

Hybrid Organometallic-Inorganic Nanomaterial: Acetyl Ferrocene Schiff base Immobilized on Silica Coated Magnetite Nanoparticles

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Abstract

In this work, a new hybrid organometallic-inorganic hybrid nanomaterial was prepared by immobilization of acetyl ferrocene on the surface of magnetite nanoparticles. Covalent grafting of silica coated magnetite nanoparticles (SCMNPs) with 3-aminopropyl triethoxysilane gave aminopropyl-modified magnetite nanoparticles (AmpSCMNPs). Then, Schiff base condensation of AmpSCMNPs with acetyl ferrocene resulted in the preparation of acferro-SCMNPs hybrid nanomaterial. Characterization of the prepared nanomaterial was performed with different physicochemical methods such as Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), vibrating sample magnetometry (VSM), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). VSM analysis showed superparamagnetic properties of the prepared nanomaterial and TEM and SEM analyses indicated the relatively spherical nanoparticles with 15 nm average size.

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1. Introduction

Recently, design and preparation of hybrid nanomaterials with tunable physical properties have attracted great interest in materials chemistry [1-6]. This field of research bridges different types of chemistry (organic, inorganic, and organometallic) to materials science and

opens many possibilities for physical properties. The ability to integrate the chemical functionality and diversity of soft matter onto a mechanically robust inorganic scaffold has long been of interest in numerous applications [7-9].

Magnetite nanoparticles (MNPs) can be used to prepare surface bound organometallic compounds. MNPs which can be easily produced

by the co-precipitation of Fe(II) and Fe(III) salts in basic conditions have superparamagnetic properties that give it exceptional behaviors suitable both for magnetic recovery [10-12]. These nanoparticles are easily dispersible and have no tendency to aggregate in solution, but are readily magnetized by an external magnetic field which favors their easy separation from the reaction mixture. The surface of magnetite nanoparticles can be functionalized to protect the magnetite core from chemical reactions and also provide functional groups for immobilization of desired compounds.

Recently, functionalization of magnetite nanoparticles with transition metal compounds has been of particular interest [13-20]. One approach is grafting of organometallic or metal-organic complexes on the surface of magnetite nanoparticles. The prepared hybrid nanomaterials exhibited interesting catalytic behaviors in the catalysis of organic reactions.

Especially, the immobilization of metallocene active sites on various supports is interesting. Although several works published on the immobilization of metallocene compounds on the surface of mesoporous materials [21-26], to the best of our knowledge, there is only one report devoted to the use of magnetite nanoparticles for preparation of ferrocene containing nanomaterial with non-covalent interaction [27].

Our current interest in the preparation of new hybrid nanomaterials based on magnetite nanoparticles [17-20] led us to investigate the preparation and characterization of a new hybrid nanomaterial based on immobilization of ferrocene Schiff base on the surface of silica coated magnetite nanoparticles modified with amine groups. The preparation of this hybrid nanomaterial is based on the functionalization of

the surface of magnetite nanoparticles with amine groups in the first step. Next reaction of the prepared nanomaterial with acetylferrocene results in the immobilization of ferrocene Schiff base on the surface of magnetite nanoparticles.

The main advantage of the system is stronger covalent interaction of acetyl ferrocene Schiff base attached on the surface of magnetite nanoparticles in comparison with earlier report [27]. On the other hand, due to the presence of magnetite core, the prepared hybrid nanomaterial has superparamagnetic properties which make its easy recovery and reuse in potential applications such as oxidation of organic compounds.

2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased from Merck chemical company and used without further purification.

Fourier transform infrared (FT-IR) spectra were recorded on Rayleigh WQF-510 spectrophotometer using pellets of the materials diluted with KBr. The carbon and nitrogen contents of the samples were analyzed using a Thermo Finnigan (Flash 1112 Series EA) CHN Analyzer. The crystalline phase of the prepared nanomaterial was identified by means of X-ray diffraction measurements using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) on a SIEFERT XRD 3003 PTS diffractometer in the 2θ range of $10\text{-}70^\circ$. 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. Thermogravimetric measurements were made on a Perkin Elmer Diamond Thermogravimeter. The temperature was increased to 700°C using a rate of $10^\circ\text{C}/\text{min}$

in static air. Scanning electron micrographs (SEM) of the samples were taken with ZEISS-DSM 960A microscope with attached camera. The transmission electron micrographs (TEM) of the nanoparticles were recorded using a Philips EM 208S instrument with an accelerating voltage of 100 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid.

2.2. Preparation of silica coated magnetite nanoparticles (SCMNPs) and aminopropyl modified SCMNPs (AmpSCMNPs)

Magnetite nanoparticles (MNPs) were prepared according to reported method [28]. For preparation of SCMNPs, 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 (50 ml). The pH of the suspension was adjusted to 4.5 using glacial acetic acid, and the mixture was then stirred and heated at 90°C for 2 h under a nitrogen atmosphere. After cooling to room temperature, the silica coated magnetite nanoparticles was separated from the reaction mixture using a permanent magnet and washed several times with distilled water and methanol. The obtained SCMNPs (2 g) were suspended in ethanol (100 ml) and then aminopropyl triethoxysilane (2 ml) was added under dry nitrogen atmosphere. The mixture was refluxed for 12 h and the resulted solid was magnetically separated, washed with methanol to remove the unreacted residue of silylating reagent and then vacuum dried at 80°C.

2.3. Preparation of supported acetyl ferrocene Schiff base on the surface of silica coated magnetite nanoparticles

The supported ferrocene Schiff base was prepared according to the standard method used for preparation of Schiff bases. The prepared AmpSCMNPs (2 g) suspended in 100 ml of ethanol with sonication were mixed with excess of acetyl ferrocene (4 mmol) and the resulted mixture was refluxed for 24 hours under dry nitrogen atmosphere. The resultant solid (acferro-SCMNPs) was separated magnetically and washed with ethanol several times to remove the unreacted residue of the acetyl ferrocene and finally dried in vacuum oven at 80°C overnight.

3. Results and discussion

3.1. Preparation of supported acetyl ferrocene Schiff base on the surface of silica coated magnetite nanoparticles (acferro-SCMNPs)

The sequence of processes in the functionalization of magnetite nanoparticles (MNPs) with ferrocene Schiff base has been shown in Figure 1. First, the external surface of MNPs was coated with a silica shell to obtain silica coated magnetite nanoparticles (SCMNPs). Then, treatment of silanol (Si-OH) groups of SCMNPs with aminopropyl triethoxysilane afforded aminopropylated silica coated magnetite nanoparticles (AmpSCMNPs). During this reaction, the silylating reagent reacts with the Si-OH groups on the surface of SCMNPs to form a stable Si-O-Si bond through which the aminopropyl chain was attached to the surface of SCMNPs. In the next step, Schiff base condensation of carbonyl group of acetylferrocene with amine group of AmpSCMNPs results in the formation of C=N bond through which the ferrocene moiety attached to the surface of

magnetite nanoparticles and preparation of acferro-SCMNPs [18,20]. Soxhlet extraction of the product was carried out subsequently in order

to remove the unreacted acetyl ferrocene from the resulted hybrid nanomaterial.

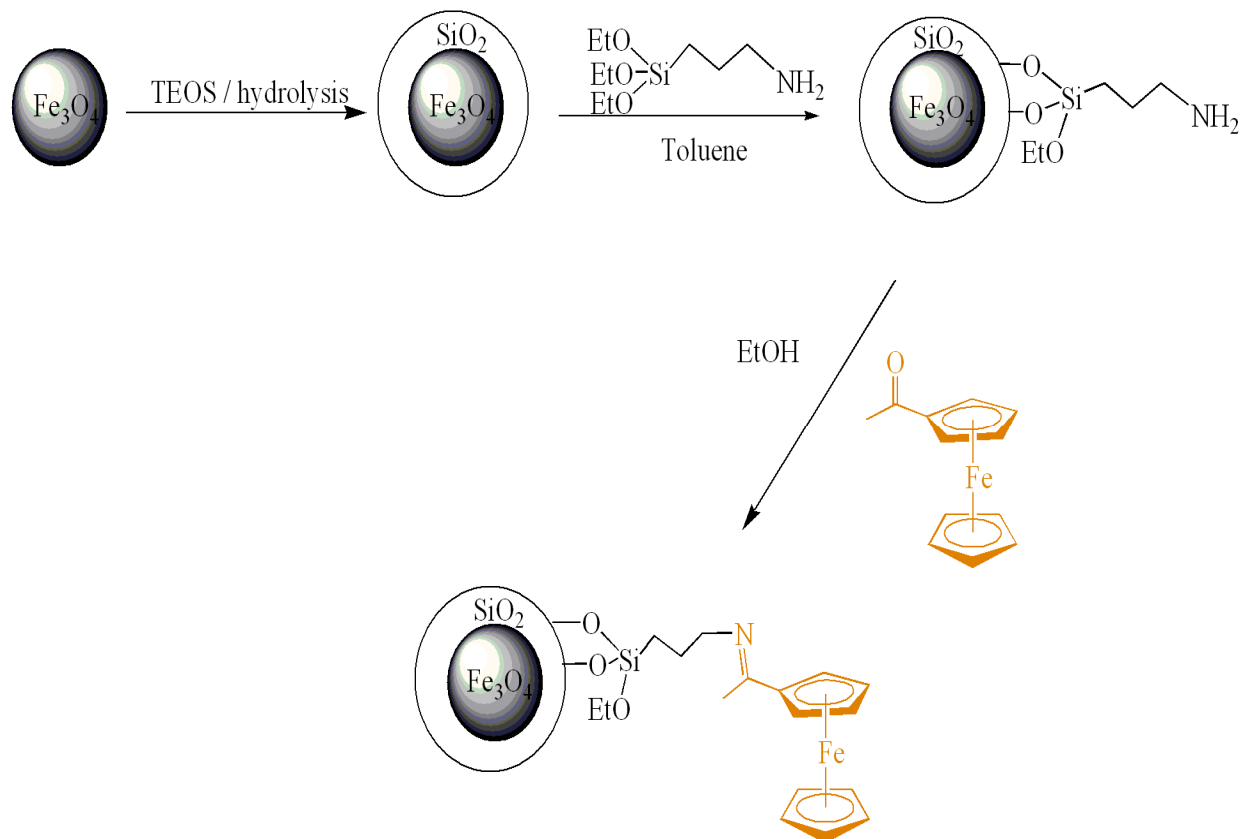


Fig. 1. The preparation steps of acferro-SCMNPs hybrid nanomaterial.

3.2. Characterization of the prepared nanomaterials

In order to verify the functionalization of the magnetite surface, the FT-IR spectra of the prepared SCMNPs, AmpSCMNPs, and acferro-SCMNPs nanomaterials were recorded and have been shown in Figure 2. The observation of two peaks at around $450\text{--}590\text{ cm}^{-1}$ indicates the characteristic absorption bands of the Fe-O bonds in the magnetite core of the prepared nanomaterials [29]. The strong and broad absorption band at about $1000\text{--}1100\text{ cm}^{-1}$ revealed the presence of Si-O-Si and Si-O-H stretching vibrations and confirmed the presence of silica

shell on the surface of magnetite nanoparticles. The presence of anchored propyl chain was confirmed by C-H stretching vibrations appeared at about 2923 cm^{-1} . In the FT-IR spectrum of acferro-SCMNPs, the peak at 1635 cm^{-1} is due to the stretching vibration of the C=N group in this material which is overlapped with H-O-H bending vibrations in this region. There are some weak peaks at $1300\text{--}1500\text{ cm}^{-1}$ that is due to the presence of cyclopentadienyl groups and confirm the covalent attachment of ferrocene Schiff base to the magnetite nanoparticles.

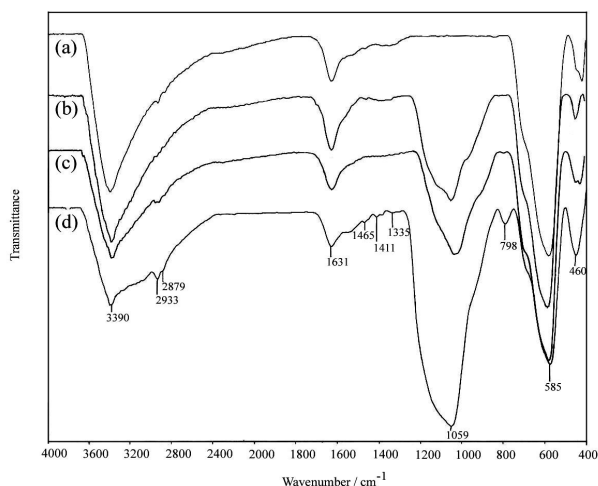


Fig. 2. FT-IR spectra of (a) MNPs, (b) SCMNPs, (c) AmpSCMNPs, and (d) acferro-SCMNPs nanomaterials.

Figure 3 shows the XRD pattern of the acferro-SCMNPs hybrid nanomaterial. The diffraction peaks can be attributed to the crystallographic planes of inverse cubic spinel structured Fe_3O_4 (JCPDS No. 19-0629). The broad peaks indicate the nanocrystalline nature of the prepared acferro-SCMNPs nanomaterial.

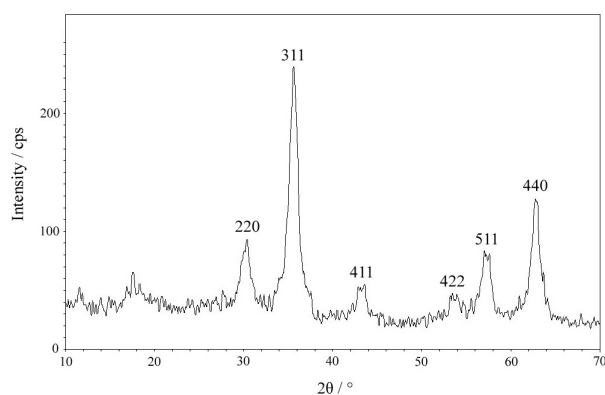


Fig. 3. XRD pattern of the prepared acferro-SCMNPs hybrid nanomaterial.

In order to investigate the magnetic properties of magnetite nanoparticles before and after modifications, the hysteresis loops of magnetite and functionalized magnetite nanoparticles were

recorded at room temperature using vibrating sample magnetometry (VSM). The magnetization curves of prepared materials were shown in Figure 4. As can be seen, the magnetization curve of MNPs exhibited no remanence effect with saturation magnetization of about 60 emu/g. Also, the silica coated magnetite nanoparticles modified with aminopropyl groups (AmpSCMNPs) showed superparamagnetic behavior with decreased saturation magnetization about 42 emu/g. The acferro-SCMNPs nanomaterial also exhibited superparamagnetic properties with saturation magnetization about 32 emu/g. The superparamagnetic properties of the prepared acferro-SCMNPs nanomaterial are critical for its application, which prevent aggregation and enables it to redisperse rapidly after removing the magnetic field.

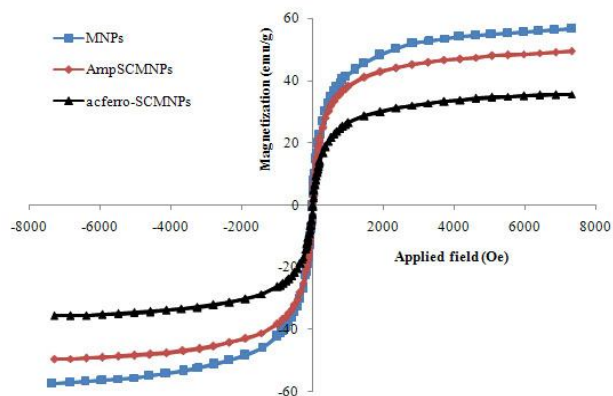


Fig. 4. Magnetization curves of prepared nanomaterials.

The thermal behavior of the acferro-SCMNPs was investigated by thermogravimetric analysis. Figure 5 shows the TGA, DTG and DTA curves for the prepared acferro-SCMNPs. The TGA and DTG curves indicate only one stage of mass reduction as a function of temperature. Due to the hydrophobic nature of the prepared nanomaterial, the amount of adsorbed water below 200°C was only 2 % wt. The main weight loss about 300-

450°C (16 %wt) was assigned to the combustion of organic compounds and cyclopentadienyl

ligands which is in good agreement with exothermic DTA peak in this region.

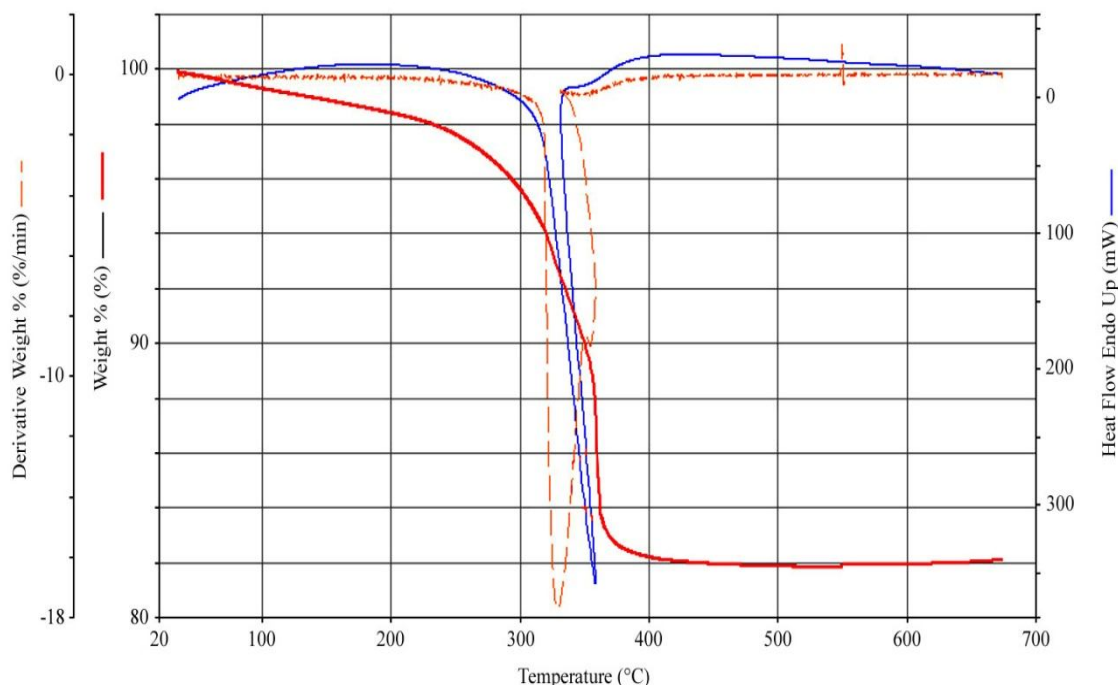


Fig. 5. TGA curves of the prepared acferro-SCMNPs hybrid nanomaterial.

Figure 6a shows the SEM image of the prepared acferro-SCMNPs nanomaterial. The SEM image indicates that the obtained product is composed of relatively monodispersed spherical nanoparticles. Aggregation gives rise to increasing the size of some of the nanoparticles as seen in the SEM image.

Transmission electron micrograph of the prepared nanomaterial has been shown in Figure 6b. As can be seen, most of the nanoparticles are aggregated. The particle size is about 15 nm as can be observed in the edges of the aggregated nanoparticles.

4. Conclusion

In conclusion, the use of modified magnetite nanoparticles to design a new organometallic-

inorganic hybrid nanomaterial has been demonstrated. First, the external surface of silica coated magnetite nanoparticles were modified with aminopropyltriethoxysilane. Afterwards, Schiff base condensation reaction resulted in immobilization of ferrocene Schiff base on the surface of modified magnetite nanoparticles. Due to the covalent attachment between the ferrocene Schiff base and magnetite nanoparticles the prepared hybrid nanomaterial has good stability in potential applications in catalysis and biological uses. Also, the results of VSM analysis showed the superparamagnetic properties of the prepared hybrid nanomaterial.

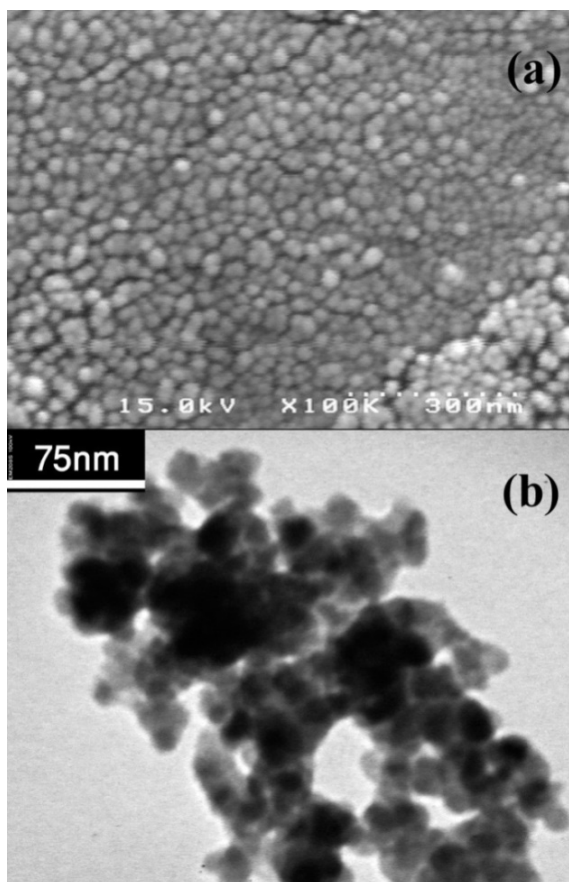


Fig. 6. (a) FE-SEM and (b) TEM images of prepared acferro-SCMNPs.

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