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Zirconia covered silver clusters through functionalized monolayers†

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We report a method of synthesis for zirconia coated silver clusters using self-assembled monolayers as templates. Formation of the zirconia cover, as monitored with X-ray diffraction and absorption spectroscopy, suggests a continuous overlayer growth that can be inhibited at any stage. Surface plasmon resonance of the silver cluster undergoes a gradual shift and decreases in intensity upon systematic build-up of the dielectric cover. The zirconia overlayer is optically transparent for smaller coverages, but becomes opaque for thicker layers. Spectroscopic studies showed that the mercaptobenzoic acid monolayer is intact in the synthetic procedure and the surface thiolate binding is unaltered. Preliminary studies suggest that metal ions can be incorporated into the oxide layer leading to a shift in the plasmon resonance band implying the possible use of these materials as ion sensors.

Introduction

Nanophase materials and nanocomposites, characterized by ultra-fine grain size (<50 nm) have generated immense interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties.[1] For instance, nanophase ceramics are of particular interest because they are less ductile at elevated temperatures as compared to the coarse-grained ceramics. Nanostructured metal clusters and colloids with appropriate oxide covers may have a special impact in catalytic applications. They may serve as precursors for new types of heterogeneous catalysts[2] and have been shown to offer substantial advantages in activity, selectivity and lifetime in chemical transformations and electrocatalysis[3] (*e.g.* fuel cells). Metal nanoparticles with core shell structures have attracted attention recently and a number of such hetero-structures have been reported in the literature.[4–7] Several methods ranging from chemical vapor deposition[8] to chemically directed self-assembly[4] and thermal deposition[5] have been used to fabricate such structures. Mulvaney and co-workers[9] have done significant work on silica encapsulation and have recently reported the preparation of thin films of such materials and their optical behavior. They used aminopropoxytrimethylsilane monolayers with the amine end binding the cluster and the silane terminal serving as a template for the growth of the silica layers. Other methods ranging from radiothermal reduction[5] to simultaneous reduction[6] of both the core and the capping species (in the case of BN covered Ag clusters) have also been reported. These approaches of metal cluster encapsulation are distinctly different from metal-cluster incorporation on ceramic oxide supports, which is a fairly developed area of research.

In this paper, we report a simple method for the synthesis of zirconia covered silver clusters. There are no previous reports on the encapsulation of metal clusters with zirconia. These oxide-covered nanoclusters are in particular more stable than the monolayer stabilized ones, which are known to lose their integrity on ageing. This enhanced stability is of great importance to applications such as catalysis. A zirconia cover is novel and has several potential applications since it is the only metal oxide with all major chemical characteristics; namely acidic, basic, oxidizing and reducing properties.[10] Zirconia is a material of immense technological applications ranging from fuel cells[11] to sensors and applications for materials such as this can be in fields as diverse as catalysis,[12] drug delivery[13] and sensors,[14] to name but a few. They can also have interesting optical properties due to the core–shell structure.[15] In the present work, the nanocomposite has been synthesized using self-assembled monolayers as template over which a shell of zirconia is grown; the thickness of which is directly proportional to the mole ratio of the zirconia precursor (zirconyl chloride) added.

Experimental

p-Mercaptobenzoic acid (MBA) and sodium borohydride ($NaBH_4$) were purchased from Aldrich. Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was from Reidel Chemicals, Germany and silver nitrate was from Qualigens Fine Chemicals, India. The solvents used in the synthesis were all laboratory grade obtained from Ranbaxy Chemicals, India, and used after distillation.

Silver clusters were synthesized by the Brust procedure.[16] A 0.0358 M toluene solution (0.3618 g in 21.6 ml) of tetra-*N*-octylammonium bromide was added to a vigorously stirred solution of 0.0288 M $AgNO_3$ (0.049 g in 10 ml) in water. The solution was allowed to equilibrate for 1 h followed by the addition of a 0.0139 M thiol solution (23.8 ml) in toluene and stirred for 10 min. This was followed by the dropwise addition of 8.25 ml (0.2378 M) of aqueous sodium borohydride over a period of 10 min. Reduction of silver ions was evidenced by the brown color of the toluene phase, which was originally colorless. The temperature during the reduction was maintained around 10 °C by cooling with ice. The toluene layer was separated and kept for reduction of volume (3–4 days) after which 100 ml of methanol was added to precipitate the cluster. It was then centrifuged, washed several times with methanol to remove unreacted reagents and air-dried.

A 0.01 g of the cluster was dispersed in 50 ml of toluene–methanol mixture (3 : 2 volume ratio) by sonication. To this zirconyl chloride octahydrate was added in a 1 : 10 (weight) ratio. The solution was equilibrated and then 5 ml of

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†Electronic supplementary information (ESI) available: XPS, IR data of the monolayer protected cluster and the nanocomposite. See http://www.rsc.org/suppdata/jm/b2/b203081k/

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triethylamine was added dropwise over a period of 15 min using a micropipette. This was followed by the addition of 50 ml of water. The solution was stirred for a period of over 24 h. The resulting mixture was centrifuged, washed with plenty of methanol and air-dried. Increasing or decreasing the concentration of zirconyl chloride was found to result in thicker or thinner shells, respectively. The product thus obtained was washed with plenty of methanol to remove excess unreacted species and was air-dried.

The composite thus formed can be suspended in methanol and does not settle for several days. The original silver clusters protected with MBA were freely soluble in methanol. Solubility decreased upon repeated precipitation. The molecular nature of the cluster did not change during storage for a month in the laboratory atmosphere as evidenced by the constancy of the infrared (IR) spectrum.

Transmission electron microscopic (TEM) measurements were done with a Philips CM12 microscope operating at 120 keV. The samples were drop-casted onto a carbon coated copper grid. X-ray diffraction (XRD) studies were carried out with a Shimadzu XD-D1 diffractometer with Cu Kα radiation (30 kV, 20 mA). The samples were spread on anti-reflecting glass slides and were wetted with acetone to obtain a uniform film. The acetone was blown dry and the slide was mounted on a diffractometer. IR spectroscopic measurements were performed with a Bruker IFS 66v FT-IR spectrometer. All samples were prepared in the form of 1% (by weight) KBr pellets. The UV–visible (UV-vis) spectra were measured in a Varian Cary 5 UV/VIS/NIR spectrophotometer. The measurements were done *in situ* with the toluene–methanol mixture as the solvent. The measurements were carried out at room temperature. X-ray photoelectron spectroscopic (XPS) measurements were carried out with a VG ESCA LAB MkII instrument in Notre Dame University, using Al Kα radiation. The binding energies were corrected with the C 1s peak at 285 eV binding energy, as the samples exhibited mild charging. Thermogravimetric (TG) analyses were carried out on a NETZSCH STA 409 thermal analysis instrument. A heating rate of 10 °C min^{-1} was used for the measurements and about 15 mg of the sample was used. Data in the range of 25–1400 °C were collected. The measurements were made in a nitrogen atmosphere.

Results and discussion

Layer-by-layer self-assembly has been used to cover the cluster with a shell of zirconia. The functionality in the thiol was chosen such that it facilitates the attachment of zirconyl chloride onto the cluster. Vijayamohanan *et al.*[17] have previously reported the synthesis of microcrystalline zirconia on flat metal surfaces using a monolayer covered gold surface as the template. In their work they used a dithiol and zirconyl chloride and suggested a reaction between the pendant –SH group and the Cl of zirconyl chloride with the elimination of HCl. We have used the –COOH group in place of the –SH since the above reaction will be even more facile in this case. The choice of solvents was made keeping in mind the solubility of the cluster (soluble in toluene) and zirconyl chloride (soluble in methanol). Prior attempts to carry out the reaction in a biphasic system of water and toluene failed to yield fruitful results. Hence we decided to use a single-phase system. Toluene and methanol were chosen since methanol is sufficiently polar, so as to dissolve the zirconyl chloride, at the same time being completely miscible with toluene. The base used for the hydrolysis is triethylamine, which is also completely miscible with the solvents. The controlled rates of hydrolysis and equilibration time are key parameters to ensure a uniform shell growth and avoid the formation of unseeded zirconia. No attempt was made to separate unseeded zirconia, if formed. The principal product was the composite as evidenced by the XRD studies (see below). The sequence of reactions employed is depicted in Fig. 1.

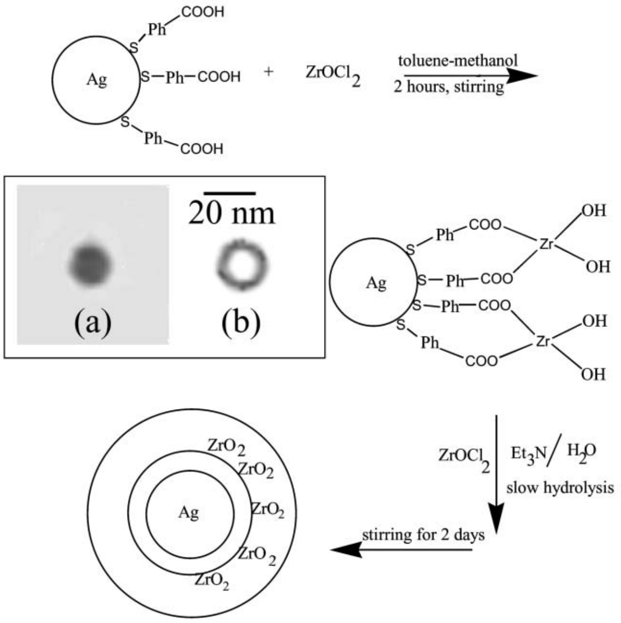

Fig. 1 Proposed reaction scheme involved in the preparation of the composite. (a) TEM image of a selected particle with its shell. (b) Image of the shell extracted with Scion Image Beta Release 2 (available from www.scioncorp.com). Observed core diameter is 15 nm and shell thickness is ~3 nm for this particle. A core size distribution of 10% is observed, but the shell thickness is about the same.

A TEM image of a selected particle with its shell is shown in Fig. 1(a). A core of 15 nm diameter and a shell of ~3 nm thickness are clearly seen. The diameter of the silver core agrees well with the XRD measurement. An enhanced image (with Scion Image Beta Release 2, available from www.scioncorp.com) showing the shell alone is presented in inset (b). The instrumental resolution is inadequate to observe the finer details of monolayer binding. Typical core size distribution is 10%, and mostly spherical morphology is seen, as in previous two-phase preparations.[18] For a given preparation, the shell thickness is about the same.

The reaction was monitored *in situ* by UV-vis absorption spectroscopy which showed changes in the cluster plasmon. The spectra are depicted in Fig. 2. Time zero represents the start of the reaction ($ZrOCl_2$ addition) with the first spectrum taken after 10 min. The parent cluster solution itself exhibits significant scattering due to aggregation. No shift in the plasmon frequency is noticed in the spectrum marked 1. As coating proceeds and the shell thickness increases, scattering occurs as light enters from the solvent (since the refractive index of zirconia is high (~2)). It may be noted that the background intensity in the last three spectra are similar and the plasmon peak has not changed significantly.

The peak maximum corresponding to the plasmon excitation occurs around 390 nm in the toluene–methanol mixture, and it red shifts as the reaction proceeds. The intensity of the peak also decreases with time and the peak is not observed at all after a period of about 24 h for a $ZrOCl_2$ concentration of 0.2 wt.%, which is ~10 times that of the cluster concentration, suggesting a larger shell thickness. The shift in plasmon on encapsulation may be principally due to the change in refractive index of the medium. Previously it was the monolayer and the solvent that served as the medium, which is nearly homogeneous. Now the oxide shell is the first cover, which has a much higher refractive index than the solvent.

For non-interacting spheres, Mie's theory[19] explains the

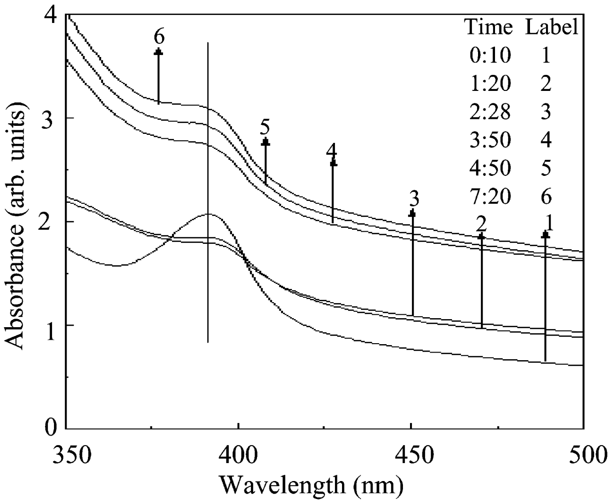

Fig. 2 UV-vis absorption spectrum of the silver cluster measured *in situ* as a function of reaction time. Note the shift in plasmon and increase in background absorbance as the reaction proceeds. Time 0:00 represents the free cluster and the other spectra correspond to the composite during the course of zirconia growth. The time count begins at $ZrOCl_2$ addition. The time label represents h:min. Line is a guide to the eye.

absorption and scattering of essentially spherical particles. This theory has been extended and modified to include several other systems such as non-spherical ones and coated spheres.[20,21] If one takes only the dipole process into account, then the classical plasmon frequency is proportional to $\sqrt{(Ne^2/Km\varepsilon_0)}$, where N is the free electron density, e is the electronic charge and m is its mass, K is the relative permittivity and ε_0 the permittivity of free space. Simple dielectric theory has been used to explain the optical absorption spectra[22] of silica coated gold particles but the onset of quantum size effects leads to deviations from bulk dielectric behavior. The nanoparticles within a thick shell resonate as though the shell is the solvent, *i.e.* the plasmon becomes independent of the refractive index of the solvent in which it is suspended. On silica encapsulation, the peak red shifts as predicted by Mie's theory.

Metal clusters have been shown to have a different absorption frequency with different surfactants[23] as stabilizers. It is quite difficult to attribute the observed shift in plasmon to a specific aspect since a large number of parameters change on coating with a shell of zirconia. On encapsulation, the relative permittivity, refractive index and mean free path of the electrons, are affected, which in turn has a profound influence on the plasmon frequency. The plasmon is also suppressed due to scattering by the oxide layer surrounding the cluster. A dampening is clearly seen upon overlayer growth (Fig. 2). The plasmon frequency red shifts upon increasing the refractive index[24] and a similar but significantly smaller shift occurs as a result of the increase in mean free path.[25] Thus the observed spectrum can be qualitatively explained though the shift is much lower than predicted. This could be due to the masking of the plasmon by light scattering. An additional point to note is that although the shift is observable, no marked change in the width of the peak is noticed. This is explained as due to the strong confinement of the free electrons within the metal by the monolayers themselves.

X-ray photoelectron spectroscopy studies reveal that the thiol part remains intact upon covering with zirconia. The study also established the presence of a zirconia cover, although an angle resolved study to probe the zirconia cover alone could not be performed. However, this study coupled with other evidence strongly suggests a core–shell structure for the product. The X-ray photoelectron spectrum in the Ag 3d, Zr 3d and S 2p regions are provided in the ESI†. From the binding energy values, it is evident that silver is in the zero oxidation state (Ag $3d_{5/2}$ at 368 eV) and also that sulfur is present as thiolate (S 2p, 162 eV). A point of more importance is that there is no inelastic scattering tail in the Ag 3d region. We do not observe an inelastic tail for zirconium as expected since it is on the top. This implies that the silver electrons come out without any energy loss and that the shell of zirconia is thinner than the escape depth of Ag 3d electrons. Hence we conclude that the shell thickness is not very large and is of the order of a few nanometres since the mean free path of the Ag 3d electrons is of the same order.[26,27] The intensity of Zr 3d is lower than Ag 3d as the atomic sensitivity factor of the former is almost half that of the latter.[28]

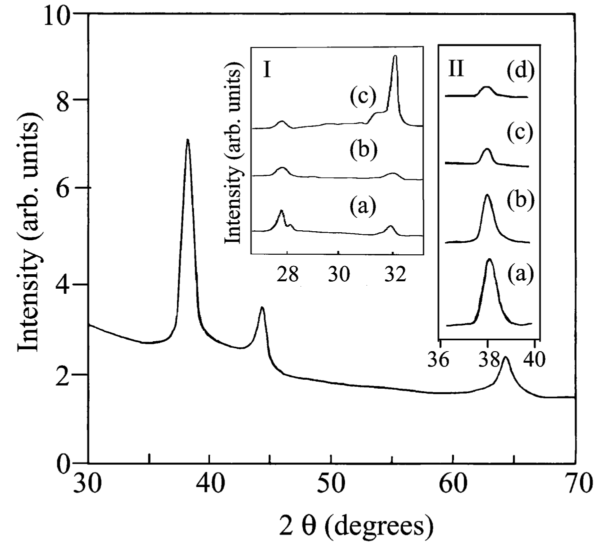

Fig. 3 X-ray diffractogram of the silver cluster protected with MBA. Inset I, X-ray diffractograms of the product showing monoclinic zirconia peaks: (a) at room temperature, (b) after heating to 200 °C, and (c) after heating to 600 °C. Inset II, reduction in intensity of the Ag(111) peak at 38° as the reaction proceeds: (a)–(d) represent increasing reaction time.

X-ray diffractograms of the material studied as a function of reaction time indicate a decrease in intensity of the (111) peak of the Ag cluster at $2\theta = 38°$ as the reaction proceeds and this peak is absent in the diffractogram when the zirconia cover is very thick. Fig. 3 depicts the X-ray diffractogram of the parent Ag cluster with its characteristic peak at 38°. The Scherrer formula[29] suggests a diameter of 14.03 nm for the silver core. The reaction was also followed by X-ray diffraction. As the reaction time increases, we observed a marked reduction in the intensity (inset I of Fig. 4) of the Ag(111) peak since the cluster

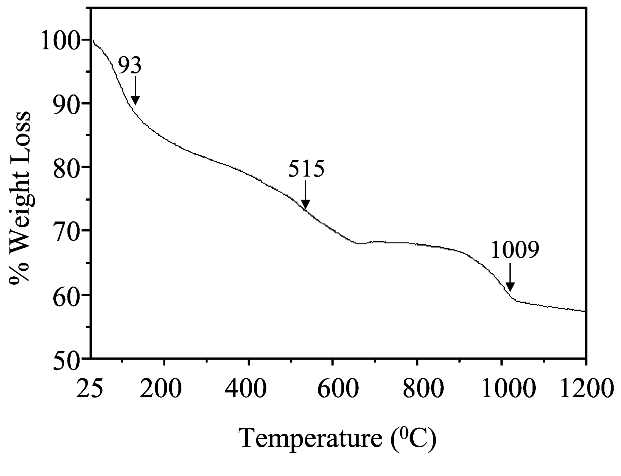

Fig. 4 Thermogram of the composite. Decomposition temperatures (°C) are indicated.

is being covered with zirconia. The X-ray diffraction study of the product (inset II of Fig. 4) shows the presence of peaks corresponding to monoclinic zirconia ($2\theta = 28^\circ$ and 32°). X-ray diffractograms of the sample after heating to 200 °C and 600 °C were also taken. Heating was done for a period of 2 h. These also showed the peaks at 28° ($11\bar{1}$) and 32° (111) of monoclinic zirconia. After heating to 600 °C, the intensity of the peak at 28° goes down while the peak at 32° intensifies, which could be attributed to some phase transition. No peak corresponding to tetragonal zirconia is observed suggesting that the sample is essentially covered by monoclinic zirconia.[30] This is along expected lines since bulk monoclinic zirconia undergoes phase transition only above 1000 °C.[31]

The thermogram of the sample is depicted in Fig. 4. The weight loss is principally a two-step process apart from a decomposition around 100 °C. The first weight loss extends to a temperature of 650 °C and is due to the loss of water from the hydrated zirconia (since it mainly exists as $Zr(OH)_2$ in the solution) and the hydrated part is converted to ZrO_2. Monolayer desorption may also occur in this region. The second loss commencing at about 900 °C could be due to the melting of the metal cluster core within the shell resulting in a loss of silver through diffusion. Weight loss in the first region amounts to about 30% while a theoretical weight loss value of 22.61% has been reported for $Zr(OH)_4$ (hydrated zirconia).[32] A weight loss of nearly 32.19% is observed for zirconium hydroxide suggesting that the oxide cover could be the hydroxide rather than the hydrated oxide. Though both the terms are used interchangeably in the literature, a recent study by Huang *et al.* has brought about some distinctions between the two.[33] A weight loss of $\sim$10% is observed in the second region. The thermogram is very different from from that of a pure zirconia sample, which shows essentially a one-step weight loss.[34] This is because on heating to higher temperatures, the cluster core can melt leading to further weight loss.

IR spectra of the thiol, cluster and the composite product were taken (spectra are provided in the ESI†). An important point is the presence of the –SH stretching frequency at 2562 cm^{-1} in the thiol and its complete absence in the other two. This confirms that the thiol is adsorbed as thiolate as reported in the literature.[35] The spectrum of the thiol also shows the presence of characteristic C–C and C–H stretching associated with the benzene ring and these features are also observed in the cluster and the product. Free –COOH was observed in the cluster around 3740 cm^{-1}, which is more pronounced than in the free thiol. This band in the case of thiol is quite narrow when compared to that of the cluster, possibly due to the presence of adsorbed methanol in the cluster. The absence of a thiol –SH stretching frequency shows that the thiol group is preferentially adsorbed over the carboxylic acid group as reported in the literature,[36] though there are reports of chemisorption on silver surfaces[37] when the acid moiety alone is present.

The spectrum of the product has a band centered about 650 cm^{-1}, which is assigned to the asymmetric stretching mode of the Zr–O–Zr bond.[38] Symmetrical Zr–O–Zr stretching is observed at 470 cm^{-1}. These bands are narrow, unlike the broad bands expected for ZrO_2, suggesting that it is present not as zirconia but as zirconium hydroxide (hydrated zirconia) which has an extended structure.[39] The bending modes are expected in the far IR region and were not probed. The –OH stretching of the hydroxide is observed as a very broad peak about 3340 cm^{-1}, which is markedly different from the –OH of the carboxylic acid of the cluster-bound monolayer. These findings, in addition to the other studies, further corroborate the presence of zirconia in the product.

Conclusions

We looked at a simple and elegant way to synthesize zirconia covered silver clusters starting from *p*-mercaptobenzoic acid stabilized silver clusters. The composite was characterized by TEM, XRD, IR, UV-vis, XPS and TG. The reaction was monitored with absorption spectroscopy, in which we observed a shift in plasmon resonance frequency as a function of the thickness of the zirconia cover. XRD shows that the zirconia cover essentially has a monoclinic structure. IR studies show that thiol part is absorbed preferentially over the carboxylic acid on the silver surface and the spectrum of the composite shows characteristic bands for Zr–O stretching. XPS studies established the presence of silver in the zero oxidation state and the observation of Ag 3d electrons shows that the shell size is less than the mean free path of photoelectrons. TG studies have proved that the material is unlike pure zirconia and has different weight loss features. The studies collectively established that the synthesis leads to a hydrated monoclinic zirconia cover. The composite was found to exhibit interesting optical absorption behavior in the presence of ions and a study is currently underway, the findings of which will be reported in a future publication.

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