

Water-solubilized aminoclay–metal nanoparticle composites and their novel properties

K. K. R. Datta, M. Eswaramoorthy and C. N. R. Rao*

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Nanoparticles of metals such as Au, Ag, Pd and Pt embedded in exfoliated sheets of aminoclays of the type $R_8Si_8Mg_6O_{16}(OH)_4$, where $R = CH_2CH_2NH_2$ are entirely water soluble. These sheets of the composite come to the organic-aqueous interface on addition of alkane thiols to the aqueous layer.

Extensive research on metal nanoparticles carried out in the last few years has been partly driven by potential applications in areas such as catalysis^{1,2} and sensors.^{3,4} Functionalization, solubilization and assembly of metal nanoparticles have been investigated by employing a variety of methods, wherein capping agents like thiols,⁵ polymers,^{6–8} surfactants,⁹ amine–borane complexes,¹⁰ and dendrimers,¹¹ have been employed. Metal nanoparticles have also been incorporated in inorganic hosts such as zeolites,¹² and clays.¹³ Such composites are however not soluble in organic or aqueous media. We have been interested in exploring the synthesis and properties of clay–metal nanoparticle composites which are readily soluble in aqueous media. For this purpose, we have employed Mg-phylo(organo)silicates containing pendant amino groups. These aminoclays have a structure analogous to 2 : 1 trioctahedral smectites, such as talc, but are covalently linked with the approximate composition $R_8Si_8Mg_6O_{16}(OH)_4$, where $R = CH_2CH_2NH_2$. The structure is made up of octahedrally coordinated brucite layers sandwiched between tetrahedral organosilicate networks.¹⁴

In the present study the property of the aminoclays wherein protonation of the amino groups in water is accompanied by exfoliation has been exploited.¹⁵ Thus metal nanoparticle composites formed by the exfoliated aminoclay sheets by carrying out the reduction of metal precursors in the presence of the clay have been investigated. Besides being entirely water soluble, the exfoliated sheets of aminoclay–Au nanoparticle composites move to the organic/aqueous interface in the presence of an alkanethiol.

The aminoclay was prepared by the method reported in the literature.¹⁶ Typically, an aminopropyl-functionalized magnesium (organo)phyllosilicate clay was prepared at room temperature by dropwise addition of 3-aminopropyltriethoxysilane (1.3 mL, 5.85 mmol) to an ethanolic solution of magnesium chloride (0.84 g, 3.62 mmol) in ethanol (20 g). The white slurry obtained after 5 min was stirred overnight and the precipitate isolated by centrifugation, washed with ethanol (50 mL) and dried at 40 °C. $H AuCl_4$, $AgNO_3$, H_2PtCl_6 and $PdCl_2$ were used as metal precursors for Au, Ag, Pt and Pd respectively. The composites were prepared in the following manner. The aminoclay was first exfoliated by dispersing 20 mg of clay in 2 mL of millipore water by sonication for

2 minutes. To this transparent clay suspension, 2 mL of 1 mM metal precursor solution was added followed by the addition of 2 mL of 0.1 M of $NaBH_4$ solution. In the case of Ag nanoparticles, the aminoclay was prepared using $Mg(NO_3)_2$ as the Mg source to avoid precipitation of $AgCl$. The transparent suspension obtained after the reduction of the metal salt by $NaBH_4$ was characterized by UV-visible spectroscopy and transmission electron microscopy (TEM). For TEM analysis, the aqueous clay suspension was first precipitated by the addition of ethanol and redispersed in ethanol by sonication before drop casting on a carbon-coated copper grid.

In the absence of the aminoclay, very large metal particles were obtained which settled within a short time.

In-situ synthesis of the clay stabilized Au nanoparticles was also carried out by dissolving 1.68 g of $MgCl_2 \cdot 6H_2O$ (8.26 mmol) in 20 mL of 3.8 mM solution of $H AuCl_4$ followed by the addition of 2 mL of 3-aminopropyltrimethoxysilane. The yellow slurry obtained was stirred overnight at room temperature and then kept at 75 °C for 24 h. It slowly turned pink in colour due to the formation of gold nanoparticles by thermal reduction. The pink transparent film obtained was washed with ethanol and then dried again.

The X-ray diffraction (XRD) pattern of the as-synthesized aminoclay shows a low-angle reflection with a d_{001} spacing of 1.4 nm corresponding to the bilayer arrangement of propylamino groups (Fig. 1a). The broad in-plane reflections at higher angles ($d_{020,110} = 0.41$ nm, $d_{130,200} = 0.238$ nm) and the characteristic (060) reflection at 0.156 nm confirm the formation of 2 : 1 trioctahedral Mg-phyllsilicate clay with talc-like structure. The XRD pattern

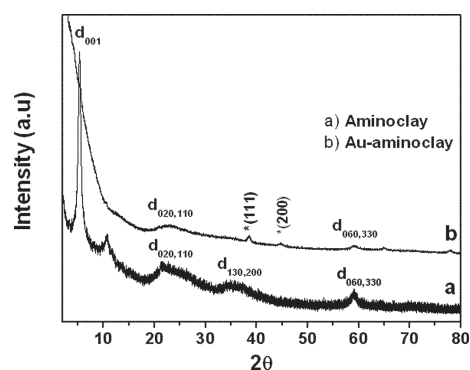


Fig. 1 X-Ray diffraction patterns of the (a) as-synthesized aminoclay and (b) the Au-aminoclay composite. Pattern (a) shows a low-angle reflection with a d_{001} spacing of 1.4 nm corresponding to the bilayer arrangement of propylamino groups. * indicates the peaks corresponding to Au nanoparticles.

Chemistry and Physics of Materials Unit and DST Unit on Nanoscience, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064, India. E-mail: cnrao@jncasr.ac.in; Fax: +91-080-22082760

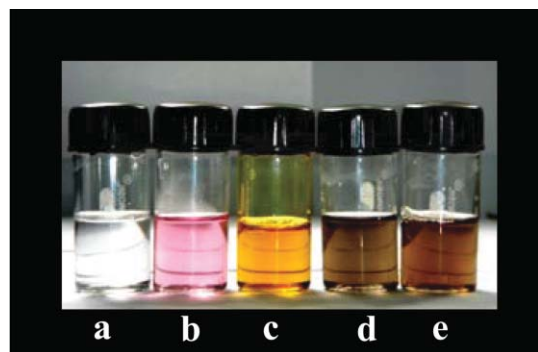


Fig. 2 Optical images of aminoclay–metal nanoparticle composites forming clear transparent solutions in water: (a) aminoclay solution, and aminoclay with (b) Au, (c) Ag, (d) Pt and (e) Pd nanoparticles.

of the metal nanoparticle–clay composite did not show the low angle peak demonstrating that exfoliation had occurred, Fig. 1(b).

Fig. 2 shows how the aminoclay–metal nanoparticle composites form clear transparent solutions in water. The solutions are pink and yellow for Au and Ag respectively and dark brown in the cases of both Pt and Pd. The reddish-brown colour observed for Au–clay nanoparticle composites immediately after the addition of NaBH_4 changed to pink with time. The solutions exhibit characteristic plasmon bands for the Au– and Ag–clay suspensions at 520 nm and 410 nm respectively as shown in Fig. 3. In the cases of Pt and Pd, the characteristic absorption band for the precursors around 260 to 280 nm was absent thereby confirming the formation of Pt and Pd nanoparticles.^{17,18} TEM images of the aminoclay–metal nanoparticle composites deposited on a carbon coated copper grid are shown in Fig. 4. The histograms show the average particle sizes to be around 3.5 and 5 nm respectively in the cases of Au and Ag nanoparticles. We could see the layered arrangements in the cases of Pt and Pd with the interspacing of 1.5 nm commensurate with the bilayer arrangement of aminoclays (see top right inset of Fig. 4b).

The aminoclay–Au nanoparticle composite was also prepared by an *in-situ* procedure, wherein the reduction was carried out thermally without the use of NaBH_4 . The clay composite so prepared also dissolves in water and shows the characteristic plasmon band at 530 nm.

The effect of addition of hexadecanethiol to an aqueous solution of the aminoclay–Au nanoparticle composite was examined and the result is shown in Fig. 5a. Immediately after the addition, the alkanethiol forms a clear nonaqueous layer on top of the pink

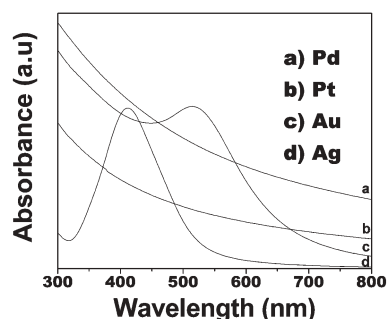


Fig. 3 UV-Vis absorption spectra of Pd, Pt, Au, Ag nanoparticles.

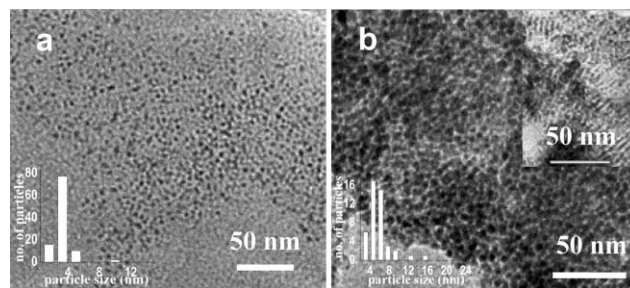


Fig. 4 TEM images of (a) Au–clay nanoparticle composites. Inset: histogram of Au nanoparticles; (b) Ag–clay nanoparticles composite. Insets (bottom left) histogram of Ag nanoparticles; (top right) Pt nanoparticles show layered arrangement.

aqueous layer. After several hours, the thiol interacts with Au nanoparticles embedded in the aminoclay and brings the sheets of composite to the aqueous/organic interface as seen in Fig. 5a(ii). This happens because the binding of metal particles to the aminoclay is very strong and the thiol is unable to dislodge it by forming metal–sulfur bonds. It is interesting that all the aminoclay appears at the interface. The presence of all the exfoliated aminoclay at the interface was confirmed by ensuring the absence of any clay in the aqueous layer. Replacing hexadecanethiol by other organic solvents such as benzene or toluene still retains the composite particles at the interface. We show the process of formation of the clay–Au nanoparticle composite schematically in Fig. 5b. This process occurs with all metal nanoparticles studied, but more effectively in the cases of Ag and Au.

In conclusion, exfoliated sheets of Mg-phyll(o)rganosilicates containing pendant amino groups have been used to stabilize Au, Ag, Pd and Pt nanoparticles. The nanoparticle-decorated clay sheets can be easily dispersed in water. These metal nanoparticles

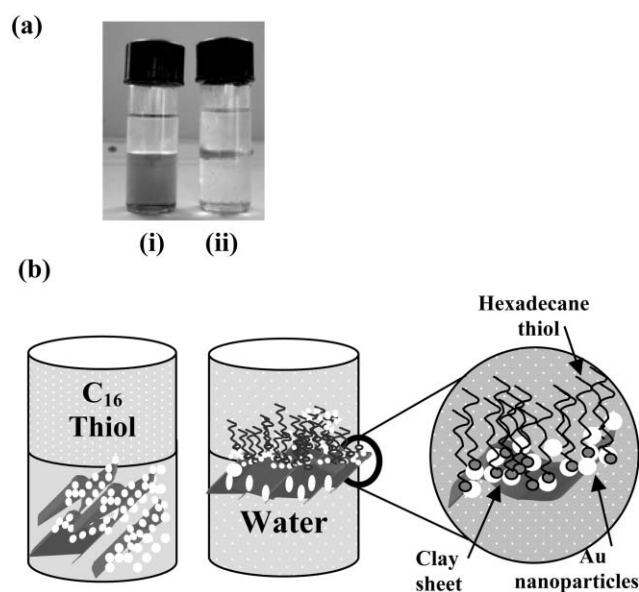


Fig. 5 (a) Optical image of aqueous Au–clay composite on addition of hexadecanethiol (i) at the time of addition (the top transparent layer is the thiol phase and the bottom layer seen as black is the aqueous phase); (ii) after 14 days the composite is at the interface (see dark ring at interface). (b) Schematic diagram of the process.

can be used to lift the clay sheets to the oil/water interface with the help of an alkanethiol. In many biphasic reactions, such as the biocatalytic transformations of steroids and epoxides, transport limitations can be overcome by carrying out reactions at the aqueous/organic interface.¹⁹ Since clays are good hosts for proteins and enzymes, stabilizing them at the oil/water interface could be useful for carrying out biphasic reactions. Although we have worked here with a family of aminoclays, other suitably functionalized clays may also exhibit similar properties.

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