

Organic-inorganic hybrid nanomaterials prepared from 4-formyl benzo-12-crown-4-ether and silica coated magnetite nanoparticles

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Abstract

Silica coated magnetite nanoparticles were covalent grafted with 3-aminopropyl trimethoxysilane to give APTSCMNPs. Reaction of the resulted nanomaterial with 4-formyl benzo-12-crown-4 ether afforded FB12C4/APTSMNPs nanocomposite material in which the crown ether moiety was attached through propyl chain spacer. Characterization of the prepared nanocomposite was performed with different physicochemical methods such as FT-IR spectroscopy, thermogravimetric analysis (TGA-DTA), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometry (VSM).

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1. Introduction

Organic-inorganic hybrid materials are of great importance and much effort has been devoted to prepare this type of materials [1-6]. Most of the works in this context have been focused on silica based materials. Silica presents attractive

properties such as adsorption capacity, acid/base chemistry and thermal stability which can be advantageously exploited for many applications. Moreover, the possibility of grafting with a variety of functional groups and high surface area make the silica valuable as support for various hybrid materials. The silica surface is being investigated

by many physicochemical techniques such as FT-IR and Raman spectroscopies, solid state NMR and electron microscopies and showed that consists of various kinds of silanol and siloxanes [7]. These groups are responsible for the chemical properties of the silica surface.

There are various methods for covalent attachment of organic groups to silica surface, such as chlorination of the silica surface followed by subsequent reaction with Grignard reagents to form silicon-carbon bond [4]. Grafting of organic groups through a trialkoxyorganosilane is another technique for functionalization of the surface of silica and several reviews have been published in this context [8-19]. Usually, organic group loading of 0.3-2 mmol per gram of the silica can be obtained. The resulted modified silica is sufficiently stable and can be further modified to give a variety of materials with different applications. Interests in application of nanosilica type materials have been increased due to the large surface to volume ratio and several works has been performed on their modification with various silylating reagents to give new hybrid nanomaterials with specific physicochemical properties [20-22]. However, the prepared nanosilica type materials suffer from difficulties in handling and filtration from reaction mixtures. Thus, in recent years, much attention has been devoted to new silica type materials i.e. silica coated magnetite nanoparticles (SCMNPs) [23-30]. These nanomaterials have superparamagnetic properties that allow them easily recovered from reaction mixtures.

Herein, we report preparation and characterization of a new organic-inorganic hybrid nanomaterial based on benzocrown ether supported silica coated magnetic nanoparticles. To the best of our knowledge there is no any work on the

immobilization of benzocrown ethers onto the surface of the silica type materials. The prepared material is predicted to have interesting properties as selective adsorbent for metal cations and also application in ion selective electrodes.

2. Experimental

2.1 Materials and characterization

Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 3-aminopropyl trimethoxysilane (APTS), tetraethyl orthosilicate (TEOS), ammonia (25 wt.%) were purchased from Merck chemical company. The 4-formyl benzo-12-crown-4 ether was prepared and characterized according to literature method [31]. All water utilized in the experiments was doubly distilled.

Fourier transform infrared spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer, using pellets of the materials diluted with KBr. The transmission electron micrographs of the nanoparticles were recorded using a Philips EM 208 Sinstrument with an accelerating voltage of 100 kV. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin Elmer Diamond Thermogravimeter. Dried samples was placed in the TGA furnace and heated at a rate of $10\text{ }^\circ\text{Cmin}^{-1}$ from room temperature to $700\text{ }^\circ\text{C}$ in static air. Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) in the magnetic field range of -8000 Oe to 8000 Oe at room temperature. The crystalline phase of the nanoparticles were identified by means of X-ray diffraction measurements using $\text{Cu } \alpha$ radiation ($\lambda = 1.54\text{ \AA}$) on a SIEFERT XRD 3003 PTS diffractometer in the 2θ range of $10\text{-}80^\circ$.

2.2. Preparation of silica coated magnetic nanoparticles (SCMNPs)

Magnetite nanoparticles were prepared with literature method [24]. After completion of the reaction, the obtained Fe_3O_4 nanoparticles was separated from the reaction medium under the external magnetic field and rinsed with distilled water. Then the product was oven dried at 353 K. In the next step, the magnetite nanoparticles (1 g) were dispersed in deionized water in a 250 ml round-bottom flask with sonication and then an aqueous solution of TEOS (10% (v/v), 80 ml) was added, followed by glycerol (60 ml). The pH of the suspension was adjusted to 4.6 using glacial acetic acid, and the mixture was then stirred and heated at 90 °C for 2 h under a nitrogen atmosphere. After cooling, the silica coated magnetite nanoparticles was separated from the reaction mixture and washed several times with distilled water and methanol.

2.3. Preparation of aminopropyltrimethoxysilyl modified silica coated magnetite nanoparticles (APTSCMNPs)

The silica coated magnetite nanoparticles was first dispersed in ethanol (100 ml) and then a solution of aminopropyltrimethoxysilane (10% in ethanol) was added to above mixture. After heating at 333 K for 2 h the resulting silanized magnetite nanoparticles were magnetically separated and then washed with ethanol several times and dried.

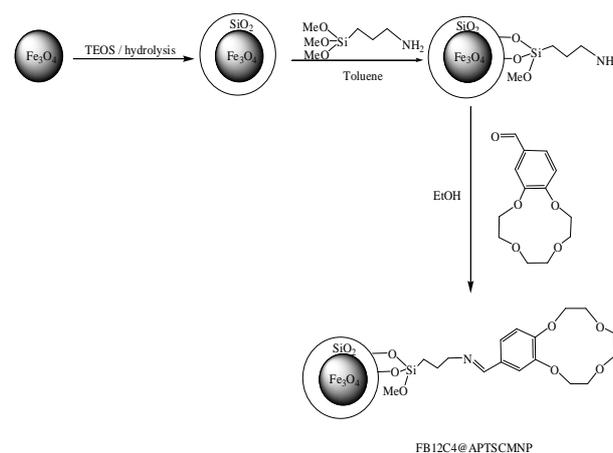
2.4. Preparation of FB12C4/APTSCMNPs

A solution of 4-formyl benzo-12-crown-4 ether (0.5 g) in ethanol (50 ml) was added to a suspension of APTS-SCMNP (2.5 g) in ethanol (100 ml). The mixture was refluxed for 6 h to complete the reaction. The resulted solid was magnetically separated and then washed several

times with ethanol to remove the excess of unreacted benzocrown ether.

3. Results and discussion

The sequence of reactions in the preparation of FB12C4/SCMNPs nanocomposite material is depicted in Scheme 1. The first step involves treatment of the prepared magnetite nanoparticles with tetraethyl orthosilicate to obtain silica coated magnetite nanoparticles (SCMNPs). In the next step, the condensation of silanol groups of SCMNPs with aminopropyltrimethoxysilane affords APTSCMNPs. Finally, Schiff base condensation of the amine groups of APTSCMNPs with carbonyl groups of 4-formyl benzo-12-crown-4 ether gives rise to the preparation of FB12C4/APTSCMNPs hybrid nanocomposite.



Scheme 1. The sequence of reactions in the preparation of FB12C4/SCMNPs nanocomposite material.

In order to confirm the coating of the magnetite surface through the silylation reaction and verify the formation of hybrid nanocomposite, FT-IR spectra of APTSCMNPs and FB12C4/APTSCMNPs in the region of 400–4000 cm^{-1} are shown in Figs. 1a-b.

The observation of two broad bands at around 430–584 cm^{-1} in these materials indicates the presence of magnetite core in the resulted

nanoparticles [24]. The silica coating of magnetite nanoparticles was confirmed by observation of a broad band about $1000\text{-}1100\text{ cm}^{-1}$ assigned to Si-O-Si and Si-OH stretching vibrations. The presence of the anchored propyl groups in APTSCMNPs were confirmed by stretching vibrations appeared at about 2930 cm^{-1} attributed to stretching vibrations of C-H bonds. Some weak bands observed at $1400\text{-}1500\text{ cm}^{-1}$ which assigned to stretching vibrations of aromatic rings in benzocrown ether and was not present in the parent APTSCMNPs.

Thus, FT-IR spectroscopy provides a good evidence for the formation of FB12C4/APTSCMNPs when comparing the FT-IR spectra of the prepared nanomaterials.

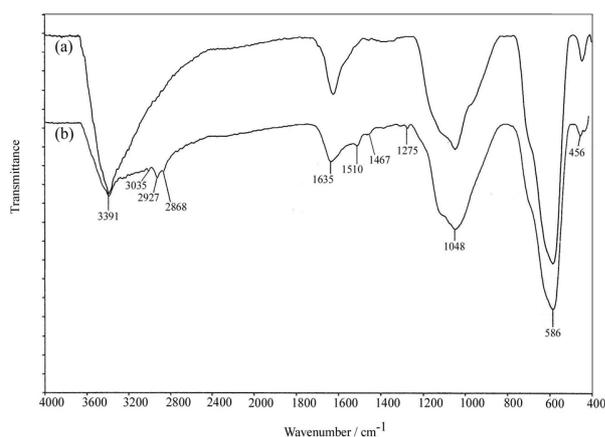


Fig. 1. FT-IR spectra of (a) APTSCMNPs and (b) FB12C4/APTSCMNPs.

Fig. 2 depicts the XRD pattern of prepared hybrid nanomaterial. The diffraction peaks can be assigned to the planes of inverse cubic spinel structured Fe_3O_4 (JCPDS No. 19-0629). The broad peaks indicate the nanocrystalline nature of the prepared material.

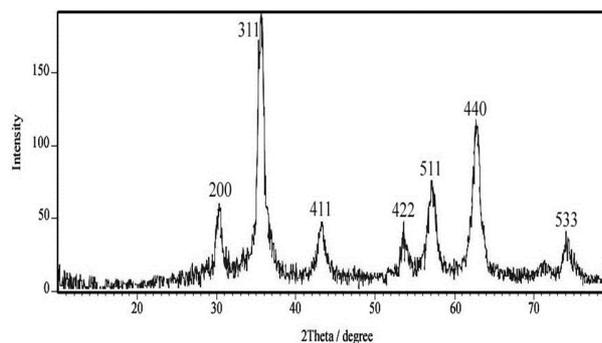


Fig. 2. XRD pattern of prepared hybrid FB12C4/APTSCMNPs.

To study the magnetic properties of magnetite nanoparticles before and after silica coating, we investigated the hysteresis loops of magnetite and functionalized magnetite nanoparticles at room temperature using vibrating sample magnetometry.

As can clearly be seen from the magnetic hysteresis loops (Fig. 3) all of the prepared magnetite nanoparticles exhibit superparamagnetism, that is, no magnetization remains when the applied magnetic field is removed. This is because of the small size of the magnetic particles. On the other hand, surface coating of the magnetite nanoparticles with silica and FB12C4 groups results in decreasing of the saturation magnetizations.

Due to the superparamagnetic property and the screening effect of the silica layer, the magnetic silica nanocomposites could be readily and stably dispersed in water and remained in suspension in the absence of external magnetic field. The magnetic silica nanocomposites could also be completely separated from the solution within minutes when subjected to a strong magnetic field and redispersed very well with a slight agitation when the magnetic field is removed.

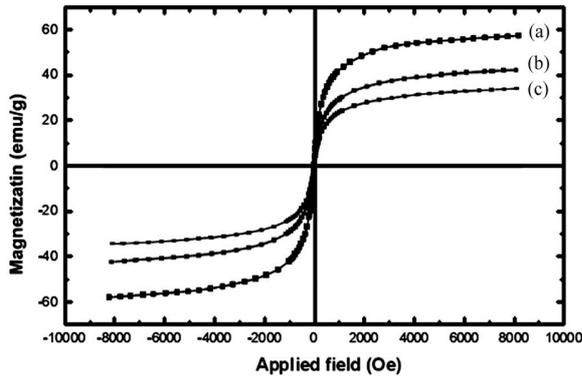


Fig. 3. Magnetization curves of (a) MNPs (b) APTSMNPs and (c) FB12C4/APTSMNPs.

The thermal behavior of the FB12C4/APTSMNPs nanoparticles was investigated by TGA-DTA analysis. Fig. 4 shows the TGA and DTA curves for the prepared FB12C4/APTSMNPs nanoparticles. The TGA curve indicates two stages of mass reduction as a function of temperature. The first stage, about 50-200 °C, was ascribed to the loss of adsorbed water. Due to the hydrophobic nature of the prepared nanocomposite material the amount of adsorbed water was only 1%wt. The corresponding DTA curve in this region is endothermic because the removal of adsorbed water is endothermic. The second stage about 200-500 °C was assigned to the combustion of organic compounds, which is in good agreement with exothermic DTA peak in this region.

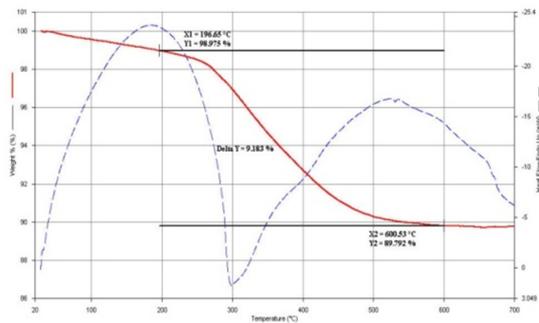


Fig. 4. TGA-DTA curves of prepared hybrid FB12C4/APTSMNPs.

A typical scanning electron micrograph of the prepared FB12C4/APTSMNPs is shown in Fig. 5a. The SEM image indicates that the obtained nanoparticles are composed of nearly uniform nanospheres with some agglomerations.

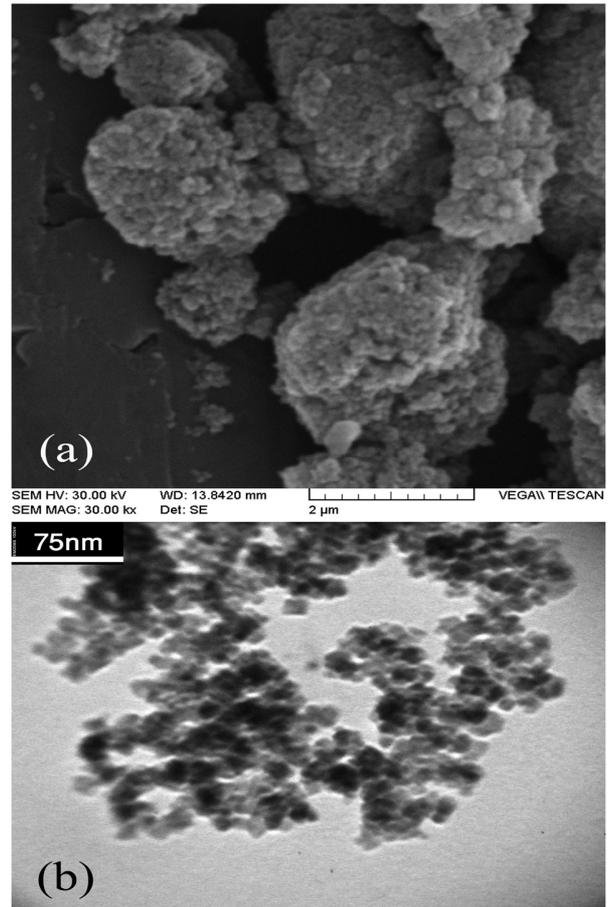


Fig. 5. (a) scanning electron microscopy and (b) transmission electron microscopy images of the prepared FB12C4/APTSMNPs nanoparticles.

The morphology and microstructure of the obtained product was further investigated by transmission electron microscopy (TEM). Fig. 5b shows the typical image of FB12C4/APTSMNPs. This image clearly shows that obtained nanoparticles have spherical morphologies and monodispersed with average diameter of about 10

nm, which is in agreement with the SEM observation.

4. Conclusion

In summary, reaction of the 4- formyl benzo-12-crown-4 ether with aminopropylsilyl modified SCMNP's afforded FB12C4/APTSMNP's nanocomposite material in which the crown ether moiety was attached through propyl chain spacer. Characterization of the prepared nanocomposite was performed with different physicochemical methods. The prepared nanomaterial predicts to have interesting properties as selective adsorbent for metal cations and also application in ion selective electrodes.

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