

Synthesis and characterization of fatty acids passivated silver nanoparticles—their interaction with PPy

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Abstract

Metal nanoparticles have applications in the area of catalysis, opto-electronics due to their size dependent optical, electrical and electronic properties. It is believed that when the size of the particle tuned to one nanometer, the quantum effect is expected in their optical properties. Silver nanoparticles exhibit size dependant absorptions in the UV–vis region and also show anti-bacterial properties. In the present paper, we report the synthesis of silver nanoparticles passivated by stearic, palmitic and lauric acids. Three reducing agents, which are moderate strong to mild, formaldehyde, dimethyl formamide and triethanol amine are used to synthesize the nanoparticles as solids. The solids are redispersible in non-polar solvents. The IR spectra showed the existence of adsorbed fatty acids. It is shown that the stability of the silver nanoparticles in toluene solvent is decreased when the chain length of the fatty acid is decreased. The toluene solution of these nanoparticles exhibited a surface plasmon resonance in the range 420–462 nm. Results showed that use of triethanol amine is the best choice in obtaining lower particle sizes. The nanoparticles are characterized by UV–vis, FTIR, XRD and AFM techniques. The interaction of these particles with the conducting polymer PPy is explored. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Fine metal particles have applications in the area of catalysis, opto-electronics due to their size dependent optical, electrical and electronic properties [1–3]. It is believed that when the size of the particle tuned to 1 nm, the quantum effect is expected in their optical properties. Silver nanoparticles are interesting class of materials that exhibit size dependant absorptions in the UV–vis region due to the surface plasmon resonance (SPR). Silver nanoparticles also exhibit anti-bacterial properties and are used as sterilizers for household articles and for purification of drinking water. Long chained molecules such as stearic acid, lauryl amine are used as stabilizers, which adsorb on the surface (passivation) of the as formed nanoparticle and prevent aggregation. The passivated nanoparticles are stable under normal conditions as solution, films and dry powders. The powders can be redispersible in non-polar solvents. Various reducing agents such as H₂, NaBH₄, N₂H₄, NH₂OH, (CH₃)₂NH·BH₃, ethanol,

ethylene glycols, Tollen's reagent, and ascorbic acids are used to effect the reductions for the syntheses of the noble metal nanoparticles [4–14].

In the present paper, we report the synthesis of silver nanoparticles passivated by stearic, palmitic and lauric acids. Various reducing agents, which are moderately strong to mild, such as formaldehyde (FA), dimethylformamide (DMF) and triethanolamine (TEA) are used. In most of the cases redispersible solids were obtained. The synthesis, characterization by XRD, AFM and UV–vis studies is discussed here.

2. Experimental

All the chemicals used were of analytical grade. Silver salts of stearic acid, palmitic acid and lauric acids were freshly prepared from their respective sodium salts and silver nitrate just before the reduction. All the experiments were conducted in a well-equipped hood. XRD experiments were carried out on Joel JDX-8030 instrument. UV–vis spectra were recorded on CARRY 50 SCAN UV–vis–NIR spectrophotometer.

In a typical reaction, finely ground silver stearate (0.5 g, 1.27 mM) was poured into 20 ml of (37% w/v) of formaldehyde

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(FA) and slowly heated up to 70–80 °C while stirring within 30 min. Heating is continued for 30 more minutes by which time the white silver stearate powder slowly turned into brown tiny lumps. At this juncture, 50 ml of toluene was added to the mixture while gentle stirring is maintained for another 15 min. The boiling brown toluene layer containing silver nanoparticles is quickly filtered through Whatman filter paper no. 42 to remove any small-unreacted lumps of silver stearate. Any remaining amount of formaldehyde is discarded by separating funnel. Toluene solvent is removed at room temperature and the brown free flowing product is desiccated. Yield is 0.200 g. These solids are re-dispersible in non-polar solvents like toluene, benzene and hexane. Similar synthetic procedure is adopted in experiments where DMF (20 ml) and triethanol amine (TEA) (10 ml) were used as reducing agents.

3. Results and discussion

3.1.1. Synthesis of nanoparticles

Three types of reducing agents, namely, formaldehyde, dimethylformamide and triethanolamine are used to prepare silver nanoparticles. When formaldehyde is used as reducing agent silver nanoparticles are readily formed from silver stearate. This readiness of formation of nanoparticles is progressively decreased from stearate to palmate to laurate. Only gray-black elemental silver is instantly formed as soon as the silver laurate is added into formaldehyde solution. This means that when the nanoparticles are formed laurate could not able to stabilize the particles by adsorption on the surface. This is due to the shorter organic chain length of lauric acid.

Highly homogeneous and light brown toluene layers were obtained from Ag–STA, Ag–PALM and Ag–LAU when triethanolamine was used as reducing agent. In this case, free flowing powders of nanoparticles were obtained after several careful washings with acetone. The stability of the toluene solutions obtained by TEA is highest up to several months. The toluene solutions of nanoparticles obtained by formaldehyde is up to few weeks and is few hours for DMF reduced nanoparticles. FT-IR spectra of the samples exhibited bands due to adsorbed fatty acids (Fig. 1). The carbonyl stretch at 1655 cm⁻¹ in the unreduced salt of Ag⁺STA⁻ is shifted to 1699 cm⁻¹ on reduction. Similarly the 1560 and 1413 cm⁻¹ bands due to carboxylate ion and methylene stretchings in unreduced salt are seen at 1540 and 1420 cm⁻¹ for nanoparticles.

3.1.2. The mechanism of reduction

Several routes are proposed for the oxidation of DMF, which is usually accompanied by evolution of H₂ or CO₂ [15,16]. However, during the synthesis of nanoparticles we did not observe any gas evolution suggesting that the reduction mechanism involved is

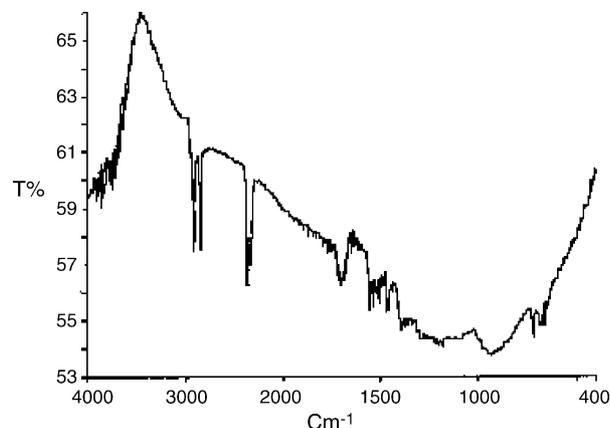
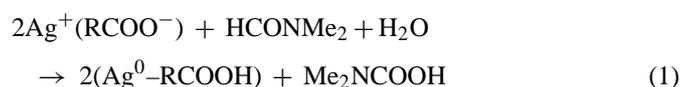
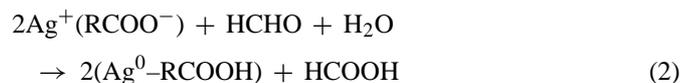
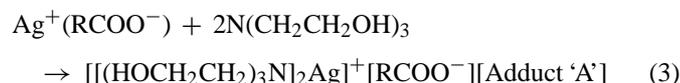


Fig. 1. FT-IR spectrum of stearic acid stabilized silver nano particles.

The reaction proceeds at a temperature range of 60–80 °C and care must be taken to quench the reaction as soon as all the white silver stearate turned into dark brown material which are quickly phase transferred into toluene layers by gentle stirring. When DMF is used as reducing agent, nanoparticles are formed for stearic acid only while they are not formed when palmate and laurate are used as stabilizers. The mechanism for formaldehyde reduction is straightforward and can be written as



When triethanolamine amine used as reducing agent different mechanism seems to operate. First, triethanolamine is expected to form an adduct with RCOOAg, at lower temperatures. It is expected that [17] silver nanoparticles are formed from this 1:2 adduct 'A' on thermal decomposition.



3.1.3. UV-visible spectra and atomic force microscopy

In general bare silver nanoparticles exhibit surface plasmon resonance at 380–400 nm [18]. This shifts to higher wavelength when the size of the nanoparticles increases. In the present systems, we observed a band in the range 420–462 nm suggesting larger size nanoparticles (Table 1). A representative UV-vis spectrum is shown in Fig. 2 for Ag–stearic acid system reduced by triethanolamine (Ag–STA/TEA). From the λ_{max} values it is expected that the size of the nanoparticles decreases from Ag–STA/DMF > Ag–PAL/FA > Ag–STA/FA > Ag–STA/TEA.

Table 1
Plasmon resonance absorptions of silver nanoparticles in toluene

System	λ_{max} (nm)
(1) Ag–STA/TEA	420
(2) Ag–STA/FA	424
(3) Ag–PAL/FA	434
(4) Ag–STA/DMF	462

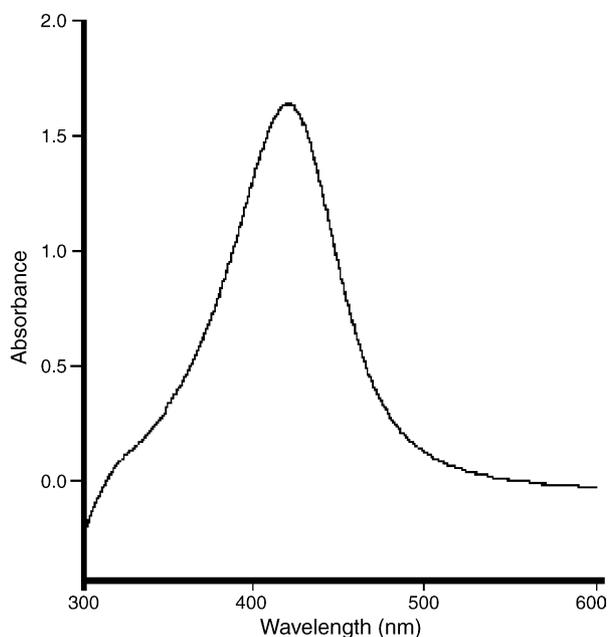


Fig. 2. UV-vis spectrum of silver nanoparticles of Ag-STA/TEA in toluene.

XRD analysis on the sample Ag-STA/TEA showed a broad pattern (Fig. 3). The peak positions can be assigned to that of an FCC silver. The peaks are substantially broadened indicating that the material is composed of very small particles. The peaks are assigned to (1 1 1), (2 0 0), (2 2 0) and (3 1 1). The portion labelled 'A' arises from the substrate base material. The size of the particle calculated from FWHM of (1 1 1) peak using Scherer formula is about 24 nm. The particle size of the sample Ag-STA/FA is analysed by atomic force microscopy. Fig. 4 shows mapping of a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area on the surface of thin film of nanoparticles, obtained by drop casting on a glass slide. Essentially, it consists of evenly distributed spherical silver particles. The size of the particle is around 200 nm. This is quite large size compared to TEA reduced system. The higher λ_{max} value of 462 nm for Ag-STA/DMF suggests still higher particle sizes compared to Ag-STA and Ag-PAL reduced

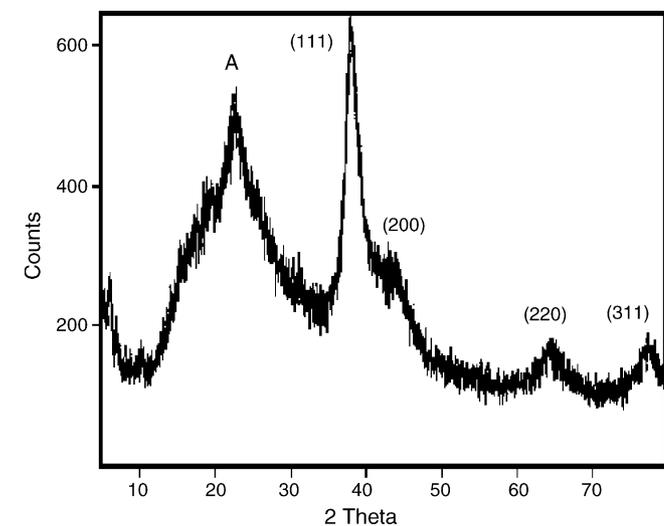


Fig. 3. XRD pattern obtained for Ag-STA/TEA system.

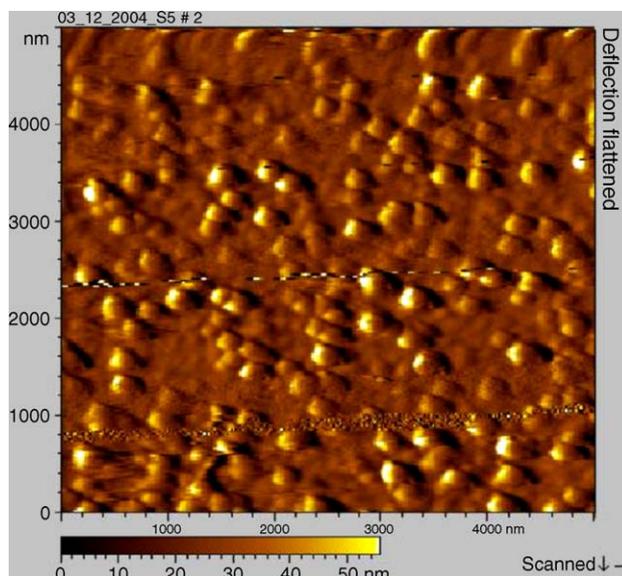


Fig. 4. AFM of Ag-STA/FA system showing the structure of nanoparticle.

by formaldehyde. Thus, on comparison, TEA is effective in achieving lower particle sizes due to formation of an adduct 'A' in the intermediate reduction step (Eq. (3)). The size of the particles is dependent on the type of reducing agent. It is found that, for the concentrations and temperatures used in this study, the size of the particles increases in the order, triethanolamine > formaldehyde > dimethylformamide and the particle size distribution is quite uniform (Fig. 4).

3.1.4. Interaction of silver nanoparticles with polypyrrole

Some interesting observations are made in reactions of silver nanoparticles with polypyrrole. When a $10\text{-}\mu\text{m}$ thick film of PPy-BF₄ (undoped film, deposited on stain less steel electrode, $2\ \text{cm} \times 5\ \text{cm}$) is dipped into toluene-nanoparticle solution (obtained by reducing 0.2 g of silver stearate with TEA and dispersed in 40 ml of toluene), the brown-yellow solution turned colourless within 5 min. All silver particles migrated on to the surface of the polymer film. The surface conductivity of the film

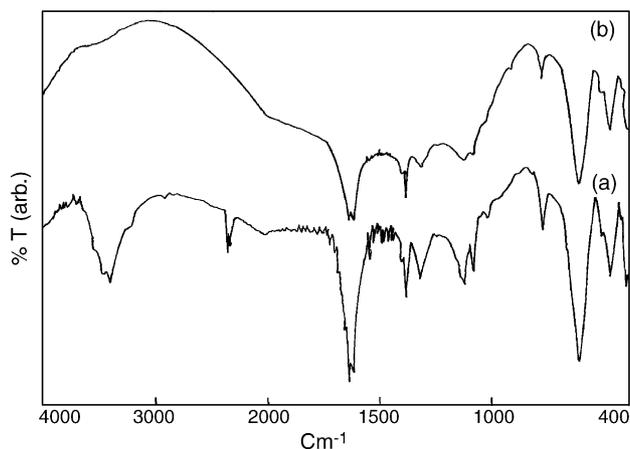


Fig. 5. FT-IR spectra of Ppy without (a) and with (b) silver nanoparticles.

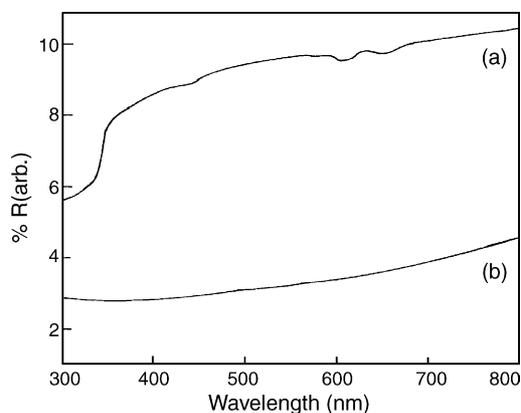


Fig. 6. UV-vis spectra of PPY film before (a) and after (b) treatment with silver nanoparticles.

increased by one order of magnitude. Fig. 5 shows the changes in FT-IR spectra of the PPy powder before (a) and after (b) treatment of silver nanoparticles. It is clear that the intensity of -NH- stretching vibration at 3240 cm^{-1} is considerably decreased due to the interaction of these groups with silver particles. This surface modification of Ppy film by silver is also reflected in UV-vis spectrum. Fig. 6 exhibits the changes in UV-vis absorption of the Ppy- BF_4 polymer films before (a) and after (b) treatment with silver nanoparticles. Thus FT-IR and UV-vis spectra provide clear evidence for $\text{-NH}\cdots\text{Ag}$ interactions in the polymer chains.

As the -NH- groups of the polymer are always positioned out side of the polymer back bone and facing the electrolyte side [19], it is believed that the nanoparticles are migrated on to the -NH- groups of the polymer and are possibly stabilized by the lone pairs of the hetero atoms. The uptake of the silver nano

particles is similar to palladium nanoparticles migration [20] on to the PPy film. However, it is to be noted that application of cathodic current is not necessary for incorporation of silver in contrast to palladium migration. This suggests existence of strong interactions between nano silver particles and polymer. Further investigations are in progress to explore the utility of these composite films in EMI shielding in marine environments and for other applications

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