltd, Bengaluru
16/06/2017	Dr. Priyadarshi Panda, GETDEW, USA
28/06/2017	Dr. Eluvathingal D Jemmis, Department of Inorganic and Physical Chemistry, IISc, Bangalore
06/07/2017	Prof. Haiwon Lee, Hanyang University, Seoul, Korea
06/07/2017	Dr. Misoon Mah, Head of the Delegation, Asian Office of Aerospace Research & Development, Tokyo
06/07/2017	Lt Col. Kristopher Ahlers, Tech Advisor, Asian Office of Aerospace Research & Development, Tokyo
06/07/2017	Lt Col. Sheena Winder, Intl. Program Officer, Asian Office of Aerospace Research & Development, Tokyo
06/07/2017	Ms. Audrey H. Gray, Admin Officer Asian Office of Aerospace Research & Development, Tokyo
11/07/2017	Dr. P. Biji, Assistant Professor, Nano Sensor Laboratory, PSG Institute of Advanced Studies, Coimbatore
13/07/2017	Mr. R. N. Bagdalkar, ED in-charge of HR and CSR, New Delhi
19/07/2017	Mr. Sudesh Menon, Managing Director, Waterlife, Hyderabad
01/08/2017	Mr. Brandon Nordin, Senior VP, ACS Publications, Hamilton College, Washington
01/08/2017	Mr. Sujan Sekhar, Manager Business Development, ACS Publications
02/08/2017	Dr. Chandra Sekhar Tiwary, Rice University, USA
04/08/2017	Mr. Varun Gupta, Director, KENT RO Systems
08/08/2017	Dr. Aloke Kumar, Department of Mechanical Engineering, IISc, Bangalore

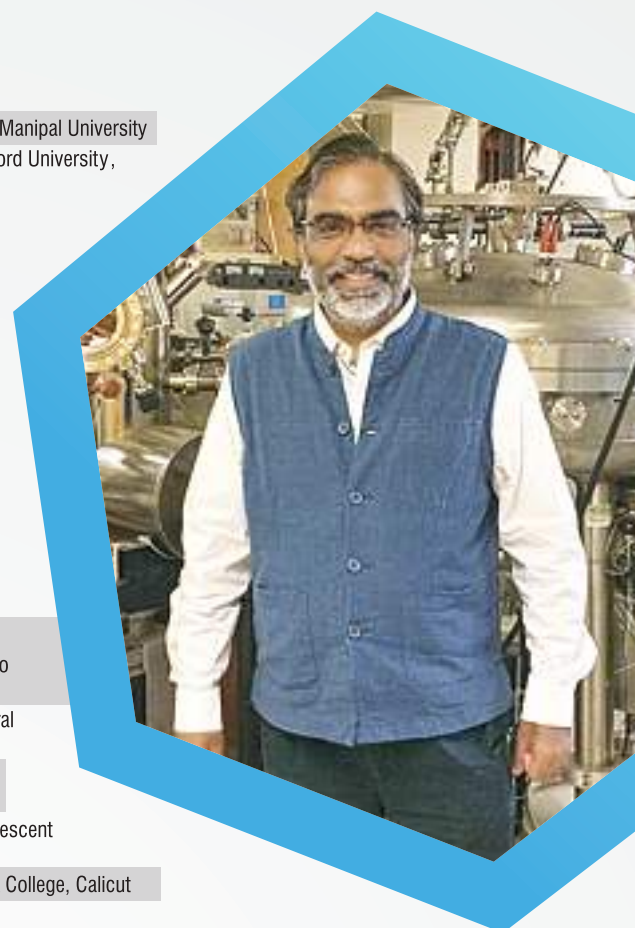


08/08/2017	Dr. Greeshma Nair, Associate Publisher-Chemistry, Elsevier, Amsterdam
16/09/2017	Dr. Jukka Hassinen, Aalto University, Finland
16/09/2017	Ms. Janika Lehtonen, Ph.D student, Aalto University, Finland
16/09/2017	Ms. Riina Honkanen, Young Research Assistants, Finland
16/09/2017	Ms. Anna Björkvist, Young Research Assistants, Finland
16/09/2017	Dr. Zakir Sultan, TWAS-UNESCO Associateship Scheme, Bangladesh
28/09/2017	Dr. Keisuke Hirata, Tsukuda Laboratory, The University of Tokyo, Japan
23/10/2017	Dr. Chaitanya, GETDEW
23/10/2017	Mr. Mayank Sharma, DewH ₂ O Inc., USA
03/11/2017	Mr. Muthu Murugappan, Murugappa Business Group, Chennai
14/11/2017	Dr. Dos Santos Pierre, Vice President Recherche, University of Bordeaux, France
17/11/2017	Dr. Shalina Begum & Students, Farook College, Kerala
20/11/2017	Dr. Abdul Khaliq Rasheed, Sunway University, Malaysia
22/11/2017	Prof. Hadas Mamane Steindel, Tel Aviv University, Israel



VISITS

11/01/2017	Brainstorming session of think tank group on Science and Policy, DST, IAS, Bangalore
07/02/2017	Inaugural address certificate course, Stella Maris College, Chennai
09/02/2017	International Symposium on new trends in Applied Chemistry, NTAC-2017, Sacred Heart College, Kochi
15/02/2017	Government College of Technology, Coimbatore
21/02/2017	Lecture, Chemical Engineering Institute, Chandigarh
16/03/2017	Vivanta by Taj President, Mumbai
17/03/2017	IIT Delhi, Delhi
23/03/2017	31st ISMAS Symposium on Mass Spectrometry, Mumbai
30/03/2017	A discussion meeting on Molecular Phenomena at the Nano-Bio Interface, Manipal University
03/04/2017	Editorial Meetings at the Spring ACS National Meeting, San Francisco, Stanford University, Lawrence Berkeley National Laboratory, Rice University, Texas, US
15/04/2017	InnoDi Meeting, Bangalore
21/04/2017	Meeting with Mr. Sourabh Das, Additional Chief Secretary, PHE Department also meeting Dr. P. B. Salim, principal secretary, Govt. of West Bengal.
21/04/2017	Keynote Lecture in SMMA-2017, IISER Kolkata
15/05/2017	Lecture in Thematic Conference in Chemical Sciences, IIT Ropar, Punjab
22/05/2017	5th NATAG-POCC Meeting, IIT Bombay
24/05/2017	Bio Nano Consulting, London, UK and KIT, Germany
05/06/2017	6th Roddam Narasimha Distinguished Lecture, IIT Gandhinagar
17/06/2017	9th International Conference on Materials for Advanced Technologies, Singapore
17/06/2017	National University of Singapore
10/07/2017	Farook College, Kozhikode, Kerala
11/07/2017	DST-SERB School on Chemical Ecology, Bangalore
26/07/2017	6th NATAG-POCC Meeting, IIT Bombay
14/08/2017	ISMPC (Symposium on Monolayer Protected Clusters), Switzerland Visit to Aalto University, Finland Attended 254th ACS National Meeting Visit to Purdue University, USA
06/09/2017	Newton Bhabha Workshop on 'Translating Clean Energy Technologies to Rural India' IISER, Pune
14/09/2017	Conference Organized by the National Academy of Sciences, India (NASI), Allahabad
21/09/2017	Conference on "Sustainable Clean Water Technology, B.S. Abdur Rahman Crescent University, Chennai
23/09/2017	International Conference on Emerging Frontiers of Chemical Science, Farook College, Calicut
09/10/2017	IIT Delhi, Delhi
02/11/2017	Lecture in Institute of Frontier Technology, RARS, A.N.G. Ranga Agricultural University, Tirupati
24/11/2017	PHED Meeting, Kolkata
29/11/2017	Inauguration and Technical talk, PSG College, Coimbatore
07/12/2017	Bangalore Nano, Bangalore
10/12/2017	InnoDi Inauguration, Bangalore
11/12/2017	11th Intl. Conference on Sustainable solutions to Achieve safe drinking water program, Bhavan's College, Mumbai
11/12/2017	150th Year Celebration - National Conference "New perspective to Advanced functional at the Dept. of Chemistry, Ravenshaw University, Cuttack, Odisha



VISITS



At Farook College, Kerala



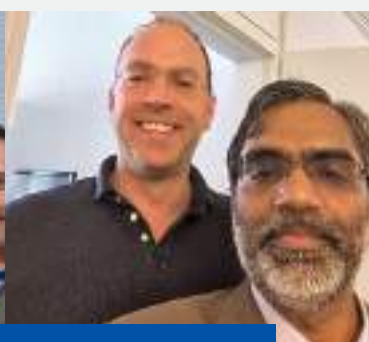
With Prof. Francesco Stellacci



With Prof. T. Tsukuda & Prof. R. L. Whetten



With Jukka Hassinen at Alto University



With Prof. Rabin Ras



With Michael Wleklinski and Erica Baker



With Prof. R. N. Zare and group



With Dr. Sakkarapalayam M. Mahalingam at Purdue University



With Prof. G. Cooks



At Purdue University



With Prof. P. M. Ajayan at Rice University



With Prashant K. Jain University of Illinois, Urbana-Champaign



With Prof. Anilkumar Amrutur at IIT Gandhinagar

THE HINDU

AGRICULTURE

When silver 'grows' in paddy fields



When the green turns silver—The rice that grows in paddy fields in the state of Kerala, India, is not just a staple food but also a source of income for the farmers. The rice is grown in the fields, and the farmers harvest it. The rice is then sold to the market, and the farmers receive money for it. The rice is a staple food for the people of Kerala, and it is also a source of income for the farmers. The rice is grown in the fields, and the farmers harvest it. The rice is then sold to the market, and the farmers receive money for it.

IIT-M develops extremely water-efficient coating



The research team at IIT-M has developed a new coating that is extremely water-efficient. The coating is made of a special material that can be used in a variety of applications. The coating is made of a special material that can be used in a variety of applications. The coating is made of a special material that can be used in a variety of applications. The coating is made of a special material that can be used in a variety of applications.

gold for india



THALAPPIL PRADEEP AND TEAM HAVE WORKED OUT TURN SILVER INTO GOLD, WITHOUT USING MAGIC.

Writer Mark Hay
Photographer Shannon Zirkle

Thalappil Pradeep and his team have developed a new process to turn silver into gold. The process is called 'silver to gold' and it is a very simple process. The process is called 'silver to gold' and it is a very simple process. The process is called 'silver to gold' and it is a very simple process. The process is called 'silver to gold' and it is a very simple process.

IIT-M develops cheaper device to purify water



The research team at IIT-M has developed a new device to purify water. The device is called 'water purifier' and it is a very simple device. The device is called 'water purifier' and it is a very simple device. The device is called 'water purifier' and it is a very simple device. The device is called 'water purifier' and it is a very simple device.

WHAT IS CAPACITIVE DEIONISATION?

Capacitive deionisation is a process that uses a special material to purify water. The process is called 'capacitive deionisation' and it is a very simple process. The process is called 'capacitive deionisation' and it is a very simple process. The process is called 'capacitive deionisation' and it is a very simple process. The process is called 'capacitive deionisation' and it is a very simple process.

THE TIMES OF INDIA

'Unsustainable use in farming depleting groundwater'

By Anand Narayan



The unsustainable use of groundwater in farming is depleting the groundwater. The unsustainable use of groundwater in farming is depleting the groundwater. The unsustainable use of groundwater in farming is depleting the groundwater. The unsustainable use of groundwater in farming is depleting the groundwater.

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CHEMISTRYWORLD



India's science start-ups

By Anand Narayan

India's science start-ups are growing rapidly. The science start-ups are growing rapidly. The science start-ups are growing rapidly. The science start-ups are growing rapidly.

India's science start-ups are growing rapidly. The science start-ups are growing rapidly. The science start-ups are growing rapidly. The science start-ups are growing rapidly.

TALKS



1. Affordable point of use water purification using nanomaterials, iNNCOTECH, Tata Chemicals Ltd. Innovation Centre, Pune, January 23, 2017.
2. Understanding science, INSA Programme on Popularization of Science, Kalpakachery, Malappuram, January 26, 2017.
3. Nanostructures and ions, Inaugural lecture at the certificate course on 'Exploring nanoscience - synthesis and characterization of nanoparticles', Center for Research in Science and Technology (CRIST), Stella Maris College, Chennai, February 7, 2017.
4. Reactions between nanoparticles, Prof. K. V. Thomas endowment international symposium on New trends in Applied Chemistry, Sacred Heart College, Thevara, Kochi, February 9-11, 2017.
5. Affordable point of use water purification using nanomaterials, Government College of Technology, Coimbatore, February 15, 2017.
6. Water, food and air: New science at the nanoscale, TATA University Connect – Meeting of CTOs, Mumbai, March 16, 2017.
7. Intercluster reactions, 31st ISMAS Symposium, BARC, Mumbai, March 23-25, 2017.
8. Reactions between nanoparticles, Discussion meeting on molecular phenomena at the nano-bio interface, Manipal University, March 30, 2017.
9. Reactions between nanoparticles, Department of Materials Science & Nanoengineering, Rice University, Houston, April 10, 2017.
10. Clean water using advanced materials: Science, incubation and industry, Smart materials: Methods and applications, IISER Kolkata, April 21, 2017.
11. Clean water using sustainable materials: Science, incubation and industry, Thematic conference in Chemical Sciences (TC2S - 2017): Sustainable Chemistry, IIT Ropar, May 15, 2017.
12. Reactions between nanoparticles, Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany, May 30, 2017.
13. Affordable clean water using advanced materials, Institute of Membrane Technology, Karlsruhe Institute of Technology, Germany, May 31, 2017.

TALKS

14. Reactions between nanoparticles, Friedrich Alexander University Erlangen - Nuremberg, June 2, 2017.
15. Clean water using advanced materials: Science, incubation and industry, Sixth lecture of the Roddam Narasimha distinguished lecture series, IIT Gandhinagar, June 6, 2017.
16. Reactions between nanoparticles, 9th International conference on materials for advanced technologies, June 19, 2017.
17. Reactions between nanoparticles, National University of Singapore, Singapore, June 20, 2017.
18. Affordable clean water using advanced materials, 9th International Conference on Materials for Advanced Technologies, Singapore, June 21, 2017.
19. New trends in mass spectrometry and imaging, NCBS, Bangalore, July 12, 2017.
20. Affordable and sustainable clean water using advanced materials, Symposium on science and engineering for sustainable development, IIT Bombay, July 26, 2017.
21. Reactions between nanoparticles, International symposium on Monolayer protected clusters, Ascona, Switzerland, August 13-16, 2017.
22. Reactions between nanoparticles, Aalto University, Finland, August 17, 2017.
23. Ion-based synthesis of functional materials, ACS 254th National Meeting, Washington DC, August 22, 2017.
24. Reactions between nanoparticles, Department of Chemistry, Purdue University, August 24, 2017.
25. How do I innovate?, UK-India newton researchers link workshop, Translating clean energy research to rural India, IISER Pune, September 6, 2017.
26. Emerging technologies for water purification with particular reference to nanotechnology, Road to Swachh Bharat – Brain storming on safe water and sanitation, NASI, Allahabad, September 15-17, 2017.
27. Nanotechnology applications for sustainable clean water, B. S. Abdur Rahman University, Chennai, September 21, 2017.
28. Reactions between nanoparticles, International conference on emerging frontiers in chemical sciences, Farook College, September 23-25, 2017.
29. From Molecular Acorns to Institutional Oaks, 2nd Institute Colloquium, IIT Madras, October 13, 2017.
30. Clean water, agriculture and our life: Impact of nanotechnology, AgriNANO-2017, Inaugural Plenary Lecture, Acharya N.G. Ranga Aricultural University, Tirupati, November 2-3, 2017.
31. Materials for clean water, recent environmental challenges, solutions and management for sustainability, Inaugural Lecture, CIT, Coimbatore, November 29-December 5, 2017.
32. Nanomaterials and Clean water, International Conference on Biological Applications of Nanoparticles, ICON-BIO 2017, IIT Madras, December 4-5, 2017.
33. Innovations for clean water: Science, technology and incubation, International Conference on Sustainable Solutions to Achieve Safe Drinking Water, Bhavan's College, Mumbai, December 11-12, 2017.
34. Reactions between nanoparticles, National Conference on New Perspective to Advanced Functional Materials, Plenary Lecture, Ravenshaw University, Cuttack, December 15, 2017.



INSTITUTE COLLOQUIUM



This presentation traced the life of the speaker at IITM from ground zero to the present, in his quest to do something meaningful in the context of Indian science. The growth of science, technology and business incubation leading to social benefits was illustrated with specific examples. The talk was designed to be motivational with limited or no chemistry or materials science.

October 13, 2017



SERVICE 2017

1. Chairman, organizing committee of the International Conference in Farook College, helped the college in conducting the first such event in science in its history.
2. Associate Editor of the Journal, ACS Sustainable Chemistry & Engineering.
3. Member of the Editorial Boards of Chemistry - An Asian Journal, Nanoscale, Scientific Reports (Nature Group), Particle, Surface Innovations, International Journal of Water, Wastewater Treatment, Chemistry of Materials (from 2018) and ACS Nano (from 2018).
4. Member, India-Japan Council of the Department of Science and Technology.
5. Member, Nanoscience Advisory Committee, Nano Mission, Department of Science and Technology.
6. Member, Proof of Concept Expert Committee, Nano Mission, Department of Science and Technology.
7. Member, Executive Committee, Neutron Scattering Society of India.
8. Vice President of the Indian Society for Mass Spectrometry.
9. Member of the Council of Materials Research Society of India.
10. Member, Bureau of Indian Standards - on drinking water products.
11. Member, Board of studies of the Department of Atomic and Molecular Physics, Manipal University.
12. Member, Board of the School of Life Sciences, Ahmedabad University.



A NEW INITIATIVE - ICCW

A new initiative to build the International Centre for Clean Water (ICCW) has begun. The vision is to create a consortium for affordable clean water for all, with global participation.

**WORLD
WATER**



INCUBATION

INNONANO RESEARCH PRIVATE LIMITED

Was incubated to take our drinking water technologies to people. The company licensed 13 of our patents. It has established production facilities. Our arsenic removal technology has reached over 600,00 people now through various installations in arsenic affected regions of India. It has been expanded to Punjab. The technologies have been approved nationally.

SAFEWATER NANO PRIVATE LIMITED

Is a company incorporated in Singapore, to take our water technologies to international markets.

INNODI WATER TECHNOLOGIES PRIVATE LIMITED

The company focuses on capacitive deionisation products. It's factory was inaugurated in December 10, 2017.

VAYUJAL TECHNOLOGIES PRIVATE LIMITED

The company is focusing on water from air. It has put together its first prototype on atmospheric water capture at 100 L/day scale using our highly efficient surfaces. It has received initial funding needed for its activities.

AQUEASY INNOVATIONS PRIVATE LIMITED

Has been established to create efficient water transport solutions. Prototypes have been tested.



During the inauguration of the factory of InnoDI, Bangalore, December 10, 2017

Summer students 2017



Our Ph.D students: Hope, determination & camaraderie



Our team: Our strength



Not pictured:



For more information:

Professor T. Pradeep

Thematic Unit of Excellence, Department of Chemistry

Indian Institute of Technology Madras

Chennai 600 036, INDIA

Tel.: +91-44-2257 4208

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Email: pradeep@iitm.ac.in

Web: www.dstuns.iitm.ac.in/pradeep-research-research-group.php

