

Polymerization of benzylthiocyanate on silver nanoparticles and the formation of polymer coated nanoparticles†

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Polymerization of benzylthiocyanate on silver nanoparticles produces organic shell covered nanoparticles with controllable thickness in a one-pot process. Gram scale quantities of core-shell materials have been synthesized by this method. The methodology involves the addition of the precursor into Ag-citrate solution and the shell nucleates over a period of three weeks with complete precipitation of the core-shell material which can be dispersed subsequently in organic solvents. The material has been characterized using transmission electron microscopy, X-ray diffraction, FT-IR, laser desorption mass spectrometry, thermogravimetry, surface enhanced resonance Raman spectroscopy (SERRS) and Raman imaging. A typical composite material consists of a silver core of 40 nm diameter coated with a polymeric shell of 8 nm thickness. The polymer exhibits characteristic features in mass spectrometry and vibrational spectroscopy. The core-shell structure of nanoparticles is imaged for the first time using the Raman intensity of the shell. Proton assisted polymerization of benzylthiocyanate occurs on the silver surface, leading to a linear chain which subsequently deposits on the nanoparticle surface resulting in the core-shell structure.

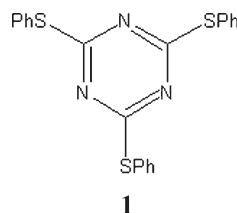
Introduction

Core-shell particles are recent additions to the large variety of nanosystems.¹ Various shells have been reported in the literature, ranging from molecular shells² to extended solids³ and from simple polymers⁴ to proteins.⁵ Diversity in cores spans from semiconductor quantum dots⁶ to metallic nanoparticles⁷ and alloys.^{2d, 8} The motivation to make such composite materials is to control and modify the properties so as to achieve photonic,⁹ catalytic,¹⁰ magnetic¹¹ and biological properties.¹² The common synthetic strategy to make such a system is to grow the shell by a post synthetic approach.^{3d} The interaction between the nanoparticle and the shell forming precursor is initiated through a chemically specific binding agent. Apart from this successful two step synthetic approach there have been several one pot approaches to make core-shell nanomaterials, the most popular being the Brust method.¹³ We have been interested in the synthesis of molecular,^{2c-e} oxide^{3a, b} and polymer^{4b} protected core-shell materials both by single and multiple step approaches and their chemistry.¹⁴

In this work we explored the possibility of initiating a polymerization reaction at the nanoparticle surface with the objective of simultaneously covering the nanoparticle surface with the resulting polymer. The approach involved adding a few more reagents to the nanoparticle growth medium, thereby

achieving the whole process in one-pot. We also wanted the reaction to yield gram quantities of material. The approach yielded a robust polymeric shell of varying thickness and the nanoparticles were precipitated in the modified form. Both the core and the shell have been characterized adequately. We believe that the chemistry reported here is an elegant approach to make larger quantities silver nanoparticles with a stable carbonaceous shell. Such materials can be incorporated into organic matrices for diverse applications.

The polymerization reported here on the nanoparticle surface does not occur normally in the solution phase, where a ring structure (**1**) containing three monomeric units is formed.¹⁵ The reaction follows an acid catalyzed route on the nano surface and the resulting linear polymer chain, being insoluble in the reaction medium, deposits at the nano surface.



Experimental

Reagents

AgNO₃ and trisodium citrate were purchased from CDH chemicals. Benzylthiocyanate was purchased from Sigma Aldrich. Isopropyl alcohol was distilled prior to use. Triply distilled water was used for all the experiments.

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Synthesis of core-shell nanoparticles

Citrate capped silver nanoparticles (Ag-citrate) were prepared according to a previously reported method.¹⁶ 125 ml of isopropanol was added to 100 ml of as prepared citrate capped silver nanoparticle solution and 1 g of benzylthiocyanate was added in to it. The resulting solution was stirred at room temperature for three weeks. The solution went through a series of gradual color changes and became dark brown (starting from the golden yellow of the parent Ag-citrate). At the end of the reaction the nanoparticles precipitated. The material was washed thrice with isopropyl alcohol. The air dried material was redispersible in most of the organic solvents such as ethanol and hexane. We refer to this material as silver capped with polybenzylthiocyanate (Ag-PBT). Gram quantities of the material have been synthesized. It was stable in the laboratory atmosphere for several months without any measurable change. The material was stored in glass bottles without additional care. The shell was found to be chemically inert and highly protective as silver was not leached out by cyanide. The silver core remained stable for a day in 2 mM NaCN (Ag-citrate disappears almost instantaneously under this condition).

Characterization

UV-visible spectra were recorded using a Perkin Elmer Lambda 25 spectrometer with a 1 cm quartz cell. Images of the nanoparticles were taken using a JEOL 2010 transmission electron microscope operating at 200 keV. Specimens for the measurements were prepared by spreading a small drop of dilute solution of the material on a 200 mesh size carbon coated copper grid. The solvent was allowed to evaporate at room temperature. The X-ray diffraction patterns were recorded with a scan rate of 4° min^{-1} in the 2θ range of 20° to 90° using a Shimadzu XD-D1 Diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). FT-IR measurements were done with a Perkin Elmer Spectrum one spectrometer. The specimen was prepared as a KBr pellet of the dry material. Raman images were measured using a Renishaw Raman System Model 2000 Spectrometer. The samples for Raman imaging measurements were drop-cast on mica sheets. The mass spectrometric studies were conducted using a Voyager DE-PRO Biospectrometry Workstation (Applied Biosystems) MALDI-TOF MS instrument. For LDI-MS measurements, the sample briefly sonicated in isopropyl alcohol, was spotted on a 100 well plate and allowed to dry at room temperature.

Results and discussion

As prepared Ag-citrate manifests time dependent changes in optical spectroscopy during the course of the reaction. After three weeks of reaction, the solution manifests a red shifted plasmon at 516 nm (Fig. 1). Note that the silver plasmon excitation shifts from 420 nm to increasing values by increasing the thickness of the monolayer shell.^{2b} This is generally achieved by varying the chain length of the thiol. A similar feature is seen in the case of ZrO₂ shell protected Ag nanoparticles as well; the peak red-shifts with increasing ZrO₂ thickness^{3b} Time dependent variation of the peak maximum is

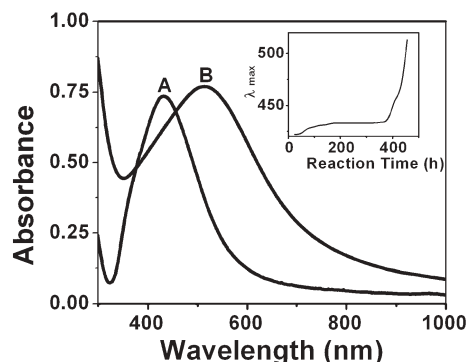


Fig. 1 UV-vis absorption spectrum of Ag-citrate in water (A) and Ag-PBT in isopropyl alcohol (B). The inset shows the position of the surface plasmon band as a function of the reaction time.

depicted in the inset of Fig. 1. The initial red shift is slow and the peak is nearly constant at around 430 nm for over 200 h and a large shift is observed subsequently. It appears that the initial polymerization is slow and the shell thickness is built up rapidly towards the end of the reaction. The extent of shift in the second stage of the reaction depends on the concentration of the benzylthiocyanate used. As will be explained later, the polymerization of benzylthiocyanate is sensitive to the pH of the medium. The protons required to initiate the reaction are produced only slowly, explaining the two step kinetics seen in the optical spectrum. By starting with a larger concentration of benzylthiocyanate one can get a thicker polymer shell (keeping the reaction time constant) as shown by an increased shift in the absorption spectrum (see the electronic supplementary information (ESI)† Fig. S1).

The sample as prepared above consists of particles with a metallic core of 40 nm diameter surrounded by a polymeric shell of 8 nm thickness (Fig. 2). The shell and the core are clearly visible in TEM. Although the particle size is large, the shell appears to be uniform in size and covers the nanoparticle surface completely. The core is polycrystalline in nature as is evident from the Moiré fringes (Fig. 2C) in the core region. The shell is amorphous but is stable under electron beam irradiation.

The diffraction pattern of the material showed peaks corresponding to the different crystallographic planes of metallic silver (Fig. 3). It can be seen that the peaks match with the cubic silver positions. The various 2θ values and the corresponding reflections are as follows: 38.41° (111), 44.39° (200), 64.80° (220), 77.76° (311) and 81.79° (222). In accordance with

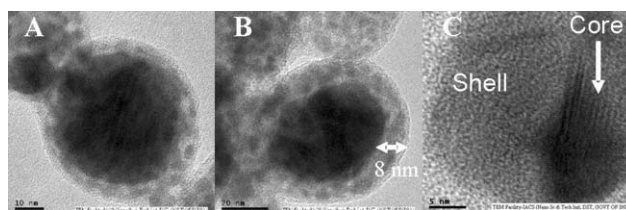


Fig. 2 TEM images of Ag-PBT showing clearly the core and the shell. The shell thickness was found to be 8 nm (Fig. 2B). Fig. 2C shows the Moiré fringes in the core region of the particle as a result of the exposure of various crystallographic planes to the electron beam.

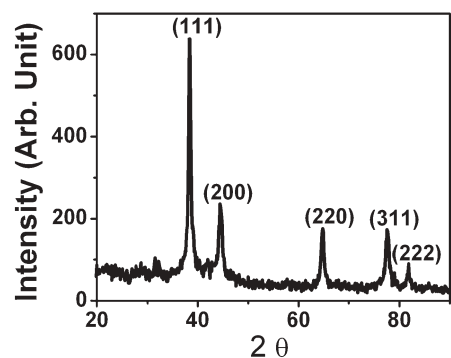


Fig. 3 X-ray diffractogram of Ag-PBT.

the TEM, the X-ray diffraction pattern suggests an average particle size of 40 nm, calculated using the Debye-Scherrer formula.

The most characteristic signatures of the polymer shell are seen in the infrared spectrum (Fig. 4). The features are distinctly different from the parent monomer which are assigned completely using data in the literature.¹⁷ Although some of the features of the two are similar, the peak at 1583 cm^{-1} in the core-shell material confirms the presence of the polymeric shell.¹⁸ This is quite different from the previous report where thiocyanate changes to thiolate during adsorption to the metal surface.¹⁹ The material showed a peak at 2147 cm^{-1} corresponding to cyanide. This is possible since a few benzylthiocyanate molecules may get trapped inside the polymeric shell as the shell, once formed, is impermeable to ions and molecules. The peaks 1425 and 1492 cm^{-1} corresponding to the $-\text{C}=\text{C}-$ stretching vibrations of the benzene ring appear both in benzylthiocyanate and in the product which confirms the presence of the benzene ring in the side chain of the polymer.

The surface enhanced resonance Raman (SERRS) spectrum (Fig. 5) of the material showed peaks corresponding to the benzene ring in the polymer. The measurement was made with 532 nm excitation which couples with the plasmon of the core, as it was shifted by the presence of the shell. It appears that the peak corresponding to the polymeric back bone ($-\text{C}=\text{N}-$) has merged with the 1600 cm^{-1} peak of benzene ring.²⁰ The material showed the $\text{C}_6\text{H}_5-\text{C}$ vibration at 1210 cm^{-1} . The intense band at 1450 cm^{-1} is attributed to the methylene

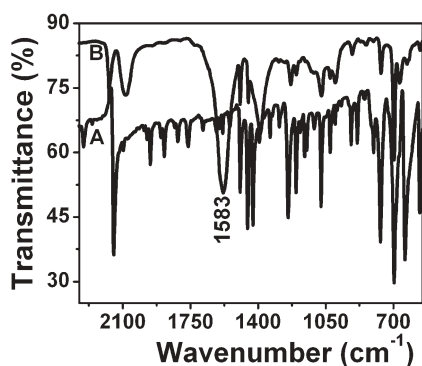


Fig. 4 FT-IR spectra of benzylthiocyanate (curve A) and Ag-PBT (curve B).

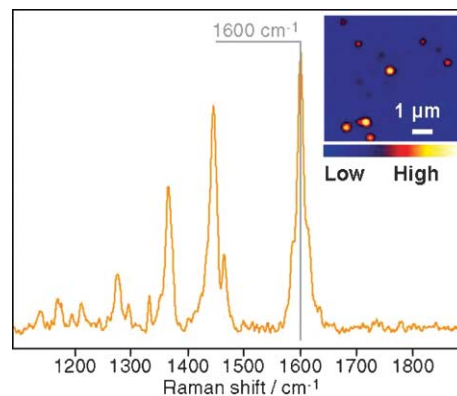


Fig. 5 SERRS spectrum of the polymer on the silver nanoparticle using 532 nm excitation. Inset shows the Raman image of Ag-PBT aggregates using the intensity of the 1600 cm^{-1} band.

scissoring mode. In order to study the course of the reaction we measured the Raman spectrum of the reaction product during the course of the reaction. This involved precipitating the core-shell material at various reaction times. As the polymerization reaction proceeds, the intensity of the peak due to the cyano group at 2145 cm^{-1} of benzylthiocyanate decreases. Thus initially the thiocyanate molecules stick to the metal surface and the adsorbed molecules gradually start reacting which is manifested by the gradual disappearance of the peak at 2145 cm^{-1} . This shows that metal surface plays a key role in the polymerization reaction.

The characteristic 1600 cm^{-1} line in the SERRS spectrum can be used for Raman mapping of the material and the Raman image obtained by summing up intensity at 1600 cm^{-1} is shown in the inset of Fig. 5. The image shows aggregates of particles with an expected intensity distribution. In an aggregate, the most intense signal will be from the centre as seen here. It is unlikely that isolated particles are imaged here, as the particle size is smaller than the spatial resolution of confocal Raman imaging. It may be noted that Raman imaging is used here for the first time to look at core-shell materials.

The nature of the polymeric shell is evident from the laser desorption mass spectrum depicted in Fig. 6. A peak separation of m/z 246 indicates the $(\text{C}_6\text{H}_5-\text{CH}_2-\text{S}-)_2$ unit and the separation of m/z 135 indicates the $\text{C}_6\text{H}_5-\text{CH}_2-\text{S}-\text{C}-$ unit. The

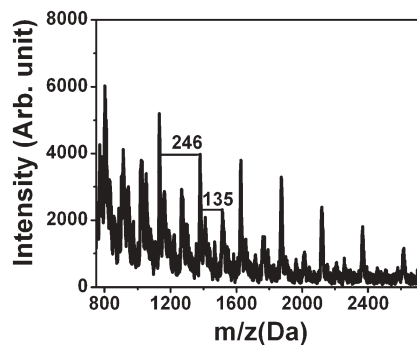
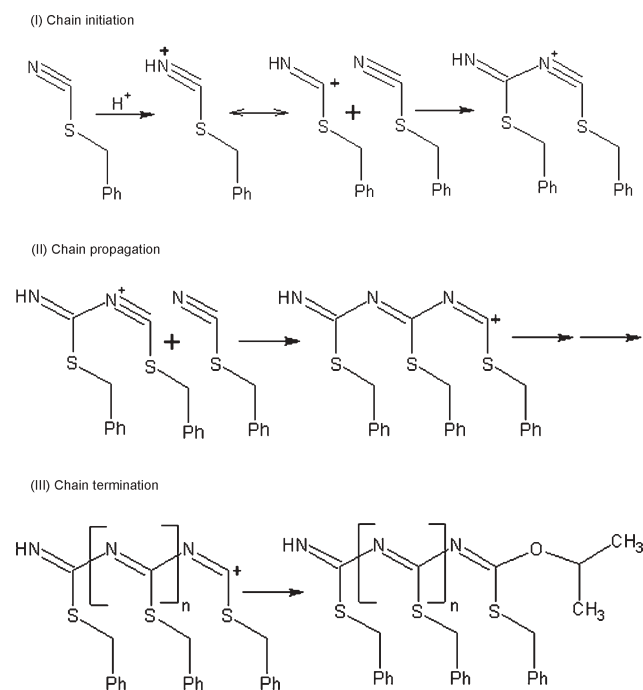


Fig. 6 LDI mass spectrum of Ag-PBT. The two distinct series observed are indicated.

origin of these two fragments can be expected from the $-(\text{C}_6\text{H}_5\text{-CH}_2\text{-S})\text{C}=\text{N}-)_n-$ backbone of the polymer. No distinct peak for the molecular ion was evident. This is expected as desorption from the metal surface is unlikely to eject the molecule as a whole. The mass spectrum therefore is a representation of the ion chemistry of the desorbed polymer fragments. The $\text{C}_6\text{H}_5\text{-CH}_2\text{-S-}$ fragment has a tendency to dimerize, and mass spectra of thiolate protected clusters in general, give the disulfide ion as the base peak. No additional features were manifested in the matrix assisted laser desorption (MALDI) mass spectrum.

The polymeric shell is thermally stable up to 200 °C. A two step thermal loss was observed in thermogravimetry (see ESI†Fig. S2). The first sharp feature occurs at 200 °C resulting in a mass loss of 17% followed by a continuous loss spread up to 1000 °C. This latter step amounts to an additional loss of 13%. The shell is resistant to ions as shown by cyanide ion reaction (see ESI†Fig. S3). At low concentration of CN^- , up to 2 mM, no metal core leaching is observed. Note that at this concentration, Ag-citrate is destroyed immediately. However, here the shell is stable even for a period of 24 h. However, at larger ionic concentration of 10 mM the core is completely destroyed within several minutes.

From the foregoing it is evident that benzylthiocyanate undergoes polymerization at the nanoparticle surface leading to polybenzylthiocyanate $-(\text{C}_6\text{H}_5\text{-CH}_2\text{-S})\text{C}=\text{N}-)_n-$. There is no evidence for the ring structure¹⁵ seen in solution phase in LDI MS. The features in IR, in conjunction with a MS data suggest a straight chain polymer, although not many reports exist on the formation of such a material.¹⁸ A distinct ring structure should have shown up in the MS and vibrational spectroscopies. On the basis of the experimental data we suggest the following mechanism for the formation of the polymer involving the following steps (Scheme 1).



Scheme 1 Probable mechanism for the formation of the polymer.

Although every step of the polymerization process is not evaluated, it may be noted that a mixture of Ag-citrate and propanol can release protons by the formation of acetone.²¹ Therefore, the initiation of polymerization is expected in our reaction mixture. In agreement with this we see that the pH of the solution shows a distinct variation during the course of the reaction, decreasing from 6.8 to 3 (at the end of the reaction). The proton attacks the nitrogen preferentially because the delocalization of d electrons of sulfur makes it less nucleophilic compared to nitrogen. This is in accordance with the previous report where during acid hydrolysis proton goes to the nitrogen of thiocyanate.²² It may be noted that the termination of the reaction could occur by other processes as well, involving other species present in the reaction mixture. The IR, Raman and LDI-MS data can be explained using such a polymeric structure.

Conclusion

In conclusion, we show that a variable thickness carbonaceous core-shell nanomaterial can be prepared directly starting from the polymer forming precursor. The nature of the polymeric shell has been thoroughly characterized by various analytical techniques. Variation of shell thickness is possible by controlling experimental parameters, this leads to controllable optical properties. Surface enhancement of the resonance Raman signal can be used for chemical mapping of the material. The polymerization reaction happens through a surface mediated path. A linear chain is obtained which covers the metal surface completely. The core is well protected and cyanide does not leach out of the core at reduced concentrations. The material has been synthesized in gram quantities.

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