

Synthesis and surface modification of aluminum oxide nanoparticles

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Nano precursor of aluminum hydroxide was synthesized by direct precipitation from aluminum nitrate and sodium hydroxide in the presence of polyethylene glycol. Al₂O₃ nanoparticles (AON) were prepared by calcinations of the precursor at 850 °C for 10 h. Aluminum oxide nanoparticles with average diameter of about (23 nm) were modified with oleic acid (OA-AON) as coupling agent. Successful surface modification of nanoparticles allows them to form stable dispersions and prevents aggregation of the nanoparticles. Then dispersibility of surface modified nanoparticles was examined in some monomers with different levels of hydrophobicity, including methylmetacrylate (MMA) butylacrylate (BuA) and Styrene (ST) having low, medium high hydrophobicity, respectively. To examine their dispersibility, aluminum oxide were dispersed in mentioned monomers, then Al₂O₃ loaded monomers were allowed to stand at room temperature for 24 h and the precipitate part of nanoparticles was separated and the amount of stable particles in dispersion was determined. The morphology and structures of nanoparticles were characterized by FT-IR, UV/VIS, X-ray diffraction (XRD) and scanning electron microscopy (SEM). These characterizations confirmed grafting of coupling agent on the surface of aluminum oxide nanoparticles, and showed that the surface modification of nanoparticles has been carried out successfully, so that their surface is rendered more hydrophobic.

Key words: Aluminum oxide, Oleic acid, Surface modification, Dispersion.

Introduction

A wide usage of metal oxide nanoparticles and nano structured materials attracts many people to research for their controlled synthesis via new method. Because, special properties of metallic or metal oxide nanoparticles exhibited several potential application in electronics, optoelectronics, catalysis and thin film coatings [1-7]. In particular, alumina nanoparticles are expected to play important roles in a variety of relevant applications, and hence, the field has generated important contributions regarding the synthesis and processing of such particles [8-11].

Different synthesis methods have been devised, including sol-gel technique [12, 13], microemulsion synthesis, mechanochemical processing [14], spray pyrolysis and drying [15], thermal decomposition of organic precursor [16], RF plasma synthesis [17], supercritical-water processing [18], self-assembling [19], hydrothermal processing [20, 21], vapor transport process [22], sonochemical or microwave-assisted synthesis [23, 24], direct precipitation [25] and homogeneous precipitation [26, 27]. However, a disadvantage to fabrication of nanodevices is the agglomeration of nanoparticles,

because of their high surface energy. To prevent the aggregation nanoparticles, the surface modification of nanoparticle can ensure their perfect dispersion. Many studies have been carried out toward the organically. Nanoparticles to enhance the surface chemical and physical properties plays the key for their successful applications [28].

Nowadays, polymer modification on inorganic particles has become a more interesting method to improve their dispersibility and compatibility in organic and or polymer composite [30]. The intercalation of guest species in crystalline layered host matrices is considered to be a versatile synthetic method for the synthesis of nanostructured hybrid materials [31, 32].

Carboxylate ligands, especially fatty acids, are often used for modifying metal oxide nanoparticles [33, 34].

The purpose of this work is to synthesize nano size aluminum oxide. In practice, these nanoparticles should to be dispersed homogeneously. To open the doors for application of aluminum oxide nanoparticles, their surface was modified by oleic acid to make them compatible with any organic media.

Experimental

Materials

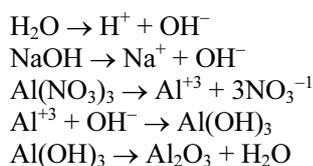
All starting materials and solvents were purchased from Merck and were used without further purification. The synthetic reactions and work-up were done in open air.

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Synthesis of nanoparticles

In a typical experimental procedure, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (9.38 g, 0.025 mol) was dissolved in distilled water to form a 0.5 M solution. The precursor solution obtained (8 ml) was added to a 100 ml conical flask containing mixed solutions of 50 ml distilled water, 3.5 ml NaOH 5 M and 2 g of PEG6000, were blended well by stirring for 15 minutes subsequently, the mixed solution was placed for 5 days at room temperature. The white crystalline products were collected by centrifugation, washed with distilled water and ethanol several times and dried, then calcinated at 850 °C for 10 h.

The formation reactions are as follows:



General procedure for the surface modification of Al_2O_3 nano-particles

For the surface modification of Al_2O_3 nano-particles with Oleic acid, different Volume amounts of Oleic acid (5-30, %wt) were used. Typically, Oleic acid (0.375 ml) was dissolved in 12.5 ml *o*-xylene to reach the concentration of 3%wt. Al_2O_3 nano particles (0.5 g) were then added to the above solution and allowed the reaction to perform for 1 h at 50 °C under stirring. Finally, the particles were collected by centrifugal separation and washed three times with toluene, then dried.

Instrument analysis

The products were characterized by wide-angle X-ray diffraction (WXR) patterns on a Rigaku D/max-2500 instrument with Cu K α radiation (40 kV, 100 mA).

The optical absorption was examined on a Perkin Elmer, lambda UV-Vis by dispersing Al_2O_3 powder in anhydrous alcohol and using anhydrous alcohol as the reference. IR spectra was obtained using KBr discs (4000, 500 cm^{-1}) on a Bruker tensor 27 FTIR spectrophotometer. The SEM images was made on analyzer (Hitachi, JAPAN. S4160).

Results and Discussion

Dispersion of Al_2O_3 nanoparticles

Al_2O_3 nano-particles can be stabilized via suspension in polar solvents, such as water; whereas, could not be suspended in a non-polar solvent, such as acrylic monomers. This finding proves that Al_2O_3 nanoparticles should have polar characteristic. However, Al_2O_3 nanoparticles modified by oleic acid were easily floated on the surface of water, and were permanently suspended in acrylic monomers (Fig. 1). This finding indicated that the polarity of nano sized Al_2O_3 powder

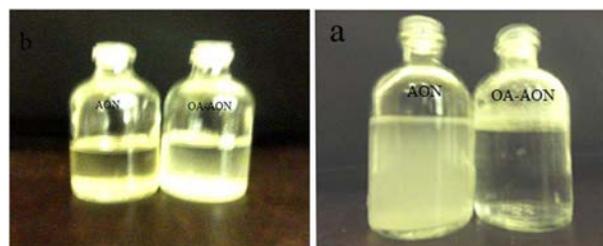


Fig. 1. Dispersion stability of Al_2O_3 nanoparticles modified with Oleic acid then dispersed in (a) water, (b) styrene.

was decreased and behaved as a non-polar material after the surface modification by a monomolecular layer of oleic acid.

In addition, the stability obviously increased in organic phase as shown in Fig. 1b in contrast, all of the aluminum oxide nanoparticles that modified by oleic acid floated totally on the water. Aluminum oxide nanoparticles that modified were dispersed well in the styrene organic layer, (Fig. 1b) indicating that they were lipophilic

Characteristics of Al_2O_3 nanoparticles

FT-IR spectra

Fig. 2 shows the FT-IR spectra of aluminum oxide nanoparticles before (AON) and after oleic acid modification (OA_AON). Comparing the spectra of AON (Fig. 2a) with that of OA_AON (Fig. 2b), the stretching vibrations bands for hydroxyl group in AON and OA-AON are observed at 3444 cm^{-1} and ~ 3451 cm^{-1} , respectively and the bending vibrations of the hydroxyl group of AON and OA-AON are observed at 1635 cm^{-1} and 1629 cm^{-1} , respectively. The stretching vibrations of AlO both in AON and OA-AON are observed at ~ 570 cm^{-1} and ~ 823 cm^{-1} [35]. However, peaks at ~ 2928 cm^{-1} , ~ 2858 cm^{-1} and at ~ 1610 cm^{-1} in OA-AON are attributed to the asymmetric, symmetric stretching vibrations of $-\text{CH}_2$ group and stretching vibrations of COO-Al, respectively, implying that the oleic acid in OA-AON.

XRD patterns

To investigate the influence of Oleic acid on the crystalline structure of Al_2O_3 nanoparticles, X-ray diffraction patterns of the particles before (AON) and after the modification process (OA-AON) are recorded (Fig. 3). All peaks from Fig 3a can be well indexed to the aluminum oxide nanoparticles. It is obviously seen that all diffraction peaks can be indexed very well as the standard data (29-0063). The obtained XRD patterns in Fig. 3b illustrated that after modification, the characteristic peaks have been broadened and weakened in intensity, suggesting that oleic acid grafted on the lattice plane of AON nanoparticles from all direction.

It is clear that the spectra OA-AON are almost the

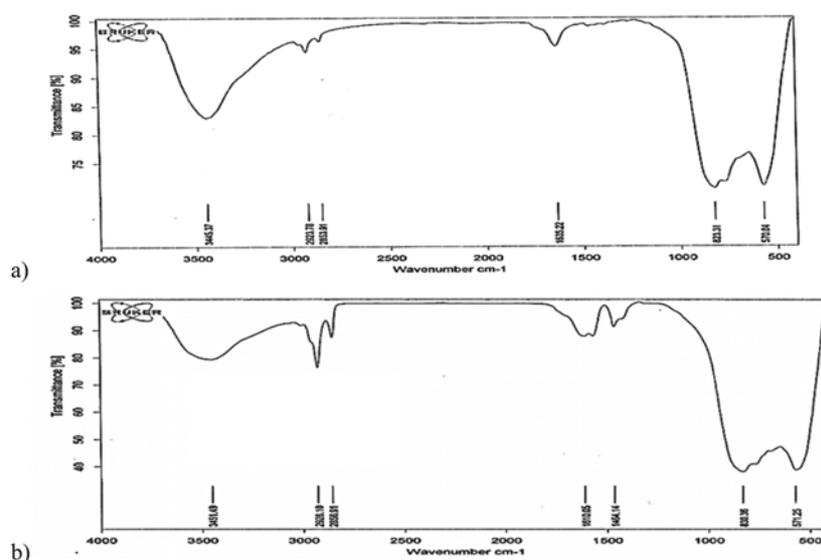


Fig. 2. FT-IR spectra of (a) Al₂O₃ nanoparticles (AON) (b) modification of Al₂O₃ nanoparticles (OA-AON).

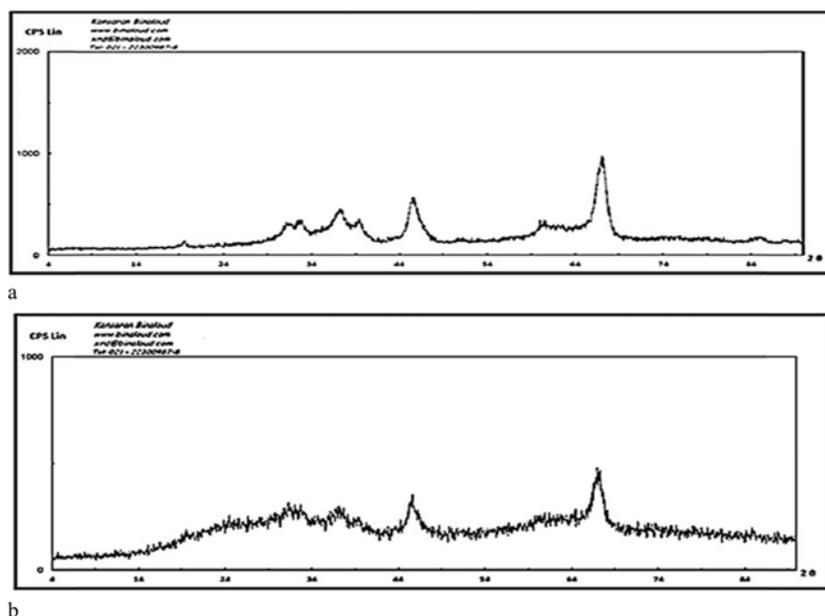


Fig. 3. X-ray powder diffraction patterns (a) AON (b) OA-AON.

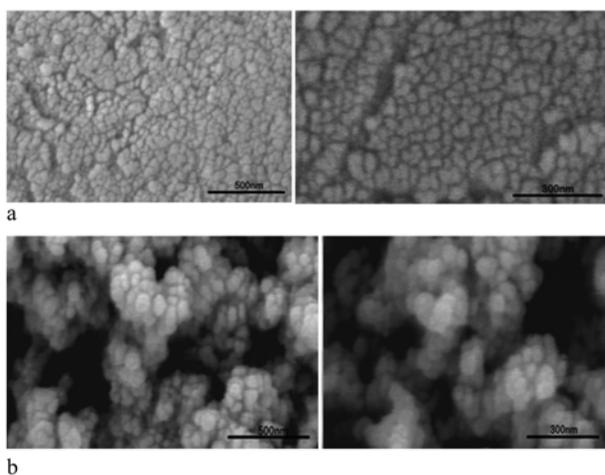


Fig. 4. SEM images of (a) AON (b) OA-AON.

same as those of AON, implying that the modification has not altered the crystalline structure of the Al₂O₃ nanoparticles.

SEM images

The scanning electron micrographs (SEM) of AON and OA-AON are shown in Fig. 4. Fig. 4a shows that most of the bare Al₂O₃ nanoparticles are quasi-spherical and their average diameter is about 10 nm. The SEM images of the Al₂O₃ nanoparticles and the oleic acid-capped Al₂O₃ nanoparticles are shown in Fig. 4b. The SEM images confirmed that the morphology of the oleic acid-capped Al₂O₃ nanoparticles is close to that of the unmodified Al₂O₃ nanoparticles. It is confirmed that the morphology of the nanoparticles before and after modified is close to that of the Al₂O₃

nanoparticles.

It is obviously seen that the Al₂O₃ nanoparticles smaller than surface modification Al₂O₃ nanoparticles particles. This is a directly evidence that the successfully grafted oleic acid on surface of Al₂O₃ nanoparticles.

Conclusions

Al₂O₃ nanoparticles were successfully synthesized with the mean size of 15 nm with a simple method and low cost and high purity.

The obtained results showed that it is possible to modify the surface of Al₂O₃ nanoparticles with oleic acid. The oleic acid-capped Al₂O₃ nanoparticles were obtained by the reaction between -OH group on the nanoparticles and -COOH of the oleic acid. FT-IR results confirm that an organic layer exists and the linkage between inorganic nuclei and organic layer is chemical bond. The surface modified nanoparticles are able to be dispersed in organic media such as acrylic and styrene monomers polymerized on the nanoparticle surfaces via the double bond of oleic acid. Surface modification of Al₂O₃ nanoparticles render their surface more hydrophobic and make them compatible with organic media

Acknowledgments

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