Chapter 2

SYNTHESIS OF METAL NANOPARTICLE DISPERSERED LAYERED SOLID: Mg/Al LAYERED DOUBLE HYDROXIDE-Pt NANOPARTICLE COMPOSITE BY DELAMINATION-RESTACKING

ABSTRACT

In this chapter, we report a general method to synthesize noble metal nanoparticle dispersed in LDH matrix. The composite is synthesized starting from delaminated LDH layers in 1-butanol and a dispersion of preformed oleylamine capped platinum nanoparticles. The delaminated layers were restacked in the presence of platinum nanoparticles to give the composite. The method can be used as a general route for the synthesis of layered solid–nanoparticle composites of varying compositions and properties.
2.1. Introduction

Metal nanoparticle supported layered solids are gaining immense attention for their applications as catalysts [1-3], optically tunable materials [4], energy conversion devices [5], sensors [6-7], and photocatalysts [8]. Layered solid–nanoparticle composites are generally prepared by impregnation [9], co-precipitation [10], ion-exchange [11] and sonochemical [12] methods. The composites prepared by the conventional wet impregnation method are not fully reproducible and gives rise to inhomogeneous distribution of the metal nanoparticles on the surface [9], while composites prepared by co-precipitation in the presence of the noble metals showed phase segregation on heating and the size of the metal particles formed was large [10]. A few composites prepared by growing nanoparticles in the interlayers of the supporting materials show uncontrolled particle growth and inhomogeneous distribution of the nanoparticles [13, 14]. An alternate and more effective way of synthesizing layered solid–nanoparticle composites is by delamination of layered solid to obtain monolayer colloidal dispersion followed by restacking the layers in the presence of nanoparticles. Nanocomposites have been prepared using monodispersed capped nanoparticles and delaminated layered solids [15]. The resulting composites show properties different from their parent solids, owing to synergistic effects between the layered solid and the nanoparticles. The improved properties result due to the fact that the components are now mixed at the level of the individual layers allowing even distribution of nanoparticles in the nanocomposite. Our group has developed a method that involves the restacking of the delaminated colloidal dispersion of organically modified layered double hydroxide (LDH) in the presence of preformed, monodispersed capped-CdSe nanoparticles in 1-butanol to get nanoparticle–LDH composites [16].

The method of synthesis, size, and the distribution of the nanoparticles in a matrix plays an important role in the stability and activity of the catalyst [16, 17].
The activity is high for smaller sized particles due to large surface area corresponding to more number of active sites [18]. Use of capping agents is one of the methods employed to stabilize the nanoparticles [19]. Distribution of nanoparticles on supports is believed to further stabilize the nanoparticles [20].

LDHs are anionic clays with positively charged metal hydroxide layers and charge compensating interlayer anions of the general formula, \([M_{1-x}^{2+}M'_x^{3+}(OH)_2]^{x+n}A^{n}\) \((M = Mg, Co, Ni; M' = Al, Cr, Fe; 0.2 \leq x \leq 0.33; A^{n} = \text{anion with charge ‘n’})\) [21]. LDHs are used as solid-base catalysts [19], catalyst supports [20] and precursors to catalysts [21]. LDH–metal composite catalysts are multifunctional materials with metal, acidic and basic sites [22].

In this work, we report the synthesis of Pt nanoparticles intercalated Mg, Al LDH composite by delamination–restacking method.

2.2. Experimental

\(\text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, \text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}, \text{sodium dodecyl sulphate (SDS), 25\% ammonia solution (specific gravity = 0.91), toluene, methanol, oleic acid, NaBH}_4\) and acetone were obtained from Merck India Pvt. Ltd. \(\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}\) and oleylamine were procured from Ranchem India Pvt. Ltd. and Sigma Aldrich respectively. All solutions were prepared using Type-II water (specific resistance 15 M\(\Omega\) cm, Millipore™ Elix-3 water purification system) and dissolved \(\text{CO}_2\) was expelled by boiling the water for 10 minutes.

2.2.1. Preparation of DS intercalated Mg,Al LDH (Mg/Al–DS LDH)

Dodecyl sulphate intercalated LDH, \(\text{Mg}_2\text{Al(OH)}_6\text{DS-2H}_2\text{O}\) (hereafter referred to as Mg/Al–DS LDH) was prepared by coprecipitation. In a typical experiment, metal nitrate mixture of \(\text{Mg}^{2+}\) and \(\text{Al}^{3+}\) with a molar ratio of 2:1 was
added drop wise into 50 ml of 1M ammonia solution which contains 6 times excess of the stoichiometric amount of SDS with continuous stirring. The slurry was aged for 18 h at 65 °C in an air oven. The solid was washed free of ions with hot decarbonated water 6–7 times, twice with acetone and dried at 65 °C overnight.

2.2.2. Preparation of oleylamine capped platinum nanoparticles (OA-capped Pt-nps)

OA-capped Pt-nps were prepared by a literature method with slight modifications [26]. A mixture of 500 mg of H₂PtCl₆·6H₂O, 660 ml toluene, 5 ml oleic acid was refluxed for 6 h and left undisturbed for 16 h. A solution containing 192 mg of NaBH₄ in 40 ml of methanol was added drop wise to the reaction mixture. The mixture was allowed to stand at room temperature for 1 h. Additional 20 mg of NaBH₄ was added directly to the reaction mixture and the mixture was left undisturbed overnight. The brownish-black solid formed was separated by centrifugation, washed with acetone (3–4 times) and dried in air at 65 °C.

2.2.3. Preparation of oleylamine Pt nanoparticles–Mg/Al-DS LDH (Pt np–Mg/Al-DS LDH) composite

100 mg of Mg/Al-DS LDH was delaminated in 150 ml of 1-butanol by sonicating (35 kHz) at 70 °C for 2 h. Simultaneously, 10 mg of OA-capped Pt–nps were dispersed in 50 ml of 1-butanol by sonication at 70 °C for 30 min. The two dispersions were mixed and sonicated for 1 h. The solvent form the mixture was then evaporated using a rotatory evaporator at 80 °C. The solid composite thus obtained was washed with acetone to remove remnant 1-butanol and was dried in an air oven at 65 °C.
2.3. Characterization

The powder x-ray diffraction (PXRD) patterns of the samples were recorded on a Philips X’Pert Pro diffractometer fitted with secondary graphite monochromator (Cukα radiation, λ=1.5418Å). The data was collected at the rate of 2° 20 per minute over the 20 range of 2 to 70°. Infrared spectra of the samples were collected using Nicolet IR200 FT-IR spectrometer (KBr pellet method, 4 cm⁻¹ resolution). The composite and the platinum nanoparticles were also characterized using Tecnai F30 transmission electron microscope (TEM) interfaced with energy dispersed X-ray spectroscopy (EDS). Samples for TEM were prepared by dispersing a small amount of the solid in about 10 ml of acetone by sonication, a drop of which was spotted on a carbon coated grid and dried at room temperature.

2.4. Results and Discussion

Figure 2.1a shows the PXRD pattern of the as synthesized OA-capped Pt-nps in which the (111), (200) and (220) reflections of platinum are seen at 20 values of 40.1° (d=2.265 Å), 46.45° (d=1.962 Å) and 67.75° (d=1.1826 Å) respectively (ICSD Number 64917; face-centered cubic, space group: Fm3m) [27]. The average crystallite size of the OA-capped Pt-nps calculated using Scherrer’s equation was ~5.5 nm. Figure 2.1b shows the PXRD pattern of dodecyl sulphate anion (DS⁻) intercalated Mg/Al-LDH. The interlayer distance of Mg/Al-DS LDH (calculated from the first basal reflection) was found to be 23.9 Å indicating the presence of DS⁻ anion in the interlayer region of the LDH with the alkyl chains of the surfactant arranged parallel to the crystallographic c-axis [28]. In addition to the basal reflections, saw tooth-shaped reflections of the (10l) and (11l) planes are also seen at 20 value of ~34 and ~61° indicating turbostraticity in the layered solid [29]. The PXRD pattern of Pt-np-Mg/Al-DS LDH composite (Figure 2.1c) shows reflections due to both the LDH and Pt-nanoparticles (reflections due to platinum nanoparticles
are visible in the enlarged inset). The interlayer distance of the Pt-np-Mg/Al-DS LDH composite was found to be 27.6 Å. The increase in the interlayer distance of the composite when compared to the Mg/Al-DS LDH precursor is due to the incorporation of the Pt-nanoparticles into the interlayer region of the LDH [17].

Figure 2.1 PXRD patterns of OA-capped Pt-nps (a), Mg/Al-DS LDH (b) and Pt np-Mg/Al-DS LDH composite (c). Inset shows an enlarged portion of (c) from 2θ = 30 to 70 °. Reflections due to Pt-nanoparticles are marked with (*).
Figure 2.2 IR spectra of Mg/Al-DS LDH (a), OA-capped Pt-nps (b) and Pt np-Mg/Al-DS LDH composite (c)

Figure 2.2 shows the IR spectra of Mg/Al-DS LDH, OA-capped Pt-nps and Pt-np-Mg/Al-DS LDH composite. The IR spectrum of Mg/Al-DS LDH (Figure 2.2 a) shows bands due to the stretching and bending modes of hydrogen bonded –OH groups of the hydroxide slabs and the adsorbed and intercalated water molecules at ~3500 and ~1640 cm\(^{-1}\) respectively. Bands due to C–H stretching vibrations of the surfactant alkyl chains are seen at 2853, 2919 and 2950 cm\(^{-1}\) suggesting an all-trans conformation [30, 31] and a band due to S=O stretching vibrations at 1222 cm\(^{-1}\) of the sulphate polar head of the surfactant are also observed. The IR spectrum of the OA-capped Pt-nps shows bands due to N–H stretching and bending modes at 3435 and 1600 cm\(^{-1}\) respectively. The bands due to C–H stretching vibrations of the
oleylamine chain appear between 2829 and 2980 cm\(^{-1}\). The IR spectrum of the composite is identical to that of Mg/Al-DH LDH except for a slight broadening at around 3500 cm\(^{-1}\) caused due to the overlapping of the O–H and N–H stretching bands.

![Image](image1.png)

**Figure 2.3** Bright field TEM images of OA-capped Pt-nps (a) and Pt-np-Mg/Al-DH LDH composite (b). Corresponding SAED patterns are shown in (c) and (d).

Figure 2.3a and b show bright field TEM images of OA-capped Pt-nps and Pt np-Mg/Al-DH LDH composite respectively. The average size of the Pt-nanoparticles in Figure 2.3a was found be about 3 nm that is much lower than the values calculated using Scherrer’s expression. Figure 2.3b shows a uniform distribution of Pt-nps over the LDH matrix. The layered structure of the Mg/Al-LDH is clearly visible in the TEM image of the composite. Selected area electron dispersion (SAED) pattern of the platinum nanoparticles (Figure 2.3c) shows characteristic features of platinum
[32] while that of the composite (Figure 2.3d) shows spots due to platinum along with those due to Mg/Al LDH [33].

![Energy dispersive x-ray spectrum](image)

**Figure 2.4** Energy dispersive x-ray spectrum of Pt-np-Mg/Al-DS LDH composite.

Energy dispersive x-ray spectrum (EDS) of Pt-np-Mg/Al-DS LDH composite shown in Figure 2.4 confirms the presence of platinum, magnesium and aluminium in the composite. The peaks due to copper are due to the grid on which the sample was loaded.

**2.5. Conclusion**

A general route for the synthesis of noble metal nanoparticle intercalated layered solids is proposed taking the synthesis of Mg/Al-DS LDH supported Pt-nanoparticle composite as a specific example. The composite was prepared by restacking the delaminated Mg/Al-DS LDH in the presence of preformed oleylamine capped Pt-nanoparticles in 1-butanol. The delamination-restacking technique employed can be applied other layered solid–nanoparticle systems of various compositions.
References


