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Fabrication and characterization of Fe_3O_4@APTES@PAMAM-Ag highly active and recyclable magnetic nanocatalyst: Catalytic reduction of 4-nitrophenol

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ABSTRACT

The surface of amine-fuctionalized magnetic nanoparticle was coated with polyamidoamine dendrimer via of alkylation of amine groups with methyl acrylate (Micheal addition route). Then silver nanoparticles were doped between the layers of dendrimer branches. The as-prepared nanocomposite is composed of a central magnetite core with a strong response to external fields, an interlayer of SiO_2, polyamidoamine dendrimer (G1) and numerous highly dispersed Ag nanoparticles with a narrow size distribution. The crystallite size from XRD (9 ± 2 nm) and particle size from TEM analysis (11.6 ± 0.2 nm) are consistent with each other. The catalytic activity of nanocomposite was tested against 4-nitrophenol. It has well magnetic separability and excellent reusability without major loss and activity (it can be conveniently recycled from the reaction system by using a magnet) and no deactivation has been observed after at least 5 cycles of reaction.

1. Introduction

Over the past decades, iron oxide nanoparticles (NPs) have been used in a broad range of applications, containing drug delivery, microwave absorption, biomedical applications or catalysis [1–3]. As an important member of magnetite nanoparticles, especially, Fe_3O_4 have recently emerged as an alternative to conventional support materials for catalytic reactions, as they can be easily recover with an external magnetic field from the reaction system, which makes the catalysis filtration unnecessary [4,5].

The catalytic reduction reactions have been investigated including several noble metal nanoparticles such as Pt [6], Pd [7], Ag [8] and Au [9]. As a relatively inexpensive noble metal, silver nanoparticles have been used in various type of catalytic reactions due to its good chemical and physical properties. However, nanoparticles tend to easily aggregate, change shape and damage the surface states during catalytic reactions since they have high surface energy because of the large surface-to-volume ratio. So in order to overcome these problems, some solid supports are necessary such as carbon [10], silica [11], zeolite [12] or metal oxides [13]. Herein, we developed a new strategy by using functional polymeric shell called dendrimer which provides as a support material to prevent aggregation of silver nanoparticles in the presence of magnetite. Since dendrimers have important properties such as functional groups and nonporous nature of it, they help to produce a uniform and stable suspension in the production of organic shell around inorganic core [14,15].

In recent years, polyvinylpyrrolidone (PVP) was often used not only as a stabilizing agent but also reducing agent in the preparation of noble metal ions like Au, Ag, Pd, Pt. For instance, Chen et al. prepared Ag–Fe_3O_4 nanocomposite by using PVP as surfactant with a one-pot solvothermal route, while in another study a research group was developed a Au-based magnetically recyclable nanocatalysts, Fe_3O_4/C/Au/PVP/p-SiO_2, for the reduction of *o*-nitroaniline to benzenediamine in the presence of PVP [16,17].

Nitrophenols arise from pesticides and synthetic dyes, and also give rise to environmental pollution. Nitrophenol compounds are among the most common organic pollutants in industrial and agricultural waste waters but the *p*-aminophenol (PAP) is an important intermediate for the manufacture of analgesic, anticorrosion lubricants and hair drying agents and antipyretic drugs [18]. Thus, 4-AP is in demand of many industries. The direct catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol becomes important, because this could be an efficient and environmental friendly process [19]. Therefore, to the best of our knowledge, the use of Fe_3O_4@APTES@PAMAM-Ag magnetic nanocatalyst for the reduction of 4-nitrophenol has hardly been reported so far.

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In this study, we present a simple strategy for the magnetically recyclable nanocatalyst with dendrimer-magnetite incorporation to encapsulate silver nanoparticle showing excellent catalytic performance and stability for the reduction of 4-nitrophenol in the presence of $NaBH_4$, which could complete the reduction of 0.005 M 4-NP within only 3 min, and no remarkable change in the catalytic activity was detected after 4 cycles. More significantly, the catalyst can be easily recovered using an external magnetic field and reused many times.

2. Experimental

2.1. Chemicals

Ferrous chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99%, Merck), ferric sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%, Merck), methyl acrylate, (MA, 99%, Aldrich), ethylene diamine (EDA, 99%, Sigma–Aldrich), Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), *p*-nitrophenol (4-NP), (3-aminopropyl) triethoxysilane (APTES) 99%, Sigma–Aldrich). All these chemicals were of analytical grade and used without any further purification.

2.2. Instrumentations

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab Diffractometer operated at 40 kV and 35 mA using Cu K_α radiation.

Fourier transform infrared (FT-IR) spectra were recorded in transmission mode with a PerkinElmer BX FT-IR infrared spectrometer. The powder samples were ground with KBr and compressed into a pellet. FT-IR spectra in the range 4000–400 cm^{-1} were recorded in order to investigate the nature of the chemical bonds formed.

Transmission electron microscopy (TEM) analysis was performed using a JEOL microscope. A drop of diluted sample in alcohol was dripped on a TEM grid.

Scanning electron Microscopy, SEM, analysis was performed in order to investigate the microstructure and morphology of the sample, using an FEI XL40 Sirion FEG Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to analysis.

The thermal stability was determined by thermo gravimetric analysis (TGA, PerkinElmer Instruments model, STA 6000). The TGA thermo grams were recorded for 5 mg of powder sample with a heating rate of 10 °C/min in the temperature range of 30–800 °C under nitrogen atmosphere.

VSM measurements were performed by using a SQUID magnetometer (Quantum Design MPMS XL). The magnetization measurements were carried out in an external field up to 15 kOe at several temperatures.

The UV–vis measurement was done using a Shimadzu UV–vis 2600.

2.3. Synthesis

2.3.1. Preparation of Fe_3O_4-APTES magnetic nanoparticles

Different solutions of ferrous chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and ferric sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) was prepared as a molar ratio of Fe^{3+}/Fe^{2+} in two. Typically, $FeCl_3{\cdot}6H_2O$ (5.8 g, 0.02 mol) and $FeSO_4{\cdot}7H_2O$ (2.70 g, 0.01 mol) were dissolved in 100 mL deionized water at 85 °C under nitrogen atmosphere to deoxygenate the mixture and vigorous stirring. Then, as an alkaline solution, ammonia was added to this mixture by stirring until the pH reaches 10 and the solution was mixed 8 h in the reflux system. Final, the black powders were collected and washed ethanol three times. The obtained magnetic nanoparticle was dispersed in ethanol/water mixture by sonication. Then, 6 mL (3-aminopropyl) triethoxy silane (APTES), was added to this mixture and the

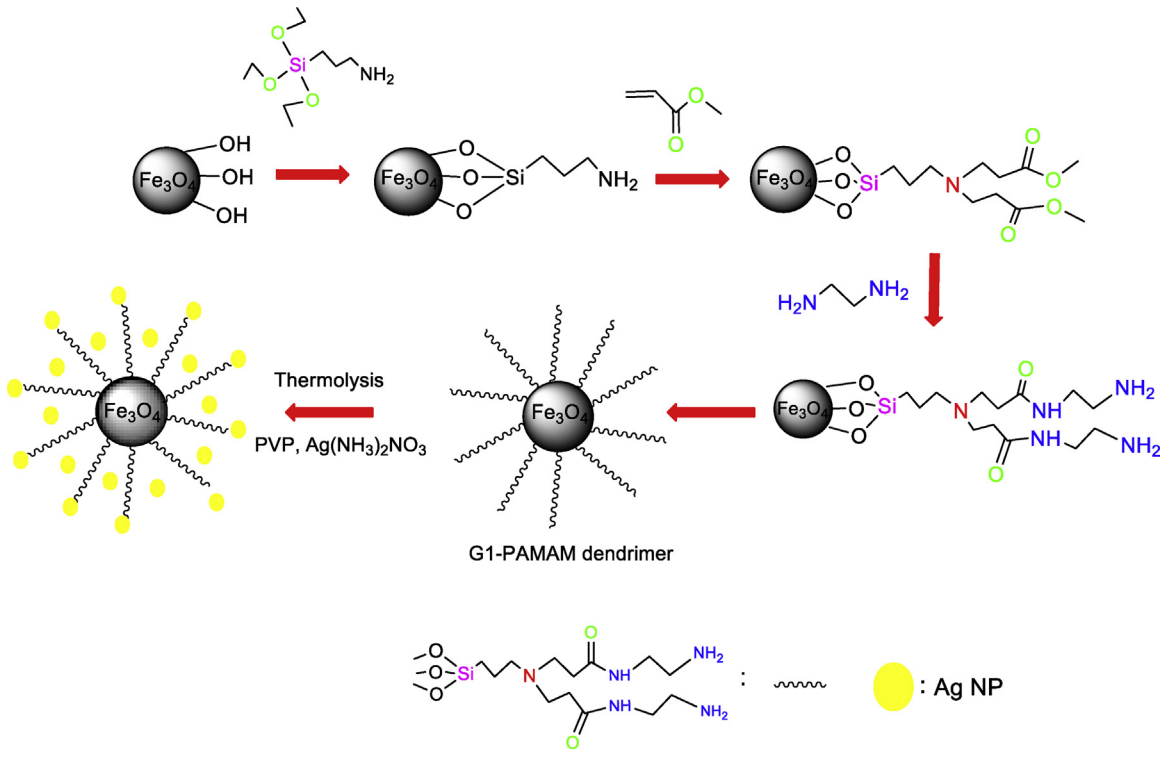

Fig. 1. Schematic illustration of the the formation of Fe_3O_4@APTES@PAMAM(G1)-Ag MRCs.