

Nanoparticles-chemistry, new synthetic approaches, gas phase clustering and novel applications

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Abstract. In this paper, an overview of the synthesis, chemistry and applications of nanosystems carried out in our laboratory is presented. The discussion is divided into four sections, namely (a) chemistry of nanoparticles, (b) development of new synthetic approaches, (c) gas phase clusters and (d) device structures and applications. In ‘chemistry of nanoparticles’ we describe a novel reaction between nanoparticles of Ag and Au with halocarbons. The reactions lead to the formation of various carbonaceous materials and metal halides. In ‘development of new synthetic approaches’ our one-pot methodologies for the synthesis of core-shell nanosystems of Au, Ag and Cu protected with TiO₂ and ZrO₂ as well as various polymers are discussed. Some results on the interaction of nanoparticles with biomolecules are also detailed in this section. The third section covers the formation of gas phase aggregates/clusters of thiol-protected sub-nanoparticles. Laser desorption of H₂MoO₄, H₂WO₄, MoS₂, and WS₂ giving novel clusters is discussed. The fourth section deals with the development of simple devices and technologies using nanomaterials described above.

Keywords. Nanoparticles; nanochemistry; gas phase clusters; flow sensors; optical limiters.

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1. Introduction

The science of metal nanoparticles is fascinating [1]. Over the past several years our research has focused on various aspects of monolayers on both planar surfaces and metal nanoparticles, focusing on their structure and dynamics [2,3]. Using spectroscopic and scattering techniques we have shown that monolayers on nanoparticles (3D-SAMs) are highly ordered systems and the dynamics evolves slowly [4–8]. Monolayer interaction leads to superlattices of these particles [9,10]. The chemistry of monolayers on the nanoparticle systems can be used to grow oxides on nanosystems leading to core-shell particles [11]. Diverse properties of these materials have

been explored such as chemical reactivity [12,13], optical nonlinearity [14–16], etc. In this paper we present a brief summary of our research. It has been divided into four sections. Focus will be more on unpublished research and published literature will be quoted only to point out the links so that an interested reader may find the details elsewhere.

2. Experimental section

Chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), silver nitrate (AgNO_3), and trisodium citrate were from CDH chemicals, India. *Ortho*-toluidine, aniline, copper chloride (CuCl_2), carbon tetrachloride and benzylchloride were from Ranbaxy Chemicals, India. Aminopropyl trimethoxy silane (APS), sodium silicate, benzylthiocyanate, zirconium (IV) propoxide, stearic acid, dimercapto succinic acid (DMSA), molybdenum sulphide (MoS_2) and tungsten sulphide (WS_2) were from Aldrich. Ciprofloxacin was purchased from Fluka. Propanethiol (PT), hexanethiol (HT) and dodecanethiol (DDT) were from Merck. Chlorpyrifos and malathion were from Chem Service Inc. USA. Polyvinyl alcohol (PVA) and polyurethane films were from local sources. The solvents used in the syntheses were from local sources and distilled before use. Water used in the experiments was of nanopure quality, obtained by further purifying the triply distilled water by a UHQ ultra-pure water purifier of ELGA. Citrate capped Ag (60–80 nm size) and Au (15–20 nm size) nanoparticles were synthesized by known methods [17,18]. The Au@SiO_2 , Ag@ZrO_2 , Au@ZrO_2 , Ag@TiO_2 and Au@TiO_2 core-shell nanoparticles were synthesized by methods reported in the literature by Ung *et al* [19] and Tom *et al* [20]. The poly(*o*-toluidine)-capped Au [21], Cu nanoparticles [22] and poly(benzylthiocyanate)-capped Ag nanoparticles [23] were synthesized as per the methods reported. Synthesis of Cu nanoparticles was similar to Au, except that polymerization was achieved slowly. Very small molecular clusters of gold were synthesized using DMSA by our own methodology, in which DMSA reduced Au^{3+} in a slow reduction [24]. Monolayer-capped Au clusters were synthesized by the modified Brust procedure [25]. The characterization techniques involved absorption spectroscopy (Perkin-Elmer Lambda 25), infrared spectroscopy (Perkin-Elmer Spectrum One), transmission electron microscopy (TEM, Philips 120 keV and JEOL 3010 high resolution instrument), powder X-ray diffraction (XRD, Shimadzu XDD1 diffractometer with $\text{CuK}\alpha$ radiation (30 kV, 20 mA)) and matrix-assisted laser desorption ionization (MALDI, Applied Biosystems Voyager DE PRO time-of-flight mass spectrometer) spectrometry. Further characterization involved differential scanning calorimetry (DSC, Netzsch PHOENIX DSC 204 instrument) and nuclear magnetic resonance (JEOL GSX 400 MHz multi-nuclei FT-NMR instrument) spectroscopy.

3. Results and discussion

3.1 Chemistry of nanoparticles

The reactivity of nanoparticles is an interesting and upcoming subject, which has tremendous potential to gift new reactions and products to chemistry [26,27].

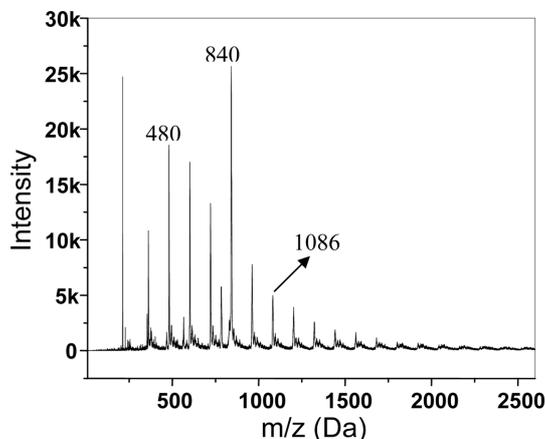


Figure 1. MALDI spectrum of the carbonaceous residue obtained from the reaction between Ag@citrate and CCl₄ in the positive mode. The matrix used is α -cyano-4-hydroxy cinnamic acid (CHCA). The carbonaceous nature of the residue is evident from the separation between the peaks (120 Da), corresponding to C₁₀ and the isotope pattern of each peak.

Citrate-capped nanoparticles of silver (Ag@citrate) and gold (Au@citrate) exhibit an unusual chemistry with halocarbons resulting in the formation of various interesting carbonaceous materials and metal halides [28]. Their reactivity depends on the size and morphology [28]. These are very important reactions of environmental significance leading to the complete mineralization of halocarbon pollutants at room temperature [29,30]. The reaction leads to the formation of C₆₀ at room temperature in a one-pot method [31]. The presence of metal halides was confirmed by powder X-ray diffraction and absorption spectroscopy [28,29]. A detailed matrix-assisted laser desorption ionization (MALDI) mass spectral investigation of the carbonaceous residue obtained by modifying the reaction conditions revealed the presence of various other carbon species as is evident from figure 1. We have found that the reactivity is highly sensitive to the shapes of the nanoparticles as well. The reactivity of halocarbons with SiO₂-protected Au nanoparticles (Au@SiO₂) leads to the formation of carbon onions of different morphologies within SiO₂ nanoshells [32]. We have extended the chemistry to ZrO₂-protected Ag and Au nanoparticles (Ag@ZrO₂ and Au@ZrO₂) respectively and products of such chemistry are the metal oxide nanobubbles [33]. It appears that carbon species formed within the shells are leached out due to their increased porosity [34]. Further studies are under way to understand the mechanistic aspects of these unusual reactions.

3.2 Development of new synthetic approaches for nanoparticles

New synthetic approaches were developed for nanoparticles of Ag, Au and Cu protected with oligomers/polymers. Extremely stable poly(*o*-toluidine)-capped Au nanoparticles and the mechanism of reduction of Au³⁺ by *o*-toluidine were

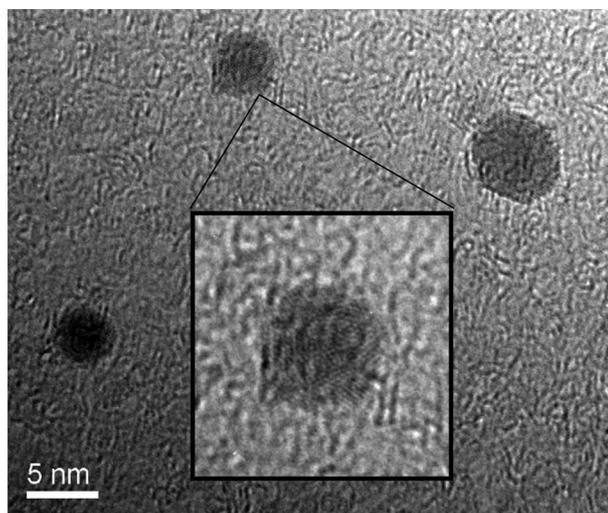


Figure 2. HRTEM image of copper nanoparticles. The average size of the particles is 3–5 nm.

investigated recently by Subramaniam *et al* [21]. A similar procedure was adopted for the synthesis of extremely stable Cu nanoparticles as well [22]. A high resolution transmission electron micrograph (HRTEM) image of the Cu nanoparticles is shown in figure 2. The average size of Cu nanoparticles synthesized by this method is 3–4 nm. The material is freely dispersible in almost all organic solvents. The material is stable for several months in the laboratory ambience. Rajeev Kumar and Pradeep [23] synthesized poly benzylthiocyanate-capped Ag nanoparticles by a one-pot synthetic route. To a mixture of Ag@citrate and 2-propanol (1:1.5 by volume), a definite amount of benzylthiocyanate was added and the mixture was subjected to mild stirring for a week, when benzylthiocyanate polymerizes on the Ag nanoparticle surface. Figure 3 shows the TEM image of the Ag nanoparticles capped with poly(benzylthiocyanate). The average size of the nanoparticles is 40–60 nm and thickness of the organic shell is ~ 10 nm. The material is freely dispersible in all organic solvents.

A procedure for the synthesis of extremely small molecular clusters of gold has been developed very recently using dimercapto succinic acid (DMSA) as the capping and reducing agent [24]. The material is crystalline and preliminary results indicate the formation of Au₃, Au₇ and higher molecular species. Direct laser desorption ionization mass spectrum of the isolated crystalline material showing Au clusters and their sulphur adducts is shown in figure 4.

A study of the interaction of biomolecules and nanoparticles has been one of our important areas in recent years. The interaction of several biomolecules with Au nanoparticles has been studied with a view to understand the binding chemistry of biomolecules, their conformational changes upon binding, improved biological action and the possibility of achieving drug delivery. Ciprofloxacin-capped Au nanoparticles have been recently reported by Tom *et al* [35]. The nature of binding has been investigated by several analytical techniques. Desorption of the drug

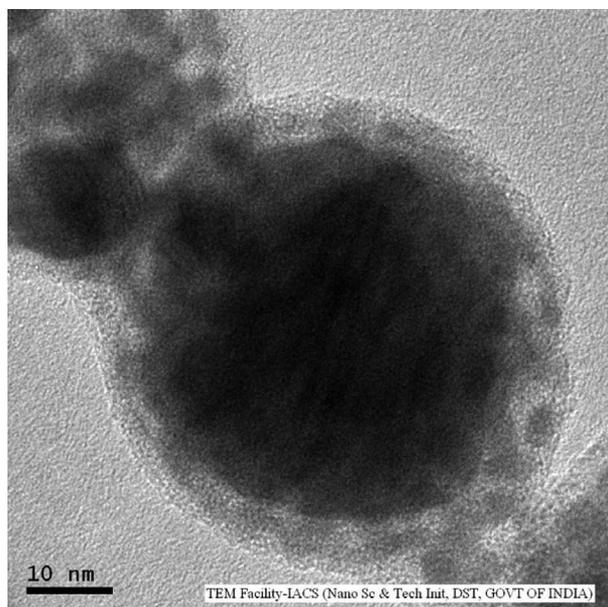


Figure 3. TEM image of the benzylthiocyanate-coated Ag nanoparticles. The average size is 40–60 nm and the shell thickness is ~10 nm.

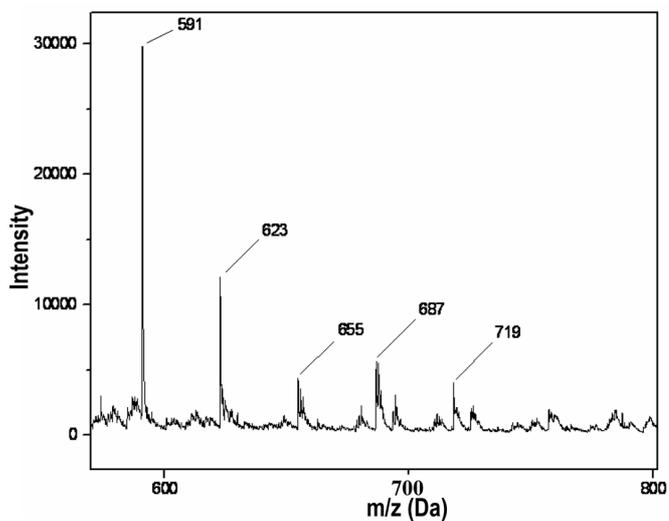


Figure 4. Direct laser desorption ionization mass spectrum of the Au@DMSA cluster showing peaks due to Au₃, Au₃S, etc.

molecules from the nanoparticles was investigated in the neutral and basic media and the kinetics of desorption [36] was shown to depend on the nanoparticle size. It was also confirmed that the nanoparticle-bound ciprofloxacin is fluorescent and this property could be utilized in biological investigations. As a preliminary step

towards realizing drug delivery possibility, we incorporated ciprofloxacin in SiO₂ nanoshells and studied its antibacterial action. We also probed the spectroscopy of the confined molecule within the nanoshell, especially using fluorescence [37,38]. Such materials behave as nanoscopic pH sensors [39]. A detailed investigation of the interaction of other relevant biomolecules with nanoparticles [40] and their delivery to human cells [41] is an active research area in our laboratory.

3.3 Clustering/aggregation of nanoparticles in the gas phase

Monolayer protected clusters of silver and gold undergo aggregation in gas phase when subjected to laser irradiation under MALDI conditions [42]. The term ‘gas phase clustering’ refers to the aggregation of monolayer-protected nano (or sub-nano)particles within the desorption region of the mass spectrometer. The direct laser desorption ionization (DLDI) mass spectra of propanethiol-, hexanethiol- and dodecanethiol-protected Au clusters (Au@PT, Au@HT and Au@DDT respectively) showed a peak maximum around 29 kDa in addition to large aggregates [42]. Column chromatography was used subsequently to isolate the 29 kDa cluster. The MALDI analyses of the 29 kDa clusters with or without matrices showed the clustering behavior in gas phase, which was confirmed to be due to the presence of monolayers. Inorganic oxides of Mo also form clusters in the gas phase when irradiated with laser [43].

We have found formation of inorganic fullerenes in the gas phase from both MoS₂ and WS₂ by direct laser irradiation and under direct laser desorption ionization (DLDI) conditions [44]. The bulk MoS₂ and WS₂ of 99.9% purity were ground well, dispersed in acetone and subjected to laser irradiation in a MALDI instrument. Experiments were also conducted with nanosized MoS₂ flakes obtained by extended sonication of MoS₂ in acetone. The DLDI mass spectra of these compounds showed a magic cluster at $m/z = 2048$, followed by another at $m/z = 2144$ as shown in figure 5. These clusters were assigned to Mo₁₃S₂₅⁻ and Mo₁₃S₂₈⁻, respectively on the basis of their isotope patterns. The stability of the ions was checked by post source decay (PSD) and the spectrum showed no fragmentation. To further confirm the stability of observed clusters, we carried out first-principles density functional theory total energy calculations with a generalized gradient approximation to the exchange correlation energy with Perdew–Burke–Ernzerhof (PBE) functional.

3.4 Nanoparticle-based sensors and devices

We have recently reported the use of citrate-capped nanoparticles of Au (Au@citrate) in the detection and extraction of endosulfan [45], a widely used pesticide in the third world countries. The adsorption of endosulfan on Au nanoparticles results in its color change, the magnitude of which depends on the concentration of the pesticide on Au. Similarly the nanoparticles of Ag and Au supported on activated alumina were used in the removal of chlorpyrifos and malathion [46], two widely used pesticides found in surface waters of developing countries. The complete removal of pesticides from water was confirmed by absorption spectroscopy

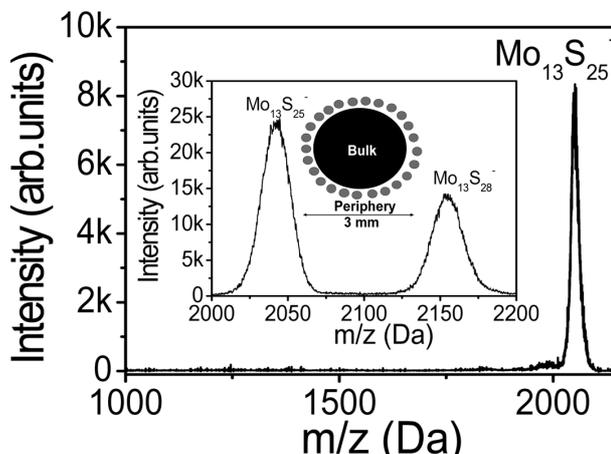


Figure 5. PSD mode spectrum showing the absence of fragmentation for $\text{Mo}_{13}\text{S}_{25}$. Inset: DLDI mass spectrum of MoS_2 in the negative mode showing the magic clusters $\text{Mo}_{13}\text{S}_{25}$ and $\text{Mo}_{13}\text{S}_{28}$. Schematic of the sample showing nanoflakes formed at the periphery is also shown in the inset.

as well as gas chromatography measurements. A low-cost antibacterial water filter has been developed by coating silver nanoparticles on commercially available polyurethane films [47]. Drinking water passed through this filter was found to be completely bacteria-free [48].

We have also reported the synthesis of monolayer functionalized nanobubbles of SiO_2 with aniline inside, $\text{C}_6\text{H}_5\text{NH}_2@ \text{SiO}_2 @ \text{stearate}$, exhibiting fluorescence and ‘excimer-like’ emission which behaves as a nanoscopic pH sensor, with complete reversibility [39]. The methodology involved adsorption of aniline on Au nanoparticles’ surface and growing silica, SiO_2 over them by Stober method. The Au nanoparticles were subsequently removed selectively by CN^- reaction or by halo-carbon chemistry. The material is stable and could be stored for extended periods without loss of fluorescence. This material is a reversible pH sensor in acidic and pH ranges. Another reversible nanoparticle-based acid–base indicator in the pH range 0.5–4 consists of $\text{Au}@ \text{poly}(o\text{-toluidine})$ [49]. This exhibits a visible, reversible, and pH-dependent color change as a result of the combined optical properties of the metallic core and the polymer shell when an acid or a base is added to it. The phenomenon is shown when $\text{Au}@ \text{poly}(o\text{-toluidine})$ is in solution or solid state, the latter is made by the incorporation of the material in polysulfone matrix to get free-standing films.

We have shown that nanoparticle assemblies can act as flow sensors [50]. These devices can generate 5–30 mV when liquids flow over a covalent assembly of metal nanoparticles made on conducting glass plates as shown in figure 6. The potential difference generated increases linearly with the flow rate and it depends on the dipole moment of the liquid. We suppose that ejection of electrons from the flowing dipoles is the main cause of the generation of potential rather than electrokinetic effects.

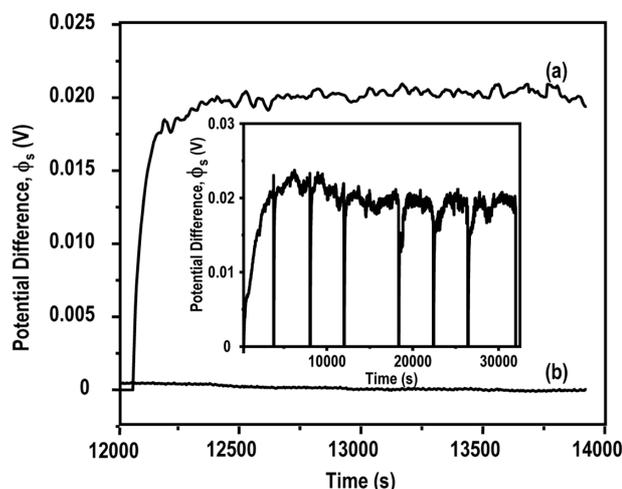


Figure 6. Plot of the potential difference vs. time for, (a) the device, showing the rise of potential and its stabilization for a fixed flow rate of 500 cc/h. The time (from the start of the experiment) between 12000 s and 14000 s is shown. Inset shows a plot of potential difference generated vs. time for a fixed flow rate of 500 cc/h during a complete cycle of measurements. Several reproducible datasets are shown. It takes some time to stabilize the potential. After the potential is stabilized, the wires were shorted bringing the potential to zero and then the measurement was resumed. Data corresponds to water. (b) Data for a device without nanoparticle (consisting of conducting glass plates only).

Developing good optical limiters has been one of the challenging tasks of scientists working in the field. Even though many substances like phthalocyanines, carbon black suspensions and fullerenes were identified as good limiters, none of them can withstand lasers of good fluence/intensity as they are prone to damage. Recently we have developed a good optical limiting material (Ag@ZrO_2 core-shell nanomaterial), which when incorporated into polyvinyl alcohol (PVA) matrix enabled us to make free-standing films which showed the highest known laser damage threshold reported hitherto [51]. Nanoparticles and clusters are found to be excellent optical limiters [52,53].

4. Conclusions

In this paper, we have presented an overview of the nanoparticle-based research carried out in our laboratory. The studies involve a range of areas such as probing the reactivity of nanoparticles (leading to novel reactions and products), developing new synthetic strategies for the synthesis of extremely stable nanoparticles and small molecular clusters, aggregation of monolayer protected clusters in the gas phase, laser-induced formation of inorganic magic clusters, interaction of biomolecules with nanoparticles and the applications of nanoparticles in pesticide removal,

sensors and the measurement of flow. Nanoparticle-based optical limiters show the highest damage threshold reported hitherto.

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