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# ANNUAL REPORT

## 2014



<http://www.dstuns.iitm.ac.in/pradeep-research-group.php>

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## Our Team

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Dr. V. Vidya, Assistant Professor in Chemistry, Bharathi Women's College, Chennai

1. Luminescent AgAu alloy clusters derived from Ag nanoparticles: Manifestations of tunable AuI-CuI metallophilic interactions, Kumaranchira R. Krishnadas, Thumu Udayabhaskararao, Susobhan Choudhury, Nirmal Goswami, Samir Kumar Pal and T. Pradeep, *Eur. J. Inorg. Chem.*, *5* (2014) 908-916 (DOI: 10.1002/ejic.201301424).
2. Development of ultralow energy (1-10 eV) ion scattering spectrometry coupled with reflection absorption infrared spectroscopy and temperature programmed desorption for the investigation of molecular solids, Soumabha Bag, Radha Gobinda Bhui, Rabin Rajan J. Methikkalam, Luke Kephart, Jeff Walker, Kevin Kuchta, Dave Martin, Jian Wei and T. Pradeep, *Rev. Sci. Instrum.*, *85* (2014) 014103 (DOI: 10.1063/1.4848895).
3. Supramolecular functionalization and concomitant enhancement in properties of Au<sub>25</sub> clusters, Ammu Mathew, Ganapati Natarajan, Lauri Lehtovaara, Hannu Hakkinen, Ravva Mahesh Kumar, Venkatesan Subramanian, Abdul Jaleel and T. Pradeep, *ACS Nano*, *8* (2014) 139-152 (DOI: 10.1021/nm406219x).
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5. Mixed-monolayer-protected Au<sub>25</sub> clusters with bulky calix[4]arene functionalities, Jukka Hassinen, Petri Pulkkinen, Elina O. Kalenius, T. Pradeep, Heikki Tenhu, Hannu J. Häkkinen, and Robin H. A. Ras, *J. Phys. Chem. Lett.*, *5* (2014) 585-589 (DOI: 10.1021/jz500052h).
6. Molecular ionization from carbon nanotube paper, R. Narayanan, D. Sarkar, R. G. Cooks and T. Pradeep, *Angew. Chem. Int. Ed.*, *53* (2014) 5936-5940 (DOI: 10.1002/anie.201311053).
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8. Manifestation of the difference in reactivity of silver clusters in contrast to its ions and nanoparticles: The growth of metal tipped Te nanowires, Anirban Som, Akshaya Kumar Samal, Thumu Udayabhaskararao, M. S. Bootharaju and T. Pradeep, *Chem. Mater.*, *26* (2014) 3049-3056 (DOI: 10.1021/cm403288w).
9. Emergence of metallicity in silver clusters in the 150 atom regime: A study of differently sized silver clusters, Indranath Chakraborty, Jayanthi Erusappan, Anuradha Govindarajan, K. S. Sugi,

- Thumu Udayabhaskararao, Atanu Ghosh and T. Pradeep, *Nanoscale*, 6 (2014) 8024–8031 (DOI: 10.1039/c4nr00679h).
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  11. Coalescence of atomically precise clusters on graphenic surfaces, Atanu Ghosh, T. Pradeep and Jaydeb Chakrabarti, *J. Phys. Chem. C*, 118 (2014) 13959–13964 (DOI: 10.1021/jp503001s).
  12. Synthesis of atomically precise silver clusters using the miscibility principle, Atanu Ghosh and T. Pradeep, *Eur. J. Inorg. Chem.*, 2014 (2014) 5271–5275 (DOI: 10.1002/ejic.201402587).
  13. Spatiotemporal mapping of three dimensional rotational dynamics of single ultrasmall gold nanorods, Kamallesh Chaudhari and T. Pradeep, *Scientific Reports (Nature)*, 4 (2014) 5948 (DOI: 10.1038/srep05948).
  14. Using ambient ion beams to write nanostructured patterns for surface enhanced Raman spectroscopy, Anyin Li, Zane Baird, Soumabha Bag, Depanjan Sarkar, Anupama Prabhat, T. Pradeep and R. Graham Cooks, *Angew. Chem. Int. Ed.*, 53 (2014) 12528–12531 (DOI: 10.1002/anie.201406660).
  15. Ag<sub>11</sub>(SG)<sub>7</sub>: A new cluster identified by mass spectrometry and optical spectroscopy, Ananya Bakshi, M. S. Bootharaju, Xi Chen, Hannu Hakkinen and T. Pradeep, *J. Phys. Chem. C*, 118 (2014) 21722–21729 (DOI: 10.1021/jp508124b).
  16. Controlled synthesis and characterization of the elusive thiolated Ag<sub>55</sub> cluster, Indranath Chakraborty, Shrabani Mahata, Anuradha Mitra, Goutam De and T. Pradeep, *Dalton Trans.*, 43 (2014) 17904–17907 (DOI: 10.1039/c4dt02476a).
  17. Reversible formation of Ag<sub>44</sub> from selenolates, Indranath Chakraborty and T. Pradeep, *Nanoscale*, 6 (2014) 14190–14194 (DOI: 10.1039/C4NR03267E).
  18. Isolation and tandem mass spectrometric identification of a stable monolayer protected silver-palladium alloy cluster, Sreya Sarkar, Indranath Chakraborty, Manoj Kumar Panwar and T. Pradeep, *J. Phys. Chem. Lett.*, 5 (2014) 3757–3762 (DOI: 10.1021/jz5019509).
  19. Approaching sensitivity of tens of ions using atomically precise cluster-nanofiber composites, Atanu Ghosh, Vedhakkani Jeseentharani, Mohd Azhardin Ganayee, Rani Hemalatha, Kamallesh Chaudhari, Cherianath Vijayan and T. Pradeep, *Anal. Chem.*, 86 (2014) 10996–11001 (DOI: 10.1021/ac502779r).
  20. Antimicrobial silver: An unprecedented anion effect, J. R. Swathy, M. Udhaya Sankar, Amrita Chaudhary, Sahaja Aigal, S. Anshup and T. Pradeep, *Scientific Reports (Nature)*, 4 (2014) 7161 (DOI: 10.1038/srep07161).

21. Optical rotation by plasmonic circular dichroism of isolated gold nanorod aggregates, Kamallesh Chaudhari and T. Pradeep, *Appl. Phys. Lett.*, *105* (2014) 203105 (DOI: 10.1063/1.4902318).
22. Simple and efficient separation of atomically precise noble metal clusters, Atanu Ghosh, Jukka Hassinen, Petri Pulkkinen, Heikki Tenhu, Robin H. A. Ras, and Thalappil Pradeep, *Anal. Chem.*, *86* (2014) 12185–12190 (DOI: 10.1021/ac503165t).
23. Vacuum ultraviolet photoabsorption of interstellar icy thiols, Radha Gobinda Bhuin, Bhalamurugan Sivaraman, J.-I. Lo, Raja Sekhar B. N., Bing-Ming Cheng, T. Pradeep, and Nigel Mason, *J. Chem. Phys.*, *141* (2014). 231101 (DOI: 10.1063/1.4903840).
24. Identification of effective substrates for the direct analysis of lipids from cell lines using desorption electrospray ionization mass spectrometry, Amitava Srimany, Jayashree Balasubramanyam, Subramanian Krishnakumar, Sailaja Elchuri and T. Pradeep, *Rapid Commun. Mass Spectrom.*, (2014) (Just accepted).
25. Size evolution of protein protected gold clusters in solution: A combined SAXS-MS investigation, Ananya Baksi, Anuradha Mitra, Jyoti Sarita Mohanty, Haiwon Lee, Goutam De and T. Pradeep, *J. Phys. Chem. C*, (2014) (Just accepted).

### Conferences conducted

1. One day discussion meeting on “*Imaging in Mass spectrometry*” January 17, 2014, IC & SR, IIT Madras.
2. International discussion meeting on “*Low Energy Ion Scattering at Molecular Solids*” January 18-19, 2014, IC & SR, IIT Madras.
3. Second international water conference on “*Emerging Technologies on Clean Drinking Water*”, October 23-24, 2014, IC & SR, IIT Madras.

### Lectures Delivered

1. Molecular ionization from carbon nanotube paper, International discussion meeting on low energy ion scattering at molecular solids, January 18-19, 2014.
2. Infinite possibilities of the infinitesimal!, Karnataka Science Congress, Gulbarga, January 30-31, 2014.
3. Biopolymer reinforced synthetic granular nanocomposites for affordable point-of-use water purification, Environmental Impact and Hazard Identification of Engineered Nanomaterials, Indo-UK seminar, Ahmedabad University, February 24-26, 2014.
4. Affordable clean water using nanotechnology, Nano for Young, ICONSAT 2014, Punjab University, Chandigarh, March 4, 2014.
5. Molecular Ionization from Carbon Nanotube Paper, Indian Society for Mass Spectrometry Workshop, Parwanoo, March 10, 2014.
6. Atomically precise clusters of noble metals, Two-Day Workshop on Nano Science and Technology April 4-5, 2014, IIT Madras.
7. Clusters, ions and advanced mass spectrometry, University of Hyderabad, April 28, 2014.
8. Affordable clean water using nanomaterials, Department of Applied Chemistry, University of Johannesburg, May 9, 2014.
9. Affordable point-of-use drinking water purification using nanomaterials, As2014, Argentina May 12-16, 2014.
10. A new form of ionization, International discussion meeting on Advanced materials: current trends & future prospects, Manali, May 28-June 1, 2014.
11. Mass spectrometry and materials science, Advances in spectroscopy, IIT Madras June 20, 2014.
12. Affordable point-of-use drinking water purification using nanomaterials, Professor CNR Rao 80<sup>th</sup> Birthday Symposium, Chemistry Centre, Burlington House, London, 23 – 24 June 2014.

13. Affordable point-of-use drinking water purification using nanomaterials, University of Alberta, July 3, 2014.
14. Affordable point-of-use drinking water purification using nanomaterials, IIT Bombay, July 11, 2014.
15. Introduction to Nanoscience and Nanotechnology, Apollo Tyres Ltd., July 12, 2014
16. Affordable point-of-use drinking water purification using nanomaterials, Amrita University, July 24, 2014.
17. Nanomaterials and emerging frontiers of mass spectrometry, Stella Maris College, Chennai July 25, 2014.
18. Nanomaterials and emerging frontiers of mass spectrometry, IIST, Thiruvananthapuram, July 28, 2014.
19. A century of chemistry!, Inaugural Lecture of the Integrated Interdisciplinary Master of Science Programme, IIRBS, M. G. University, Kottayam, August 19, 2014.
20. Luminescent gold molecules, IIT Madras, August 23, 2014.
21. Metals...not yet, SN College for Women, Kollam, September 29, 2014.
22. New ways of ambient ionization, JNC Conference on Chemistry of Materials, Thiruvananthapuram, October 11-13, 2014.
23. Affordable point of use drinking water purification using nanomaterials, Plenary talk at Asia NANO 2014, Jeju, Korea, October 26-29.
24. New ways of ambient ionization, Department of Chemistry, Seoul National University, Korea, October 29, 2014.
25. Drinking water purification for tomorrow, National Academy of Sciences 3<sup>rd</sup> Policy Support Brainstorming on Safe Water and Sanitation, Allahabad, November 18-20, 2014.
26. New ways of ambient ionization for plant sciences, Department of Plant Biology & Biotechnology, Loyola College, Chennai, November 26, 2014.
27. New ways of ambient ionization, 5<sup>th</sup> DAE-BRNS Interdisciplinary Symposium on Materials Chemistry, BARC, Mumbai, December 9-13, 2014.
28. Affordable point-of-use water purification using nanomaterials, INAE Annual Convention, Jaipur, December 12-13, 2014.
29. A century of chemistry!, Science Talent Enrichment Programme (STEP) - Dec 15-19, 2014, IISER Thiruvananthapuram.



## Student Activities

1. Avijit Baidya visited Aalto University, Finland to work under Prof. Robin Ras on *Applications of superhydrophobic surface*, 24th June -17th Sept, 2014.
2. Ananya Bakshi attended Gordon Research Conference on *Noble Metal Nanoparticle*, Mount Holyoke College, South Hadley, MA, USA and visited Prof Vicky Wysocki's lab at The Ohio state University.
3. Indranath Chakraborty attended Gordon Research Conference on *Noble Metal Nanoparticle*, Mount Holyoke College, South Hadley, MA, USA and visited Prog Bigioni's lab at The University of Toledo
4. Radha Gobinda Bhuin attended 62<sup>nd</sup> ASMS Conference on *Mass Spectrometry and Allied Topics*, June 15-19, 2014, Baltimore, MD, USA.
5. Radha Gobinda Bhuin visited National Synchrotron Radiation Research Center, Taiwan, August 4-11, 2014.
6. Radha Gobinda Bhuin visited Seoul National University, South Korea to work with Prof. H Kang, August 12- October 10, 2014
7. Rabin Rajan J Methikkalam attended International Mass Spectrometry Conference, IMSC-2014, Geneva, Switzerland.

## Patents/Technologies

### Patents

- Vertical growth of nanoparticles leading to micrometer long brushes by ambient electrolytic spray deposition, T. Pradeep, Depankar Sarkar, M. K. Mahita, Anirban Som, R. Graham Cooks, Anyin Li, 6669/CHE/2014, filed on December 29, 2014.
- Method of extraction of silver by glucose, T. Pradeep, Ananya Baksi, Mounika Gandhi, Swathi Chaudhari, Soumabha Bag, 6730/CHE/2014, December 30, 2014.
- Method for accumulation of silver by rice and possible metal extraction by agriculture, T. Pradeep, Soujit Sengupta, Ananya Baksi, Debal Deb, 6846/CHE/2014, December 31, 2014.

### Technology Development

- AMRIT is undergoing installations across the country. It has now reached West Bengal, Bihar, Uttar Pradesh and Karnataka.
- A new AMRIT purifier with RFID-based delivery and internet-based data collection was displayed at Bangalore India Nano 2014.
- On-line AMRIT water purifiers attached to hand pumps have been developed recently.
- The pesticide removal technology has reached about Rs. 1.5 cores in royalty earnings, translating to the production of nearly 1.5 million filter units. The technology must have reached about 5 million people so far.

## Grants

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

## Cover Pages



DOI: 10.1002/ejic.201402985



COVER PROFILE

Read the full text of the article at 10.1002/ejic.201402587

## Synthesis of Atomically Precise Silver Clusters by Using the Miscibility Principle



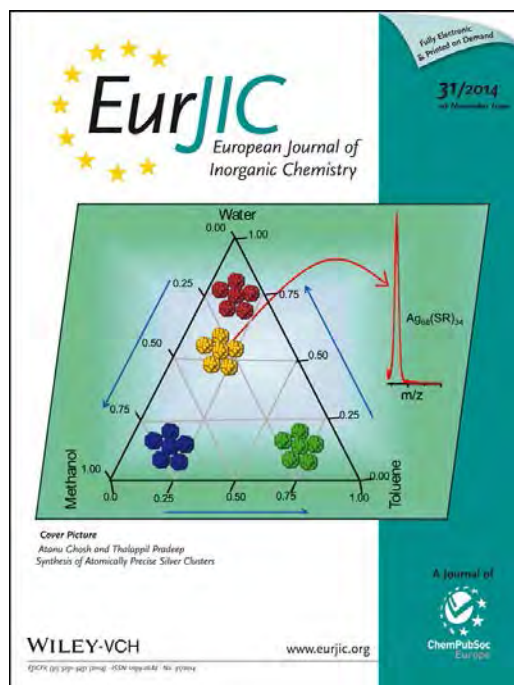
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विज्ञान और प्रौद्योगिकी विभाग

GOVERNMENT OF INDIA  
Ministry of Science and Technology  
Department of Science and Technology  
Technology Bhavan, New Mehrauli Road  
New Delhi - 110016

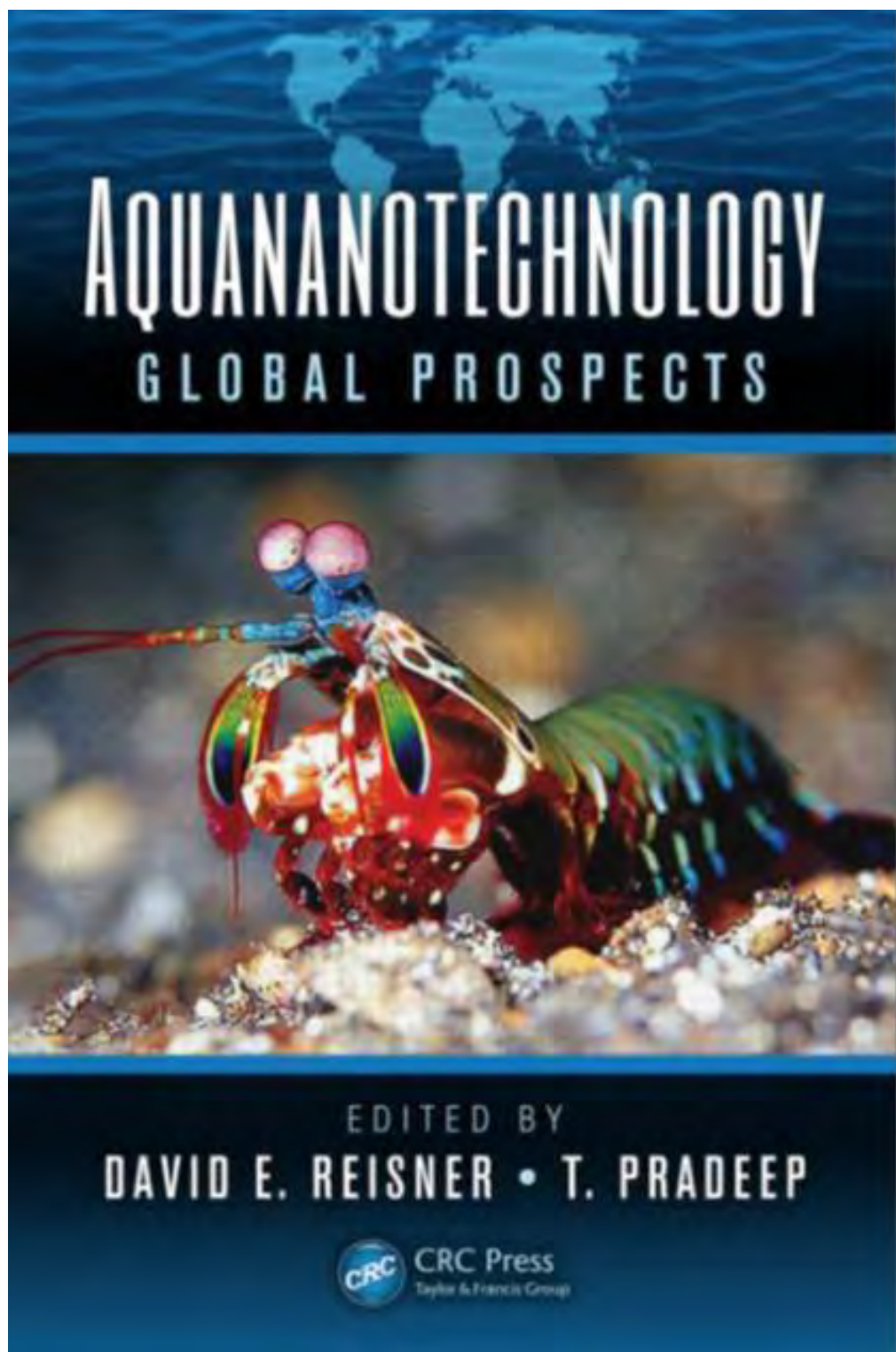


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Invited for the cover of this issue is Thalappil Pradeep at the Indian Institute of Technology Madras, India. The cover image shows a schematic phase diagram of the three-component solvent system used for preparing monolayer-protected silver clusters. The different clusters obtained by keeping the reactants the same but adjusting the solvent system by moving to different regions of the phase diagram are shown in different colors.



**Books (Front Cover of a Book Released This Year)**



***Aquananotechnology: Global Prospects.***

David E. Reisner, T. Pradeep, CRC Press, New York, 837 Pages

## commentary



**Figure 4** | Promising example of commercialized nanotechnology. **a**, A silver nanocomposite, Ag-BM, used for metal decontamination of water, formed from silver nanoparticles (yellow spheres) embedded in a matrix of alumina (brown rods) templated on chitosan fibrils (ochre filaments). **b**, A resulting product for arsenic and metal decontamination of water named AMRIT, undergoing installation in the arsenic- and iron-affected regions of the Murshidabad District, West Bengal (inset), and currently serving 30,000 people. The technology has resulted in the incubation of the Indian Institute of Technology Chennai-based company InnoNano Research. Panel **a** adapted with permission from ref. 11, © 2013 NAS. Inset, © Daniel Kaesler/Alamy.

8/12/2014

# THE HINDU

S & T » Science

## Honey, I shrunk the mass spectrometer



Innovative: Rahul Narayanan of the Department of Chemistry, IIT Madras and the lead author of the paper performs an experiment using nanotube-coated paper.—photo: Special Arrangement

### PAPER SPRAY IONIZATION WITH A 3-V BATTERY

Like most ambient sample ionization methods used for mass spectrometry, paper spray usually requires voltages in the kilovolt range. Such high ionization voltages can be dangerous and require large power supplies. Rahul Narayanan, Depanjan Sarkar, and Thalappil Pradeep of the Indian Institute of Technology, Madras, in Chennai, and R. Graham Cooks of Purdue University now show that they can ionize samples with potentials as low as 3 V by using paper coated with carbon nanotubes (*Angew. Chem. Int. Ed.* 2014, DOI: 10.1002/anie.201311053). In a demonstration, the group used the low-voltage method to collect mass spectra of pesticides, medicines, amino acids, and other compounds. Without the nanotube coating, more than 500 V is required to produce any signal, they say. Electron micrographs of the coated paper show that nanotubes protrude from the surface. The researchers suggest that the nanotubes act as electrodes that induce an electric field between the paper tip and the mass spectrometer inlet. More recently, the team has found that they could obtain spectra by applying just 1 V, Pradeep says.—CHA

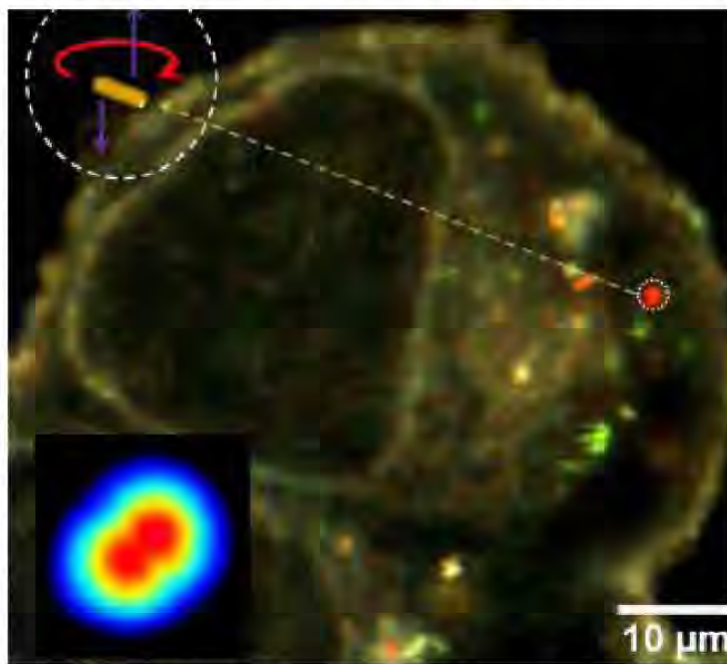
# Turning a simple optical microscope into a powerful tool

R. PRASAD

Small modifications to an ordinary optical microscope have helped turn it into a powerful instrument that can be used for studying complex cellular biology in real time at the nanoscale level. And such is the resolution that the modified optical microscope can study the cellular biology of a living single cell. All biological events – transport mechanism, protein synthesis – happen at the nanoscale level.

The work carried out by an IIT Madras duo – Kamalesh Chaudhari, a research scholar from the Department of Biotechnology and Prof. T. Pradeep of the Department of Chemistry – has made it possible to observe the three dimensional dynamics of tiny nanoparticles with “simpler instrumentation.” “Simple optical microscopes have never been used for observing detailed dynamics of simple nanoscale objects,” said Prof. Pradeep. The results of the study were published on August 5 in *Scientific Reports*.

Popular methods for studying biological events at nanoscale use fluorescence; the other is tagging a nanoparticle to an object of interest and studying it. “So far people have tried to label fluorescent particles/small molecules and study them. But in those cases the cell is fixed, and if the cell is live, the fluorescence of the small molecules lasts at most for 20 minutes,” said Mr. Chaudhari.



*Various motions of a gold nanorod in a human cell and the polar map derived from the study can unravel complex cellular biology in real time.*

Optical scattering is one of the other methods used for studying biological events. But it would be useful only if an object produces intense scattering of incident light at a given wavelength. Gold nanorods are excellent scatterers of light. So if you observe scattering at a specific wavelength we know a nanoparticle is there,” Prof. Pradeep said. But it was the use of a polariser with a small

angular tilt that produces an asymmetry in the scattering pattern that has made the technique unique for studying biological events.

Since the scattered light from the nanorod will be polarised in a preferential direction, the direction of the polarisation analyser is changed to transmit light of specific polarisation.

Unlike a spherical nanoparticle, a nanorod produces

two types of scattering – one is along the longitudinal axis and the other is in the transverse axis. While the longitudinal scattering is enhanced in the red region, the transverse scattering is in the green region. “With an optical microscope, we can’t see nanorods, but can distinguish the scattering pattern,” the senior author said. Based on the colour of the scattered light it becomes possible to

say if the rod is perpendicular or horizontal with respect to the incident light.

“If a particle is spherical then polarisation has no effect because the scattering of an isotropic sphere is independent of orientation,” said Prof. Pradeep. But in the case of a rod, the scattering is orientation dependent – whether the rod is vertical or horizontal with respect to the incident light.

“We get a polar pattern by varying the polarisation angle,” the senior author said. In the case of nanorods, the pattern produced by scattering resembles the figure eight. Based on the polar pattern, it is possible to deduce how the nano rods move/rotate inside a cell or if they are sticking to the surface of a cell. According to him, the scattering is very different when the rod is freely moving than when it is sticking to a cell surface.

“We can see small changes as rods move up and down and also track the vertical and horizontal rotation,” said Prof. Pradeep. “When the rod is inside a cell, we can track the motion as a movie with an optical microscope. So tomorrow, selective delivery into an organelle inside a cell and how a particle moves inside the organelle can be studied.” The team used nanorods of 30 by 10 nanometre. In comparison, the size of a cell is 20 microns (20,000 nanometre). The size of a nanoparticle should be much smaller than a cell so it does not alter the chemistry inside the cell.

## Novel way to produce safer drinking water

R. PRASAD

**M**aking drinking water a lot safer by killing an overwhelming number of bacteria and most viruses is now possible. A novel research to this end was carried out by a team led by Prof. T. Pradeep, Department of Chemistry, Indian Institute of Technology (IIT), Madras.

In May 2013, the same team was able to achieve only 100 times reduction in bacterial load and negligible reduction in viral load through sustained release of 50 parts per billion (ppb) of silver ions in drinking water.

But in the latest study, the team was able to achieve 1,00,000 times reduction in bacterial load and 1,000 times reduction in viral load by synergistically combining silver with carbonate ions. The drastic improvement in antimicrobial performance was achieved despite the team using only 25 ppb of silver ions, half the amount used in the earlier work.

"A novel way has been found to save 1,300 tonnes of silver annually, which would have been unrecoverable otherwise, amounting to a saving of Rs.4,600 crores," Prof. Pradeep told this Correspondent.

The amount of carbonate and silver used was well below the permissible level in drinking water. Tap water was used for the experiments. The results of the study were published a couple of days ago in Nature Group's journal *Scientific Reports*.

"A fundamental result that came out of our earlier study



was that the antibacterial activity of silver can be tuned by simple methods," Prof. Pradeep said. "Everybody was studying silver in isolation but we looked at synergistically combining silver with some other ions."

Explaining what prompted him to combine silver with another ion, he said: "It was intuition (based on chemistry). When you say there is an effect of an ion on an organism, what it means is that the ion has to get into the body of an organism. The penetration has to go through several steps. Each one is a chemical binding process. Therefore, silver can be tuned by ions or molecules."

The search for ions that can be combined with silver without causing toxicity to humans eventually led to carbonates.

"It's a very common ion in water. It is also cheap and easily deployable. So we

stayed with carbonate," Prof. Pradeep said.

The team had earlier found that silver was able to destroy the integrity of the cell membrane and also damage the DNA. In the case of carbonates, several peripheral membrane-bound proteins get removed. "We found that the peripheral proteins of the organisms were cleaned up after treatment with carbonates," he said.

As a result, more silver ions were able to penetrate the exposed cell surfaces of bacteria and virus much more effectively and quickly. Hence, a large quantity of pathogenic microorganisms was destroyed.

Antibacterial and antiviral effects were tested on *E. coli* and *Staphylococcus aureus* and MS2 bacteriophage (virus). Both bacteria and virus were destroyed within 15 minutes of contact time.

Carbonates and silver were

released into water at the same time but their contact areas with water were controlled by playing around with their sizes. "By controlling the size of the particles, one can effectively control the concentration of ions in water," he said.

Since carbonate gets dissolved more quickly than silver, carbonate particles were sand-sized while silver was nanosize. "We want more dissolved carbonates than silver in water as carbonates have to first remove the peripheral proteins of a cell," he said. The amount of dissolved ions in water is 25 parts per billion (ppb) of silver and 20 parts per million (ppm) of carbonate.

Prof. Pradeep is confident that there is scope for more improvement. "You can still make it better by controlling the activity of silver by synergizing with other ions," he said.

# NANOTECH ON TAP

Indian technology offers **CLEAN WATER** at low cost

**GROUNDWATER** in the Indian state of West Bengal naturally contains arsenic, causing ailments including skin diseases and cancer. Thanks to nanotechnology, thousands of people there have gained access to arsenic-free water since 2013, with the installation of treatment tanks using porous granules developed by a team at the Indian Institute of Technology (IIT), Madras, led by chemistry professor Thalappil Pradeep. The technology has received government support for field-testing as an option for low-cost, point-of-use water treatment.

The granules are nanocomposites made from ferric oxyhydroxide and a biopolymer, chitosan. Iron oxides remove arsenic ions from water by adsorption. The team boosted their metal oxyhydroxide's activity by reducing the particle size to nanoscale, thereby increasing the surface-to-volume ratio, and anchoring the material within a network of chitosan. With this structure, which resembles sand and is made at room temperature, embedded particles don't leach into water, and the captured arsenic stays put. What goes on "in the atomic scale is not completely understood," Pradeep says, but that has not stopped the material's real-world use.

At the Ambattur industrial estate, in a suburb of the Indian city of Chennai, a facility makes about 36 kg of the ferric oxyhydroxide-chitosan nanocomposite per day. Production at the plant—run by InnoNano Research, a start-up founded by the IIT Madras team—is enabling field trials in West Bengal.

With funding from the state government, about 100 community water purifiers using the nanocomposites, typically in 600-L tanks, have been installed in the district of Murshidabad, says an InnoNano cofounder known only as Anshup.

Each one, he estimates, serves 50–100 families and lasts one to two years. In the lab, the composite reduces a 1-ppm arsenic load to less than 10 ppb, the limit set by the World Health Organization (WHO). In field trials, natural arsenic loads of up to 330 ppb, the highest found in the field according to the team, drop to less than 10 ppb.

COURTESY OF THALAPPIL PRADEEP



Globally, 137 million people are exposed to arsenic levels greater than the WHO limit. And some 780 million people do not have clean drinking water, according to the Centers for Disease Control & Prevention (CDC). "Every 20 seconds, a child dies from a water-related disease, especially in the developing world," says Emmanuel I. Unuabonah, a researcher from Redeemer's University in Nigeria who also develops water treatment materials.

**TO REMOVE MICROBES**, the Ambattur plant produces smaller quantities of another material developed by the team, an aluminum oxyhydroxide-chitosan composite (*Proc. Natl. Acad. Sci. USA* 2013, DOI: 10.1073/pnas.1220222110). When impregnated with silver nanoparticles, the material kills microbes by gradually releasing  $\text{Ag}^+$ , a microbicide. Team member Udhaya Sankar estimates that 120 g of the composite could continuously provide 10 L of microbe-free drinking water daily for a year.

In the lab, microbial loads of  $10^5$  colony-forming units (100 times the amount in natural drinking water) drop to zero. Lab studies also show that together, the Fe and Al composites remove both arsenic and microbes; limited field trials corroborate the lab results, says team member Amrita Chaudhary.

**INVENTORS** The InnoNano team in front of a water treatment tank that uses the materials they developed. From left, Anshup, holding a cartridge of ferric oxyhydroxide-chitosan nanocomposite; Chaudhary; Anil Kumar; Pradeep; and Sankar.

The composites can be made to remove other contaminants, such as lead or mercury, and assembled for specific needs. The antimicrobial material is housed at the roof of a vessel fed with untreated water from the top. The vessel volume can vary from a few liters for a household to hundreds of liters for a small community. A multilayer block of composites for specific contaminants sits behind the water tap.

InnoNano's materials join many water purification techniques, including ultraviolet radiation, chlorine treatment, and various filtration methods. "You need a basket of technologies," Pradeep says, to address the diverse needs around the world.

A powder called the P&G Purifier of Water, developed by CDC and Procter & Gamble, is perhaps the best-known water purification technology for use in impoverished or disaster-stricken areas. The product, which contains ferric sulfate and calcium hypochlorite, costs 3.5 cents per sachet. One sachet treats 10 L of water in about 30 minutes, removing metals, including arsenic, and killing microbes. For a family using 10 L of drinking water per day, treatment would cost \$12.80 per year, a month's earnings for many West Bengalis. InnoNano's

filters would deliver the same amount of drinking water for \$2.00–\$3.00 per year, Chaudhary says.

The nanocomposites stand a good chance of being used on a large scale, Redeemer's Unuabonah says. However, more evidence of their robustness is needed, and the arsenic-scavenging material needs to be tested on higher levels of contamination.

The technology is already popular in Murshidabad. The system works well, says Rajeev Kumar, a former Murshidabad district magistrate, and because community units—such as schools or offices—are responsible for operating the tanks, people have a sense of ownership. In a documentary prepared for IIT Madras, residents ask for installations in their villages. The district has ordered at least 100 more purifiers.

For its part, InnoNano wants not only to provide a purification solution, but also to maintain the installations. "Originally, we were thinking of keeping our role to materials manufacturing," Pradeep says, "but that alone is not enough."—VIRAT MARKANDEYA, *special to C&EN*



## Awards and Recognitions

### **T. Pradeep:**

- Fellow of the Royal Society of Chemistry (FRSC).
- Elected fellow Indian National Academy of Engineering
- Associate editor, ACS Sustainable Chemistry and Engineering

### **Students:**

- Malhotra Wiekfield Award, Indranath Chakraborty
- Best Poster Award at ICONSAT 2014 , Indranath Chakraborty
- Best poster award at Bangalore Nano, Ananya Bakshi
- The Best Exhibitor Award for the year 2014 in the category of Innovative Display which was presented by Department of Information Technology, Biotechnology and Science & Technology, Government of Karnataka and Vision Group on Nanotechnology to Anil Kumar, Prakash, Ramesh.

### **Alumni:**

- M S Bootharaju joined KAUST, Saudi Arabia as a Post-Doctoral Fellow.
- C Subramaniam joined Department of Chemistry, IIT Bombay as an Assistant Professor.
- C Subramaniam received the Young Science Gold Award from IUMRS.
- T. S Sreeprasad joined Rice University as a senior Post-doctoral fellow.
- P. L. Xavier joined Max Plank Institute for Structure and Dynamics of Matter as a PhD student.
- Sreya Sarkar joined Purdue University, Indiana as a PhD student.

## **Graduation**

**Soumabha Bag**, Department of Chemistry, IIT Madras, 2014

*Low energy ion scattering at molecular solids*

**M.S Bootharaju**, Department of Chemistry, IIT Madras, 2014

*Noble metal nanomaterials for water purification*

**Robin John**, Department of Physics, IIT Madras, 2014

*Investigations of the formation and inter-conversion of low dimensional carbon systems*

**Kamalesh Chaudhari**, Department of Biotechnology, IIT Madras, 2014 (to be awarded in 2015)

*Single particle interactions of nano-bio interactions*

**Ammu Mathew**, Department of Chemistry, IIT Madras, 2014 (to be awarded in 2015)

*Functional noble metal clusters: Synthesis, surface chemistry and applications*

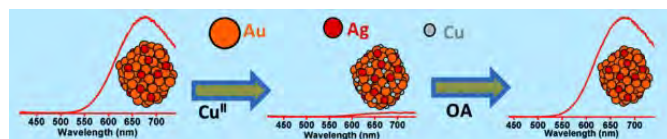
## Abstracts of Journal Papers

### Luminescent AgAu Alloy Clusters Derived from Ag Nanoparticles – Manifestations of Tunable Au<sup>I</sup>–Cu<sup>I</sup> Metallophilic Interactions

Kumaranchira R. Krishnadas, Thumu Udayabhaskararao, Susobhan Choudhury, Nirmal Goswami, Samir Kumar Pal and T. Pradeep, *Eur. J. Inorg. Chem.*, 5 (2014) 908-916 (DOI: 10.1002/ejic.201301424).

#### Abstract

Luminescent AgAu alloy quantum clusters are synthesized by a simple method that utilizes the galvanic reduction of polydisperse plasmonic silver nanoparticles. The clusters are characterized by ultraviolet–visible (UV/Vis) absorption spectroscopy, photoluminescence (PL) spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and matrix-assisted laser desorption ionization mass spectrometry (MALDI MS). Selective and tunable quenching of cluster luminescence by Cu<sup>II</sup> ions is observed and depends highly on the solvent as well as the protecting ligands. Metal-ion selectivity is exclusively caused by Metallophilic interactions with the cluster core, and the tunability depends on the nature of the protecting ligands as well as solvent effects. Detailed XPS and time-resolved luminescence measurements reveal that the tunability of luminescence quenching is achieved by the systematic variation of the metallophilic interactions between the Au<sup>I</sup> ions of the alloy cluster and Cu<sup>I</sup> ions formed by the reduction of Cu<sup>II</sup> ions by the cluster core. This is the first report of tunable Metallophilic interactions between monolayer-protected quantum clusters and a closed-shell metal ion. We hope that these results will draw more attention to the field of quantum cluster– metal ion interactions and provide useful insights into the stability of these clusters, origin of their intense luminescence, mechanisms of metal-ion sensing, and also help in the development of methods for tuning their properties.

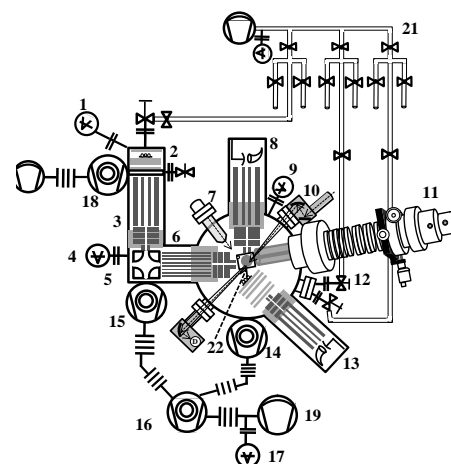


### Development of ultralow energy (1-10 eV) ion scattering spectrometry coupled with reflection absorption infrared spectroscopy and temperature programmed desorption for the investigation of molecular solids

Soumabha Bag, Radha Gobinda Bhui, Rabin Rajan J. Methikkalam, Luke Kephart, Jeff Walker, Kevin Kuchta, Dave Martin, Jian Wei and T. Pradeep, *Rev. Sci. Instrum.*, 85 (2014) 014103 (DOI: 10.1063/1.4848895).

#### Abstract

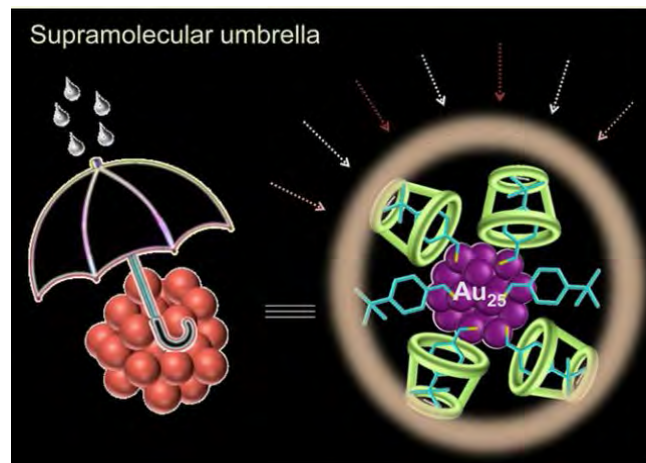
Extremely surface specific information, limited to the first atomic layer of molecular surfaces, is essential to understand the chemistry and physics in upper atmospheric and interstellar environments. Ultra low energy ion scattering in the 1–10 eV window with mass selected ions can reveal extremely surface specific information which when coupled with reflection absorption infrared (RAIR) and temperature programmed desorption (TPD) spectroscopies, diverse chemical and physical properties of molecular species at surfaces could be derived. These experiments have to be performed at cryogenic temperatures and at ultra-high vacuum conditions without the possibility of collisions of neutrals and background deposition in view of the poor ion intensities and consequent need for longer exposure times. Here we combine a highly optimized low energy ion optical system designed for such studies coupled with RAIR and TPD and its initial characterization. Despite the ultralow collision energies and long ion path lengths employed, the ion intensities at 1 eV have been significant to collect a scattered ion spectrum of 1000 counts/s for mass selected CH<sub>2</sub><sup>+</sup>.



Ammu Mathew, Ganapati Natarajan, Lauri Lehtovaara, Hannu Hakkinen, Ravva Mahesh Kumar, Venkatesan Subramanian, Abdul Jaleel and T. Pradeep, *ACS Nano*, 8 (2014) 139-152 (DOI: 10.1021/nm406219x).

**Abstract**

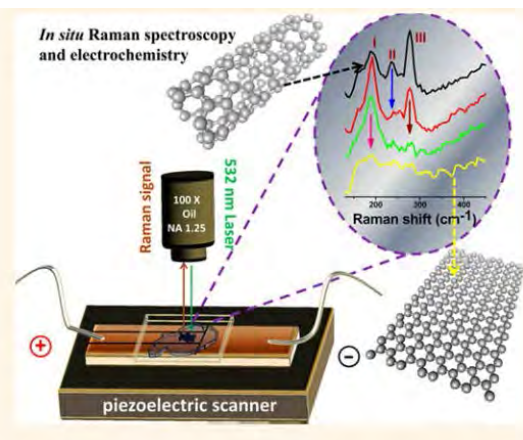
We present a versatile approach for tuning the surface functionality of an atomically precise 25 atom gold cluster using specific hostguest interactions between  $\beta$ -cyclodextrin (CD) and the ligand anchored on the cluster. The supramolecular interaction between the Au<sub>25</sub> cluster protected by 4-(t-butyl)benzylmercaptan, labeled Au<sub>25</sub>SBB18, and CD yielding Au<sub>25</sub>SBB18@CD<sub>n</sub> (n = 1, 2, 3, and 4) has been probed experimentally using various spectroscopic techniques and was further analyzed by density functional theory calculations and molecular modeling. The viability of our method in modifying the properties of differently functionalized Au<sub>25</sub> clusters is demonstrated. Besides modifying their optoelectronic properties, the CD moieties present on the cluster surface provide enhanced stability and optical responses which are crucial in view of the potential applications of these systems. Here, the CD molecules act as an umbrella which protects the fragile cluster core from the direct interaction with many destabilizing agents such as metal ions, ligands, and so on. Apart from the inherent biocompatibility of the CD-protected Au clusters, additional capabilities acquired by the supramolecular functionalization make such modified clusters preferred materials for applications, including those in biology.



Robin John, Dhanraj B. Shinde, Lili Liu, Feng Ding, Zhiping Xu, Cherianath Vijayan, Vijayamohanan K. Pillai and T. Pradeep, *ACS Nano*, 8 (2014) 234-242 (DOI: 10.1021/nm403289g).

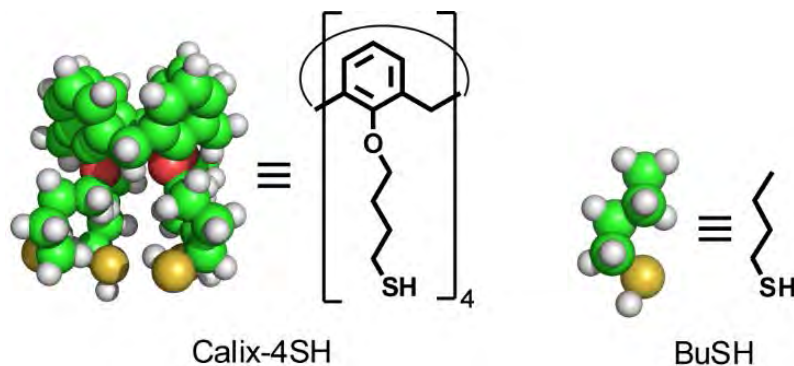
**Abstract**

We report an in situ Raman spectroscopic and microscopic investigation of the electrochemical unzipping of single-walled carbon nanotubes (SWNTs). Observations of the radial breathing modes (RBMs) using Raman spectra mapping reveal that metallic SWNTs are opened up rapidly followed by gradual unzipping of semiconducting SWNTs. Consideration of the resonant Raman scattering theory suggests that two metallic SWNTs with chiralities (10, 4) and (12, 0) get unzipped first at a lower electrode potential (0.36 V) followed by the gradual unzipping of another two metallic tubes, (9, 3) and (10, 1), at a relatively higher potential (1.16 V). The semiconducting SWNTs with chiralities (11, 7) and (12, 5), however, get open up gradually at (1.66 V). A rapid decrease followed by a subsequent gradual decrease in the metallicity of the SWNT ensemble as revealed from a remarkable variation of the peak width of the G band complied well with the variations of RBM. Cyclic voltammetry also gives direct evidence for unzipping in terms of improved capacitance after oxidation followed by more important removal of oxygen functionalities during the reduction step, as reflected in subtle changes of the morphology confirming the formation of graphene nanoribbons. The density functional-based tight binding calculations show additional dependence of chirality and diameter of nanotubes on the epoxide binding energies, which is in agreement with the Raman spectroscopic results and suggests a possible mechanism of unzipping determined by combined effects of the structural characteristics of SWNTs and applied field.



JukkaHassinen, Petri Pulkkinen, Elina O. Kalenius, T. Pradeep, HeikkiTenhu, Hannu J. Häkkinen, and Robin H. A. Ras, *J. Phys. Chem. Lett.*, 5 (2014) 585–589 (DOI: 10.1021/jz500052h).

Although various complex, bulky ligands have been used to functionalize plasmonic gold nanoparticles, introducing them to small, atomically precise gold clusters is not trivial. Here, we demonstrate a simple one-pot procedure to synthesize fluorescent magic number Au<sub>25</sub> clusters carrying controlled amounts of bulky calix[4]arene functionalities. These clusters are obtained from a synthesis feed containing binary mixtures of tetrathiolatedcalix[4]arene and 1-butanethiol. By systematic variation of the molar ratio of ligands, clusters carrying one to eight calixarene moieties were obtained. Structural characterization reveals unexpected binding of the calix[4]arenes to the Au<sub>25</sub> cluster surface with two or four thiolates per moiety.

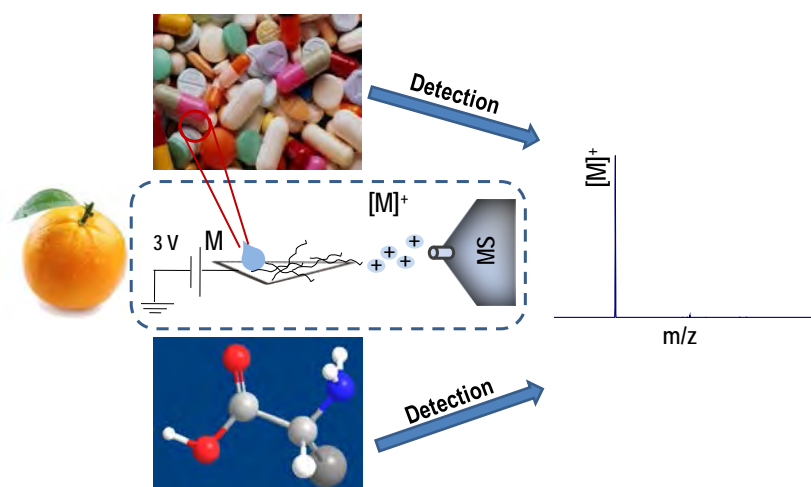


## Molecular ionization from carbon nanotube paper

R. Narayanan, D. Sarkar, R. G. Cooks and T. Pradeep, *Angew. Chem. Int. Ed.*, 53 (2014) 5936 –5940 (DOI: 10.1002/anie.201311053).

### Abstract

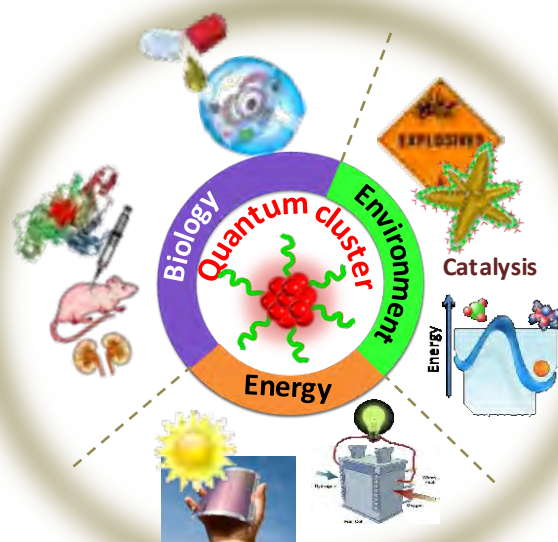
Ambient ionization is achieved by spraying from a carbon nanotube (CNT)-impregnated paper surface under the influence of small voltages (>3 V). Organic molecules give simple high-quality mass spectra without fragmentation in the positive or negative ion modes. Conventional field ionization is ruled out, and it appears that field emission of microdroplets occurs. Microscopic examination of the CNT paper confirms that the nanoscale features at the paper surface are responsible for the high electric fields. Raman spectra imply substantial current flows in the nanotubes. The performance of this analytical method was demonstrated for a range of volatile and non-volatile compounds and a variety of matrices.



Ammu Mathew and T. Pradeep, *Part. Part. Syst. Charact.*, 31 (2014) 1017-1053 (DOI: 10.1002/ppsc.201400033).

Abstract

Sub-nanometer-sized metal clusters, having dimensions between metal atoms and nanoparticles, have attracted tremendous attention in the recent past due to their unique physical and chemical properties. As properties of such materials depend strongly on size, development of synthetic routes that allows precise tuning of the cluster cores with high monodispersity and purity is an area of intense research. Such materials are also interesting owing to their wide variety of applications. Novel sensing strategies based on these materials are emerging. Owing to their extremely small size, low toxicity, and biocompatibility, they are widely studied for biomedical applications. Primary focus of this review is to provide an account of the recent advances in their applications in areas such as environment, energy, and biology. With further experimental and theoretical advances aimed at understanding their novel properties and solving challenges in their synthesis, an almost unlimited field of applications can be foreseen.

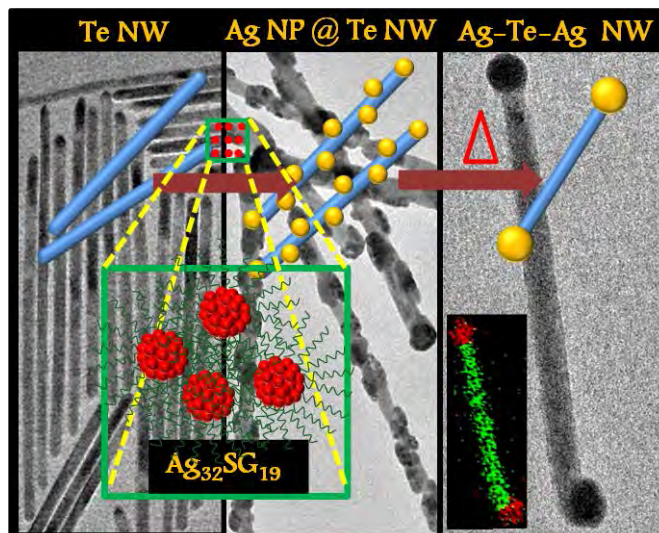


Manifestation of the difference in reactivity of silver clusters in contrast to its ions and nanoparticles  
The growth of metal tipped Te nanowires

Anirban Som, Akshaya Kumar Samal, ThumuUdayabhaskararao, M. S. Bootharaju and T. Pradeep, *Chem. Mater.*, 26 (2014) 3049–3056 (DOI: 10.1021/cm403288w).

Abstract

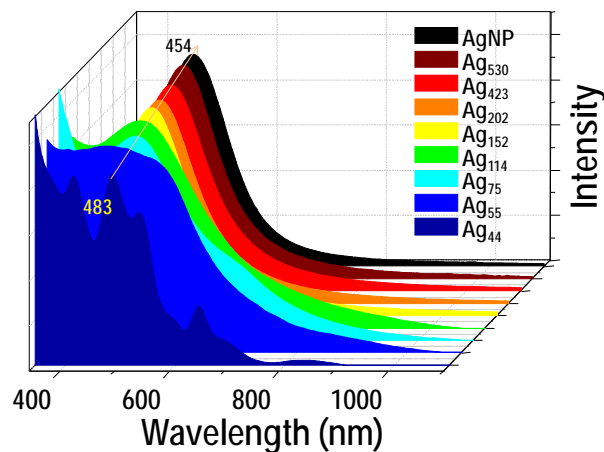
Reactivity of two different nanosystems of silver, namely nanoparticles and atomically precise clusters, toward 1D tellurium nanowires (NWs) was probed and compared with the reaction of silver ions. While the reaction of nanoparticles and ions led to silver telluride nanowires, a different reactivity was exhibited by clusters which resulted in silver islands at different positions on the Te NWs. These hybrid Ag nodule-decorated Te NWs are sensitive to temperature, and they transform to dumbbell-shaped silver-tipped Te NWs upon solution phase annealing. Differences in chemical reactivity of nanoparticles of two different size regimes with nanowires are demonstrated. Synthetic methods of this kind will be useful in creating complex nanostructures which are difficult to be made in the solution phase.



Indranath Chakraborty, Jayanthi Erusappan, Anuradha Govindarajan, K. S. Sugi, Thumu Udayabhaskararao, Atanu Ghosh and T. Pradeep, *Nanoscale*, 6 (2014) 8024–8031 (DOI: 10.1039/c4nr00679h).

Abstract

We report the systematic appearance of a plasmon-like optical absorption feature in silver clusters protected with 2-phenylethanethiol (PET), 4-fluorothiophenol (4-FTP) and (4-(t-butyl)benzenethiol (BBS), as a function of cluster size. A wide range of clusters, namely,  $\text{Ag}_{44}(\text{4-FTP})_{30}$ ,  $\text{Ag}_{55}(\text{PET})_{31}$ ,  $\sim\text{Ag}_{75}(\text{PET})_{40}$ ,  $\sim\text{Ag}_{114}(\text{PET})_{46}$ ,  $\text{Ag}_{152}(\text{PET})_{60}$ ,  $\sim\text{Ag}_{202}(\text{BBS})_{70}$ ,  $\sim\text{Ag}_{423}(\text{PET})_{105}$ , and  $\sim\text{Ag}_{530}(\text{PET})_{100}$  were prepared. The UV/Vis spectra show multiple features up to  $\sim\text{Ag}_{114}$  and thereafter from  $\text{Ag}_{152}$  onwards, the plasmonic feature corresponding to a single peak at  $\sim 460$  nm EVOLVES which points to the emergence of metallicity in clusters composed of  $\sim 150$  metal atoms. A minor blue shift in the plasmonic peak was observed as cluster size increases and merges with the spectrum of plasmonic nanoparticles of

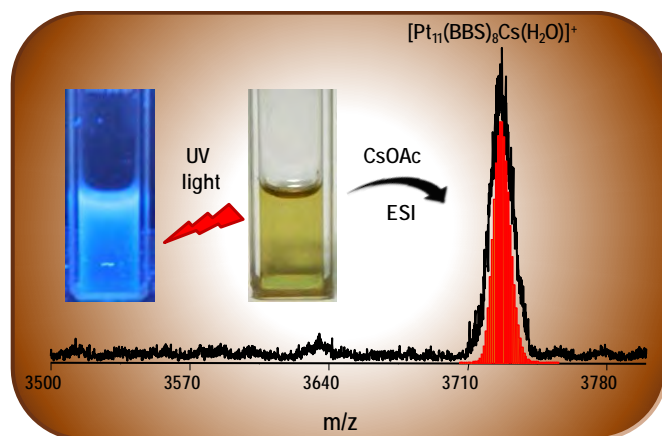


Blue emitting undecaplatinum cluster

Indranath Chakraborty, Radha Gobinda Bhui, Shridevi Bhat and T. Pradeep, *Nanoscale*, 6 (2014) 8561-8564 (DOI: 10.1039/C4NR02778G).

Abstract

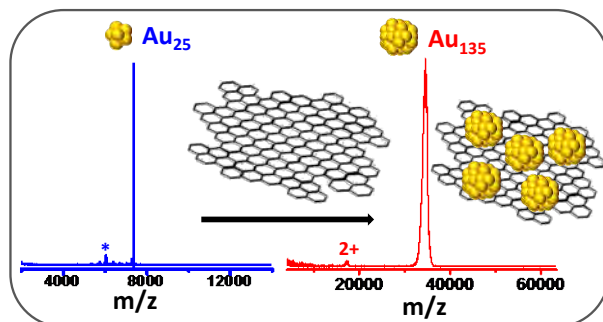
A blue luminescent 11-atom platinum cluster showing step like optical features and absence of plasmon absorption was synthesized. The cluster was purified using high performance liquid chromatography (HPLC). Electrospray ionization (ESI) and matrix assisted laser desorption ionization (MALDI) mass spectrometry (MS) suggest a composition,  $\text{Pt}_{11}(\text{BBS})_8$  which was confirmed by a range of other experimental tools. The cluster is highly stable and compatible with many organic solvents



Atanu Ghosh, T. Pradeep and JaydebChakrabarti, *J. Phys. Chem. C*, 118 (2014) 13959–13964 (DOI: 10.1021/jp503001s).

### Abstract

The interaction of ultrasmall metal clusters with surfaces of graphene is important for developing promising future applications of graphenic materials. In the experiment, chemically synthesized reduced graphene oxide (RGO) in water was mixed with Au<sub>25</sub>SR<sub>18</sub> (where SR, SCH<sub>2</sub>CH<sub>2</sub>Ph, is a ligand protecting the cluster core) in tetrahydrofuran, and a completely new cluster, larger in mass, was formed at the liquid–liquid interface. Matrix assisted laser desorption/ionization mass spectrometry of the product attached to RGO show that the peak due to Au<sub>25</sub>SR<sub>18</sub> disappears gradually upon reaction and a single sharp peak referred to here as “135 ± 1 kDa cluster” appears. The composition of the new cluster is very close to the well-known magic cluster, Au<sub>144</sub>SR<sub>60</sub> while the peak maximum is at Au<sub>135</sub>SR<sub>57</sub>. The formation of 35 ± 1 kDa cluster from the parent Au<sub>25</sub> is proposed to be governed by the trapping of smaller clusters in a deep potential well generated at the graphene surface. We theoretically model the active role of the surface in stabilizing the large clusters. Our studies indicate a general mechanism of stabilization of clusters of precise size via the competition between the interfacial fluctuations and the energy scales of interaction of the clusters with the surface. The chemical transformation occurs at deformable surfaces at reduced particle densities which is in good agreement with the theoretical model. Transformations of this kind are important in controlled tuning of particles at graphenic surfaces.

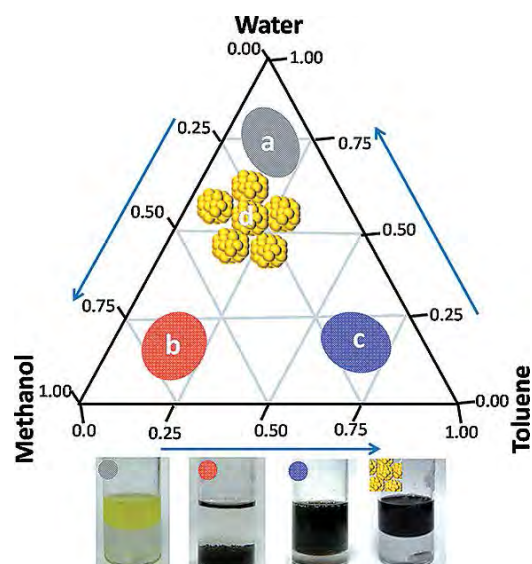


### Synthesis of atomically precise silver clusters using the miscibility principle

Atanu Ghosh and T. Pradeep, *Eur. J. Inorg. Chem.*, (2014) 5271–5275 (DOI: 10.1002/ejic.201402587).

### Abstract

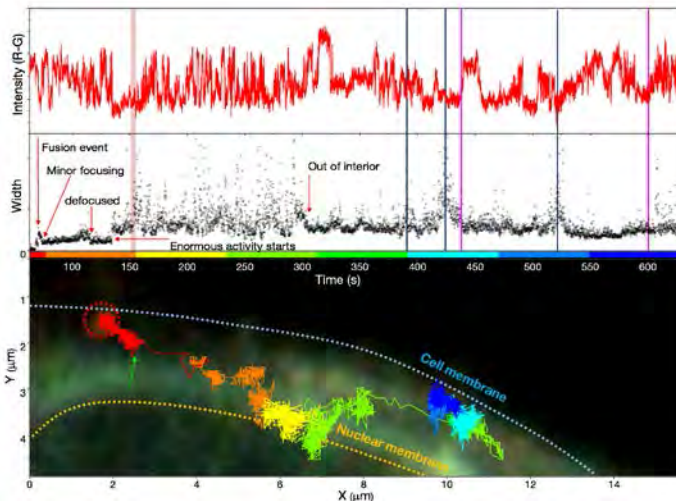
A new strategy to synthesize a diverse array of organic-soluble, atomically precise silver clusters has been developed. The technique is based on the miscibility principle of solvents and uses no phase-transfer agents; various clusters of masses 8.0, 13.4, 22.8, 29.2, and 34.4 kDa were synthesized by changing the reactant composition. We have also synthesized the well-known Au<sub>25</sub>(SR)<sub>18</sub> cluster by the same method. Among the silver clusters formed, we have studied the new 13.4 kDa species, which has unique steplike features in its UV/Vis spectrum, in detail by mass spectrometry and other analytical techniques. The compound has been assigned as Ag<sub>68</sub>(SR)<sub>34</sub>, which is reported for the first time. By time-dependent studies, we have shown that the synthetic route follows the bottom-up approach. The material forms microcrystals. We hope that the proposed synthetic strategy will extend the area of atomically precise clusters.



KamaleshChaudhari and T. Pradeep, *Scientific Reports (Nature)*, (2014) (DOI: 10.1038/srep05948).

### Abstract

Spatiotemporal mapping of the position and orientation of nano-machinery inside complex and dynamic cellular environments is essential for the detailed understanding of many bio-physical processes. For the genuine observation of such biomolecular dynamics with high signal to noise ratio and reduced disturbance from the labeling probes, reduction in the size of nano-bio labels and simplification of techniques for their observation are important. Here we achieve this using polarized dark field scattering micro-spectroscopy (PDFSMS), in its simplest form so that it is deployable in several experiments. We not only locate tiny gold nanorods (GNRs) of size 30 (length) 3 10 nm (diameter) inside HEK293 cells but also demonstrate mapping of their in-situ polarization patterns using a novel method. Real time observations of rotating GNR with DFSMS and PDFSMS are used to resolve in-plane and out-of-plane rotational modes of GNR. We have shown that PDFSMS itself can provide complete information about the state of GNR. A step ahead, we demonstrate the application of PDFSMS to track three dimensional rotational dynamics of transferrin-conjugated GNRs inside live HEK293 cells. These first-time observations of the three dimensional intracellular rotational dynamics of tiny GNRs using PDFSMS present a new landmark in single particle scattering spectroscopy.

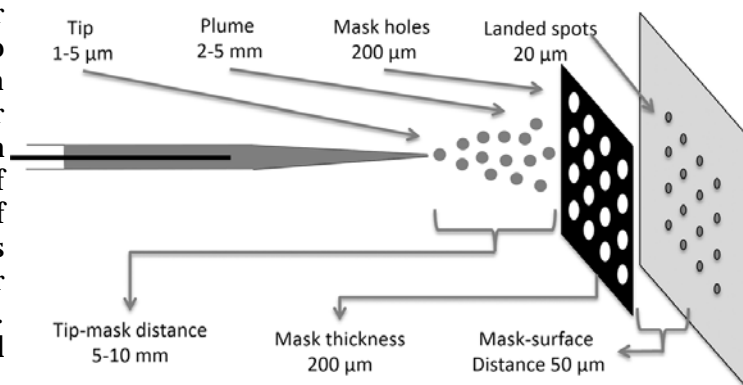


## Using ambient ion beams to write nanostructured patterns for surface enhanced Raman spectroscopy

Anyin Li, Zane Baird, Soumabha Bag, Dejanjan Sarkar, AnupamaPrabhath, T. Pradeep and R. Graham Cooks, *Angew. Chem. Int. Ed.*, 53 (2014) 12528-12531 (DOI: 10.1002/anie.201406660).

### Abstract

Electrolytic spray deposition was used to pattern surfaces with 2D metallic nanostructures. Spots that containsilver nanoparticles (AgNP) were created by landing solvatedsilver ions at desired locations using electrically floated masksto focus the metal ions to an area as little as 20 mm in diameter. The AgNPs formed are unprotected and their aggregates canbe used for surface-enhanced Raman spectroscopy (SERS). The morphology and SERS activity of the NP structures werecontrolled by the surface coverage of landed silver ions. The NP structures created could be used as substrates onto whichSERS samples were deposited or prepared directly on top ofpredeposited samples of interest. The evenly distributed hotspots in the micron-sized aggregates had an average SERSenhancement factor of 108. The surfaces showed SERS activitywhen using lasers of different wavelengths (532, 633, and 785 nm) and were stable in air.

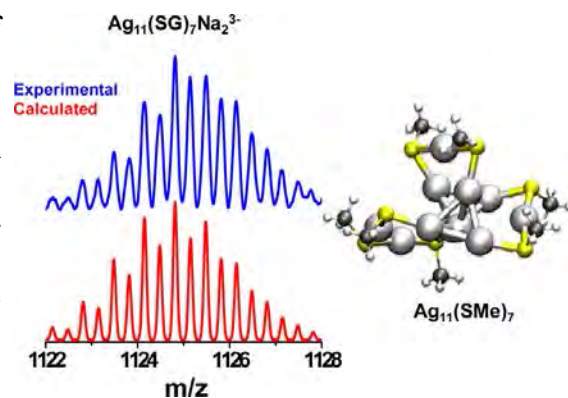




Ananya Baksi, M. S. Bootharaju, Xi Chen, Hannu Hakkinen and T. Pradeep, *J. Phys. Chem. C*, (2014) (DOI: 10.1021/jp508124b).

Abstract

We report a one-step and high yield synthesis of a red luminescent silver cluster with the molecular formula, Ag<sub>11</sub>(SG)<sub>7</sub> (SG: glutathionate) via reduction of silver ions by sodium borohydride in the presence of the tripeptide, glutathione (GSH). The as-prepared cluster shows prominent absorption features at 485 and 625 nm in its UV-vis absorption spectrum. Aging of the as-prepared cluster solution led to the disappearance of the 625 nm peak, followed by broadening of the 485 nm peak to give three maxima at ~487, 437, and 393 nm in its absorption spectrum. These peaks remain unchanged even after polyacrylamide gel electrophoresis (PAGE), where a single band was observed confirming high purity of the cluster formed. Electrospray ionization mass spectrometry (ESI MS) reveal the composition of the cluster to be Ag<sub>11</sub>(SG)<sub>7</sub> with multiple sodium attachments to the ligand to give -3 and -2 charged species. These compositions match well with their calculated isotope patterns. Extensive MS/MS was performed to understand the fragmentation. Potential atomic structures are discussed based on density functional theory calculations and comparisons for optical absorption spectra using Ag<sub>11</sub>(SCH<sub>3</sub>)<sub>7</sub> as the model. Photoluminescence of this cluster was selectively quenched in the presence of Hg(II) and Cu(II) separately. Detection limit was found to be below their permissible limits in drinking water set by US EPA. Ag<sub>11</sub>(SR)<sub>7</sub> cluster is reported for the first time.

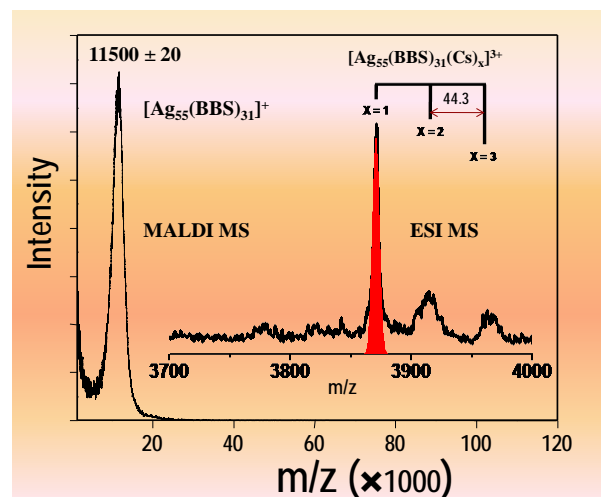


Controlled synthesis and characterization of the elusive thiolated Ag<sub>55</sub> cluster

Indranath Chakraborty, Shrabani Mahata, Anuradha Mitra, Goutam De and T. Pradeep, *Dalton Trans.*, 43 (2014) 17904–17907 (DOI: 10.1039/c4dt02476a).

Abstract

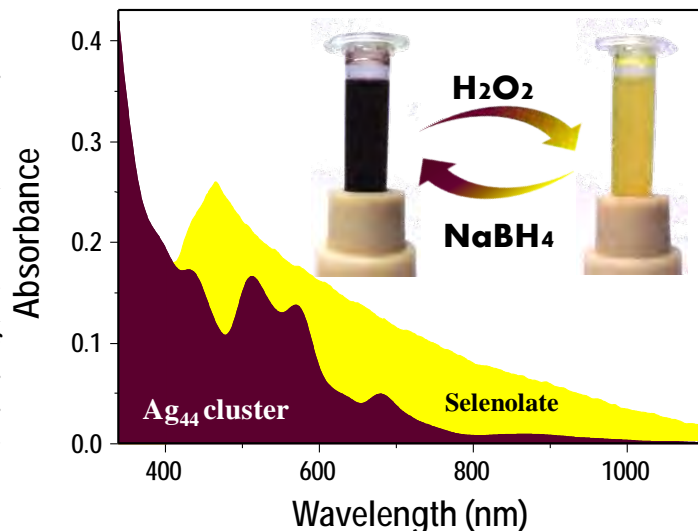
A stable, Ag<sub>55</sub> cluster protected with 4-(tert-butyl) benzyl mercaptan (BBSH) was synthesized which exhibits two prominent absorption bands with maxima at 2.25 and 2.81 eV. A molecular ion peak at  $m/z$  11 500 ± 20 in matrix assisted laser desorption ionization mass spectrum (MALDI MS), assigned to Ag<sub>55</sub>(BBS)<sub>31</sub> was observed. Electrospray ionization (ESI MS) shows a prominent truncation along with higher charged species. An analogous Ag<sub>55</sub>(PET)<sub>31</sub> (PET = 2-phenylethanethiol, in the thiolate form) was also synthesized under optimized conditions which proves the amenability of this cluster and the synthetic methodology to other ligands.



Indranath Chakraborty and T. Pradeep, *Nanoscale*, 6 (2014) 14190-14194 (DOI: 10.1039/C4NR03267E).

Abstract

The cluster Ag<sub>44</sub>SePh<sub>30</sub>, originally prepared from silver selenolate, upon oxidative decomposition by H<sub>2</sub>O<sub>2</sub> gives the same cluster back, in an apparently reversible synthesis. Such an unusual phenomenon was not seen for the corresponding thiolate analogues. From several characterization studies such as mass spectrometry, Raman spectroscopy, etc., it has been confirmed that the degraded and as-synthesized selenolates are the same in nature, which leads to the reversible process. The possibility of making clusters from the degraded material makes cluster synthesis economical. This observation makes one to consider cluster synthesis to be a reversible chemical process, at least for selenolates.

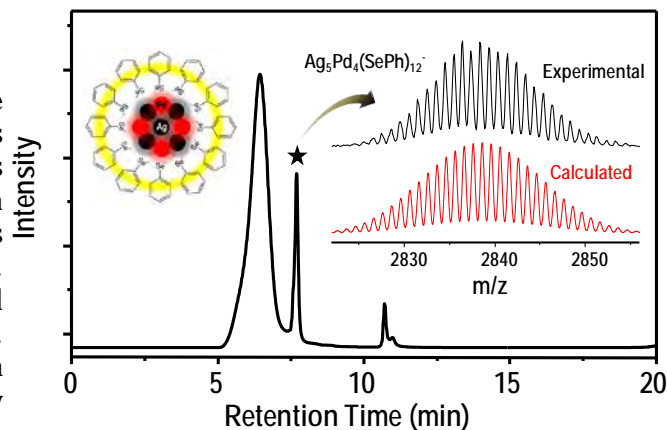


Isolation and Tandem Mass Spectrometric Identification of a Stable Monolayer Protected Silver Alloy Cluster

Sreya Sarkar, Indranath Chakraborty, Manoj Kumar Panwar and T. Pradeep, *J. Phys. Chem. Lett.*, 5 (2014) 3757–3762 (DOI: 10.1021/jz5019509).

Abstract

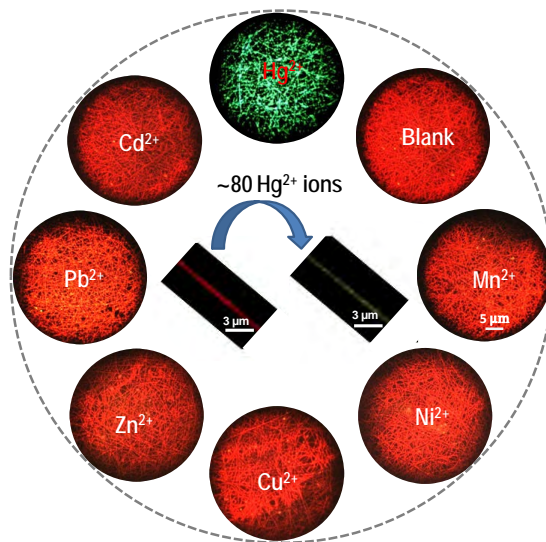
A selenolate-protected Ag–Pd alloy cluster was synthesized using a one-pot solution-phase route. The crude product upon chromatographic analyses under optimized conditions gave three distinct clusters with unique optical features. One of these exhibits a molecular peak centred at m/z 2839, in its negative ion mass spectrum assigned to Ag<sub>5</sub>Pd<sub>4</sub>(SePh)<sub>12</sub><sup>-</sup>, having an exact match with the corresponding calculated spectrum. Tandem mass spectrometry of the molecular ion peak up to MS<sup>9</sup> was performed. Complex isotope distributions in each of the mass peaks confirmed the alloy composition. We find the Ag<sub>3</sub>Pd<sub>3</sub><sup>-</sup> core to be highly stable. The composition was further supported by scanning electron microscopy, energy-dispersive spectroscopy, and X-ray photoelectron spectroscopy.



Atanu Ghosh, VedhakkaniJeseentharani, MohdAzhardin Ganayee, Rani Hemalatha, KamaleshChaudhari, CherianathVijayan and T. Pradeep, *Anal. Chem.*, 86 (2014) 10996–11001 (DOI: 10.1021/ac502779r).

### Abstract

A new methodology has been demonstrated for ultratrace detection of  $\text{Hg}^{2+}$ , working at the limit of a few tens of metal ions. Bright, red luminescent atomically precise gold clusters, Au@BSA (BSA, bovine serum albumin), coated on Nylon-6 nanofibers were used for these measurements. A green emitting fluorophore, FITC (fluorescein isothiocyanate), whose luminescence is insensitive to  $\text{Hg}^{2+}$  was precoated on the fiber. Exposure to mercury quenched the red emission completely, and the green emission of the fiber appeared which was observed under dark field fluorescence microscopy. For the sensing experiment at the limit of sensitivity, we have used individual nanofibers. Quenching due to  $\text{Hg}^{2+}$  ions was fast and uniform. Adaptation of such sensors to pH paper-like test-strips would make affordable water quality sensors at ultralow concentrations a reality.

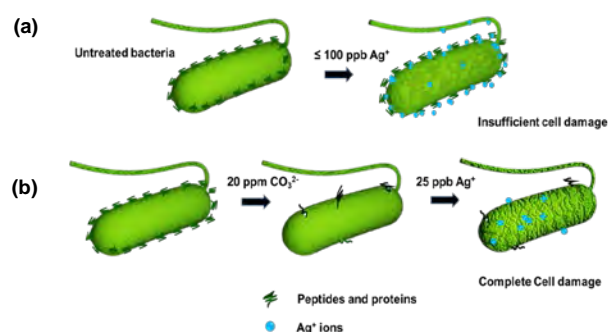


### Antimicrobial silver: An unprecedented anion effect

J. R. Swathy, M. UdhayaSankar, Amrita Chaudhary, SahajaAigal, S. Anshup and T. Pradeep, *Scientific Reports (Nature)*, 4 (2014) 7161 (DOI: 10.1038/srep07161).

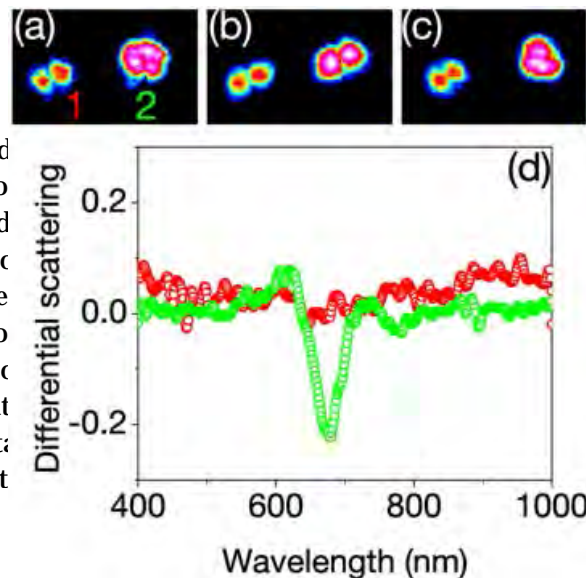
### Abstract

Silver is an indispensable metal but its use has to be minimised for sustainable growth. Much of the silver lost during use is unrecoverable; an example being its use as an antimicrobial agent, a property known since ages. While developing methods to create an affordable drinking water purifier especially for the developing world, we discovered that 50 parts per billion (ppb) of  $\text{Ag}^1$  released continuously from silver nanoparticles confined in nanoscale cages is enough to cause antimicrobial activity in conditions of normal water. Here we show that the antibacterial and antiviral activities of  $\text{Ag}^1$  can be enhanced, 1,000 fold, selectively, in presence of carbonate ions whose concentration was maintained below the drinking water norms. The protective layers of the organisms were affected during the carbonate-assisted antimicrobial activity. It is estimated that, 1,300 tons of silver can be saved annually using this new way to enhance its antimicrobial activity.



KamaleshChaudhari and T. Pradeep, *Appl. Phys. Lett.*, 105 (2014) 203105 (DOI: 10.1063/1.4902318).

Abstract



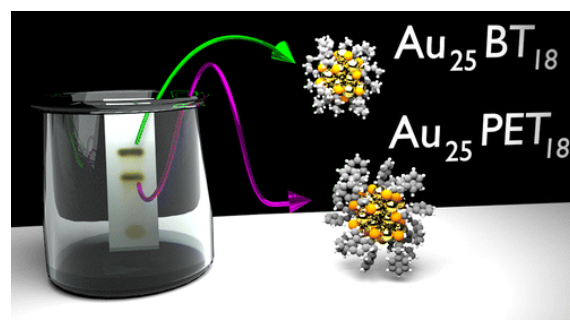
We show that plasmonic chirality in single gold nanorod (GNR) aggregates lead to the rotation of polarization of the scattered light. 3D glasses in conjunction with linearly polarized dark field scattering microspectroscopy were used to study the chirality of single GNR aggregates. Using this hetero-polarizer setup, we not only detect but also quantify their chirality. A polar mapping strategy was used for providing direct evidence for the emergence of light of different polarization angles when chiral GNR aggregates were excited with circularly polarized light of different handedness. Further, we have developed a methodology to eliminate fluctuations in the scattering intensity by averaging and normalizing the data. This allows calculation of plasmonic circular dichroism scattering spectra with

Simple and efficient separation of atomically precise noble metal clusters.

Atanu Ghosh, Jukka Hassinen, Petri Pulkkinen, Heikki Tenhu, Robin H. A. Ras, and Thalappil Pradeep, *Anal. Chem.*, (2014) (DOI: 10.1021/ac503165t).

Abstract

There is an urgent need for accessible purification and separation strategies of atomically precise metal clusters in order to promote the study of their fundamental properties. Although the separation of mixtures of atomically precise gold clusters  $Au_{25}L_{18}$ , where L are thiolates, has been demonstrated by advanced separation techniques, we present here the first separation of metal clusters by thin-layer chromatography (TLC), which is simple yet surprisingly efficient. This method was successfully applied to a binary mixture of  $Au_{25}L_{18}$  with different ligands, as well as to a binary mixture of different cluster cores,  $Au_{25}$  and  $Au_{144}$ , protected with the same ligand. Importantly, TLC even enabled the challenging separation of a multicomponent mixture of mixed-monolayer-protected  $Au_{25}$  clusters with closely similar chemical ligand compositions. We anticipate that the realization of such simple yet efficient separation technique will progress the detailed investigation of cluster properties.

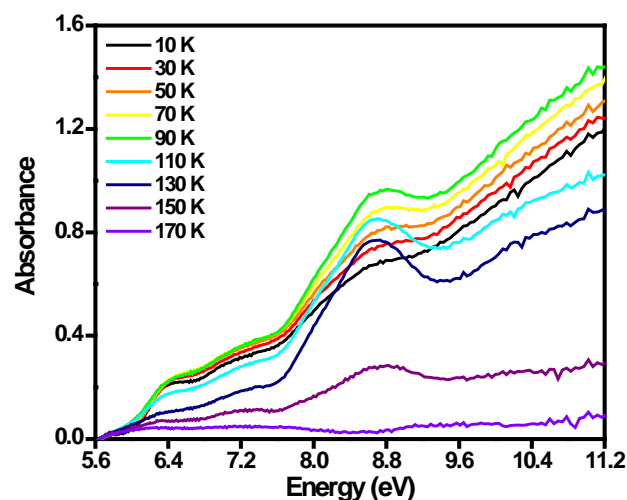


## Vacuum ultraviolet photoabsorption of interstellar icy thiols

Radha Gobinda Bhuin, Bhalamurugan Sivaraman, J.-I. Lo, Raja Sekhar B. N., Bing-Ming Cheng, T. Pradeep, and Nigel Mason, *J. Chem. Phys.*, (2014).

### Abstract

Following the recent identification of ethanethiol in the interstellar medium (ISM) we have carried out Vacuum UltraViolet (VUV) spectroscopy studies of ethanethiol ( $\text{CH}_3\text{CH}_2\text{SH}$ ) from 10 K until sublimation in an ultrahigh vacuum chamber simulating astrochemical conditions. These results are compared with those of methanethiol ( $\text{CH}_3\text{SH}$ ), the lower order thiol also reported to be present in the ISM. VUV spectra recorded at higher temperature reveal conformational changes in the ice and phase transitions whilst evidence for dimer production is also presented.



## Identification of effective substrates for the direct analysis of lipids from cell lines using desorption electrospray ionization mass spectrometry

Amitava Srimany, Jayashree Balasubramanyam, Subramanian Krishnakumar, Sailaja Elchuri and T. Pradeep, *Rapid Commun. Mass Spectrom.*, (2014) (DOI: 10.1002/rcm.7111)

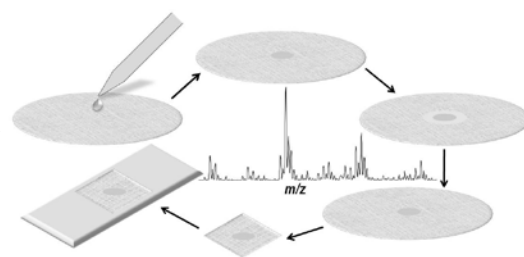
### Abstract

**RATIONALE:** Various disease conditions, particularly tumours, can be understood easily by studying changes in the lipid profile of cells. While lipid profiles of tissues have been recorded by desorption electrospray ionization mass spectrometric (DESI-MS) imaging, there is paucity in standardized protocols for sample preparation involving cell cultures to generate reliable results. In this study, we report a method for the direct analysis of lipids from cultured cells by incorporating them onto Whatman 42 filter paper as a substrate for reliable DESI-MS analysis.

**METHODS:** The WERI-RB1 cell line was spotted on commonly used substrates for DESI-MS analysis, such as glass slides, Teflon coated glass slides, thin layer chromatography (TLC) plates, and Whatman 42 filter paper. A comparison of mass spectrometric images with two different lipids was made to understand the behaviour of different surfaces when the same sample was spotted on them. Relative intensities of different lipid peaks in the WERI-RB1 cell line were compared and relative lipid abundances were also compared across two different human retinoblastoma cell lines; WERI-RB1 and Y79.

**RESULTS:** The study demonstrates that good lipid signals can be obtained by DESI-MS when the cells are spotted on Whatman 42 filter paper. Tandem mass spectrometry was performed to identify the lipids as glycerophosphocholines (PC). Better lipid images from assembly of cells were obtained with distinct boundary when they were spotted on Whatman 42 filter paper than other surfaces.

**CONCLUSIONS:** We demonstrate the use of a simple substrate for reliable DESI-MS analysis of cultured cells. This method has the potential to understand various interactions of cells with other external agents. The current method would help in the application of DESI-MS for biology in general and medical sciences in particular.





For additional information, please visit: <http://www.dstuns.iitm.ac.in/>

# Photographs from Bangalore India Nano 2014



सत्यमेव जयते

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