

MAGNETIC POLYMER MICROSPHERE STABILIZED GOLD NANOCOLLOIDS AS A FACILELY RECOVERABLE CATALYST*

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Abstract Magnetically responsive hierarchical magnetite/silica/poly(ethyleneglycol dimethacrylate-co-4-vinylpyridine) ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$) tri-layer microspheres were used as stabilizers for gold metallic nanocolloids as a facilely recoverable catalyst with the reduction of 4-nitrophenol to 4-aminophenol as a model reaction. The magnetic microsphere stabilized gold metallic nanocolloids were prepared by *in situ* reduction of gold chloride trihydrate with borohydride as reductant *via* the stabilization effect of the pyridyl groups to gold nanoparticles on the surface of the outer shell-layer of the inorganic/polymer tri-layer microspheres.

Keywords: Gold metallic nanocolloids; Magnetic functional polymer microspheres; Catalyst.

INTRODUCTION

Metallic nanoparticle is one of the most attractive research fields owing to its unique physical and chemical properties, which are different from those of either single atom or bulk metallic materials. Due to the tailorable physicochemical and chemical properties by deliberate modulation of their size, shape and composition, metallic nanocolloids are promising for potential applications in a new generation of optical, electronic, chemical devices and catalysts^[1–5]. Gold nanocolloids have been one of the most widely studied metallic colloids owing to their interesting quantum size related properties and applications in many fields, such as labels and sensors for heavy metal ions^[6, 7], carbohydrates^[8] and other biomolecules^[9], catalysts^[10] and nanotechnology^[11]. To date, most publications have centered on the synthesis and characterization of water/organic solvent-‘soluble’ metallic nanoparticles.

Although the soluble metallic nanocolloids stabilized by either polymer or surfactant have high activity, stability and selectivity in homogeneous catalytic reactions^[12–14], it is neither economic nor convenient for the recovery of the catalyst from the products by conventional techniques, such as filtration and ultracentrifugation. The immobilization of the metallic nanocolloids on supports seems to be a way for such catalysts to retain high activity during recycling. Hirai *et al.* immobilized ultrafine rhodium particles on a polyacrylamide gel through the formation of an amide bond between the primary amino group of the support and methyl acrylate residue in the protective polymer^[15]. Liu and co-workers reported the capture of colloidal metallic particles on the solid surface by ligand coordination^[16] and a modified coordination technique^[17]. Pal’s group investigated the immobilization of gold nanoparticles in an anion-exchange resin and their quantitative regeneration by means of efficient cationic surfactants^[18]. Akashi *et al.* described the *in situ* synthesis of platinum^[19] and silver

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nanoparticles^[2] on poly(*N*-isopropylacrylamide)-coated polystyrene microspheres. Gao *et al.* utilized superparamagnetic nanoparticles as a novel type of matrices *via* the complexing of Pd and *N*-heterocyclic carbenes (NHCs) for supporting catalytic homogeneous Suzuki, Heck and Sonogashira cross-coupling reactions^[20], which proceeded much faster than its counterpart on resins without significant loss of catalytic activity after several reaction cycles. Ying and co-workers reported the utilization of silica-coated magnetic nanoparticles ($\text{SiO}_2/\text{Fe}_2\text{O}_3$) as a supported-catalyst for palladium (Pd) magnetic nanocomposites with 3-(mercaptopropyl)-triethoxysilane (MPS) and *N*-(2-aminoethyl)-3-aminopropyl trimethoxysilane (AAPS), which behaved excellent catalytic activity and reusability for the hydrogenation of nitrobenzene during the ease recycling *via* magnetic separation^[21]. Yin's group^[22] described the fabrication of hierarchical assemblies of silica colloids and their utilization as a recoverable support for gold nano-catalysts, which possessed relatively high surface-area with high activity and facile recovery of the catalyst by using an external magnetic field.

In our previous work, polymer microspheres with different functional groups as supports for gold metallic catalysts were studied due to the possibility of tailoring the loading capacity, size and catalytic activity of the metallic nanocolloids *via* the different interaction between the functional groups in the gel-layer and on the surface of the polymer microspheres and the gold nanocolloids during the *in situ* reduction of tetrachloroauric acid trihydrate (HAuCl_4) with sodium borohydride (NaBH_4) as reductant^[23–26]. Here, the gold metallic nanocolloids stabilized by pyridyl groups on the surface and gel-layer of the magnetite/silica/poly(ethyleneglycol dimethacrylate-*co*-4-vinylpyridine) ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$) microspheres were *in situ* prepared by reduction of HAuCl_4 with NaBH_4 in presence of tri-layer magnetic inorganic/polymer microspheres as stabilizers. Further, the catalytic reduction of 4-nitrophenol (4-NP) with NaBH_4 as reducing reagent to 4-aminophenol (4-AnP) was used as a model reaction to investigate the catalytic activity and the facile reusability of the magnetic microsphere-stabilized gold metallic nanocolloids *via* the efficient interaction between pyridyl groups and gold nanoparticles during the recycling of the catalyst in an external magnetic field.

EXPERIMENTAL

Chemicals

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Tianjin Guangfu Fine Chemical Engineering Institute. Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was bought from Shanghai Gongxuetuan Reagents II Co. Ammonia (25%, aqueous solution) was got from Tianjin Dongzheng Fine Chemical Reagent Factory. Trisodium citrate was available from Tianjin Chemical Reagents I Co. Tetraethylorthosilicate ($\text{Si}(\text{OEt})_4$, TEOS) and ethyleneglycol dimethacrylate (EGDMA) were provided by Aldrich and used without further treatment. 3-(Methacyloxy)propyltrimethoxysilane (MPS) was purchased from Aldrich and distilled under vacuum. 4-Vinylpyridine (4-VPy) was available from Acros and distilled under vacuum. 2,2'-Azobisisobutyronitrile (AIBN) was provided by Chemical Factory of Nankai University and recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagent II Co.) was dried over calcium hydride and purified by distillation before use. Tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was obtained from Shenyang Research Institute of Nonferrous Metals, China. Sodium borohydride (NaBH_4) was purchased as analytical grade from Tianjin Chemical Reagents III Co. 4-Nitrophenol (4-NP, Tianjin Chemical Reagent Factory) was recrystallized from petroleum ether and ethyl acetate. The other reagents were used without further purification.

Preparation of Narrow-disperse $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$ Tri-layer Microspheres

Magnetite/silica ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) core-shell nanoparticles were prepared according to the method in the literature through the hydration of TEOS in presence of magnetite nanoparticles as templates with aqueous ammonia as catalyst^[27], in which magnetite nanoparticle cores were synthesized by chemical co-precipitation of Fe^{2+} ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 9.82 g, 0.046 mol) and Fe^{3+} ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 24.0 g, 0.088 mol) under basic condition. Coating of magnetite/silica particles with MPS was achieved by introducing MPS (1.0 g, 4.0 mmol) into the above ethanol suspension of magnetite/silica particles under stirring, and the mixture was stirred for 48 h further at room

temperature. The resultant MPS-modified magnetite/silica particles were purified by centrifugation, decantation, and resuspension in ethanol for three cycles to remove the excessive MPS. The final MPS-modified magnetite/silica particles were dried in a vacuum oven at 50°C till constant weight.

The growth of polymer outer shell-layer to afford tri-layer magnetite/silica/poly-(ethyleneglycoldimethacrylate-*co*-4-vinylpyridine) ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$) microspheres was similar to the technique reported in our previous paper^[28]. In the present work, the MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were used as seeds, while the comonomers were EGDMA crosslinker and 4-VPy functional monomer for distillation precipitation polymerization. The typical procedure for the distillation precipitation polymerization was as following: MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles (0.02 g), EGDMA (0.04 mL, 0.21 mmol), 4-VPy (0.04 mL, 0.36 mmol) and AIBN (0.0016 g, 2 wt% relative to the comonomers) were dissolved in 40 mL of acetonitrile in a dried 50 mL two-necked flask under ultrasonic-bathing. Then the two-necked flask attached to a fractionating column, a Liebig condenser and a receiver was submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 10 min, and the reaction mixture was kept under reflux state for further 15 min. Then the solvent was distilled off the reaction system and condensed into the receiver. The reaction was stopped after 20 mL of acetonitrile was distilled from the reaction system within 60 min. When the reaction mixture was cooled to ambient temperature, EGDMA (0.1 mL, 0.52 mmol), 4-VPy (0.1 mL, 0.90 mmol), AIBN (0.004 g, 2 wt % relative to the comonomers) and 20 mL acetonitrile were dissolved into such residual reaction mixture to start the second-step distillation-precipitation polymerization, which was the same as the first-step polymerization. The resultant $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$ microspheres were purified by three cycles of ultracentrifugation, decanting and resuspension in acetonitrile under ultrasonic-bathing. Then these nanoparticles were dried in a vacuum oven at ambient temperature till constant weight.

The loading capacity of the accessible pyridyl groups on the surface of tri-layer $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$ microspheres was determined by an acid-base titration similar to the procedure in our previous work^[23].

Preparation of Magnetic Microsphere Stabilized Gold Nanocolloids

Gold nanocolloids stabilized by pyridyl groups on the surface of magnetic tri-layer $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$ microspheres were *in situ* prepared by the reduction of HAuCl_4 with NaBH_4 as reductant in presence of magnetic microspheres as stabilizers. A typical procedure was as following: 0.02 g $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})$ microspheres were suspended in 4 mL of acetonitrile in a 25 mL round flask. Then 0.3 mL of 6.27 mmol/L HAuCl_4 aqueous solution (containing 1.9×10^{-6} mol Au) was added to the suspension with ultrasonic irradiation. The molar ratio of pyridyl groups to Au atoms was 20:1. After the suspended solution was stirred at room temperature for 24 h, 0.5 mL of 0.14 mol/L NaBH_4 aqueous solution (containing 7.0×10^{-5} mol NaBH_4) was rapidly poured into the reaction with stirring. The suspension turned purple immediately, indicating the formation of the gold nanocolloids. Then the reaction system was stirred further for 12 h at room temperature. The resultant magnetic polymer microsphere stabilized gold nanocolloids ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})@Au$) were purified by three cycles of ultracentrifugation, decanting and resuspension in acetonitrile with ultrasonic irradiation and then dried in a vacuum oven at room temperature till constant weight.

Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol by NaBH_4

Catalytic activity of magnetic polymer microsphere stabilized gold nanocolloids was investigated *via* the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AnP) by NaBH_4 as reductant under ambient temperature in aqueous solution as a model reaction. A typical experiment was carried out as follows: aqueous solution of 4-NP (2 mL, 0.1 mmol/L, 2.0×10^{-7} mol) and NaBH_4 (4 mL, 0.1 mol/L, 4×10^{-4} mol) were mixed together with stirring. After adding 0.3 mL of the suspension (1.0 g/L) with magnetic polymer microsphere stabilized nanocolloids ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-}co\text{-VPy})@Au$, containing 2.8×10^{-8} mol Au) into the reaction system with mild stirring. The bright yellow solution faded gradually as the reaction proceeded. The catalytic activity was determined by a UV-Vis spectrometer with a decrease of peak at 399 nm corresponding to 4-NP in UV-Vis spectra and a simultaneous increase of peak at 297 nm assigning to 4-AnP.

To compare the catalytic property of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ catalyst with neat gold nano-colloids, sodium citrate stabilized Au nanoparticles aqueous solution with diameter of 23 nm was prepared. Typically, 100 mL of 0.25 mmol/L HAuCl_4 aqueous solution was heated to boiling state with mechanical stirring. Then, 1 mL of 5 wt% sodium citrate aqueous solution was quickly added. The reaction was maintained till the color of the reaction mixture changing into wine red. The wine red mixture was cooled to room temperature and centrifuged for 40 min at 8000 r/min to obtain concentrated Au nanoparticles aqueous solution. Then, 75% of the colorless supernatant was removed and the retained solution was redispersed under gentle shaking. To study the catalytic behavior of the as-obtained Au nanoparticles, 12 drops of such concentrated aqueous solution (containing 1.4×10^{-7} mol mol of Au atoms) were added into 2 mL of 0.1 mmol/L 4-NP (2×10^{-7} mol) aqueous solution with gentle shaking. Then, 4 mL of 0.1 mol/L NaBH_4 (4×10^{-4} mol) aqueous solution was introduced into such mixture with gentle shaking. The catalytic reaction was detected by UV-Vis spectroscopy.

The magnetic polymer microsphere stabilized gold nanocolloids were recycled by decantation under an external magnetic field with further washing by deionized water for the next cycle. The recovery of the catalyst was proven further by the activity of recycling for four times.

Characterization

The size of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ magnetic microspheres was determined by scanning electron microscopy (SEM, Quanta200F, FEI), and the morphology of the magnetic polymer microsphere stabilized gold nanocolloids was characterized by transmission electron microscopy (TEM, FEI Technai-20, Germany). UV-Vis spectra were performed on a JASCO V-570 spectrometer ranging from 250 nm to 600 nm. Fourier-transform infrared spectra (FT-IR) were scanned over the range of 400–4000 cm^{-1} with a potassium bromide slide on a Bio-Rad FTS135 FT-IR spectrometer. The magnetic properties of the particles were studied with a vibrating sample magnetometer (9000 VSM BDJ Electronics Inc, Troy, MI) at room temperature.

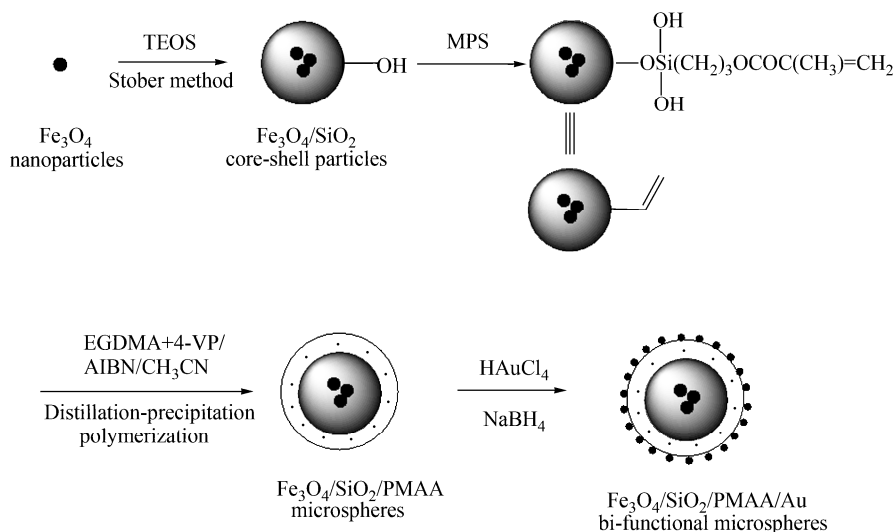
RESULTS AND DISCUSSION

Coating magnetic nanoparticles with silica shell is a convenient and important approach to expand the utilization of magnetic nanoparticles in both fundamental research and industrial application. Usually, an inert silica coating on the surface of magnetic nanoparticles can prevent their aggregation in suspension, improve their chemical stability and provide protection against toxicity. Furthermore, the presence of surface silanol groups can easily react with various coupling reagents to covalently attach a specific ligand to these magnetic particles for further application^[27]. In the present work, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticles were prepared according to the literature^[28] and used as seeds for distillation precipitation copolymerization to grow a polymer shell-layer with pyridyl groups further as stabilizer for gold nanocolloids. The TEM micrograph of the resultant $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles in Fig. 1(a) had a core-shell structure and relatively uniform dispersion with a mean diameter of 238 nm. The deeper contrast in the center of each particle corresponding to the magnetic nanoparticles as core implied that the lighter silica shell-layer was effectively encapsulated over the magnetic nanoparticles, which permitted the further development of tri-layer inorganic/polymer hybrid microspheres.

Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ Tri-layer Magnetic Hybrid Microspheres

Scheme 1 illustrated the synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ tri-layer magnetic hybrid microspheres, in which MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were used as seeds during the distillation precipitation copolymerization of EGDMA crosslinker and functional 4-VPy monomer in neat acetonitrile and then magnetic inorganic/polymer microsphere stabilized gold nanocolloids were *in situ* synthesized by the reduction of HAuCl_4 with NaBH_4 as reductant.

Distillation precipitation polymerization has been proven to be a convenient and effective method to synthesize monodisperse polymer microspheres with various functional groups^[29–31], core-shell^[32] and multi-layer structure^[33]. In the present work, MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core-shell nanoparticles were used as seeds for the preparation of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ tri-layer inorganic/polymer hybrid microspheres as



Scheme 1 Synthesis of magnetic polymer microsphere stabilized gold metallic nanocolloids $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$

shown in Scheme 1. The vinyl groups on the surface of MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds played a key role during the distillation precipitation polymerization of EGDMA as crosslinker and VPy functional monomer to result in tri-layer magnetic polymer microspheres, which was much similar to the role of the residual vinyl groups of polydivinylbenzene (PDVB)^[29] and poly(ethyleneglycol dimethacrylate) (PEGDMA)^[30] microspheres to capture the newly formed oligomers and monomers from the polymerization medium for the growth of the polymer particles. Following the strategy of our previous work^[26], MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were synthesized *via* the condensation of MPS with the reactive hydroxyl groups on the surface of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles to introduce the reactive vinyl groups on the surface of inorganic seeds. The modification of MPS was confirmed by the FT-IR spectrum in Fig. 2(a) with presence of the peaks at 1634 and 1703 cm^{-1} corresponding to the stretching vibrations of the vinyl group and the carbonyl components of MPS segments, respectively. These results proved the successful incorporation of the reactive vinyl groups onto the surface of the magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles, which permitted further the development of tri-layer inorganic/polymer microspheres. The reactive vinyl groups on the surface of MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds captured the newly formed oligomers and monomers during the distillation precipitation polymerization of EGDMA and VPy to result in tri-layer $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres without secondary-initiated particles and segments as shown by TEM micrograph in Fig. 1(b). To get $\text{P}(\text{EGDMA-co-VPy})$ shell-layer with thickness enough for the stabilization of gold metallic nanocolloids without secondary-initiated particles, two-stage polymerization was adopted. Otherwise, small secondary-initiated particles (TEM micrograph not shown here) would occur in the case of total monomers (EGDMA and VPy) loading higher than 0.3 mL in the present work. The result in Fig. 1(b) indicated that outer-layer with thickness around 6 nm was successfully encapsulated onto MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds in absence of any secondary-initiated particles after the two-stage polymerization, which implied that the capture ability of the incorporated reactive vinyl groups was efficient and enough for the construction of tri-layer inorganic/polymer magnetic hybrid microspheres *via* the capture of the oligomers and monomers during the distillation precipitation polymerization. The yields of these two steps distillation precipitation polymerization were 5% and 9%, respectively. The low yields during the polymerization steps were resulted from the low concentration of the comonomers in the reaction medium. Further, the loading capacity of the accessible pyridyl groups on the surface of the tri-layer magnetic polymer microspheres was 1.90 mmol/g determined by titration.

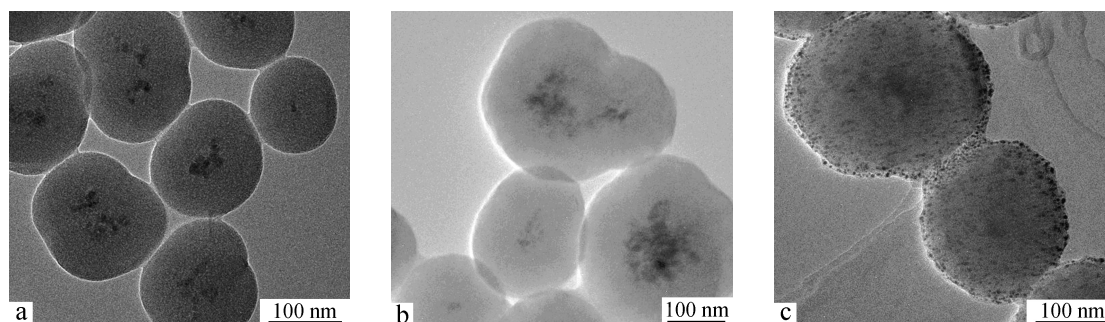


Fig. 1 TEM micrographs: (a) MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds, (b) tri-layer $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres and (c) magnetic polymer microsphere stabilized gold metallic nanocolloids $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$

The successful encapsulation of $\text{P}(\text{EGDMA-co-VPy})$ outer shell-layer onto MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds was further confirmed by FT-IR spectrum as shown in Fig. 2(b). Comparing with the FT-IR spectrum of MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds in Fig. 2(a), the FT-IR spectrum in Fig. 2(b) had strong absorption peaks at 1597 and 1731 cm^{-1} corresponding to the typical vibration of pyridyl groups and the carbonyl group of the ester in PEGDMA component, respectively. In a word, the crosslinked $\text{P}(\text{EGDMA-co-VPy})$ shell-layer with loading capacity of 1.90 mmol/g pyridyl groups and shell-thickness of 6 nm was successfully coated onto the surface of MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds by the two-stage distillation precipitation polymerization *via* the efficient capture procedure with the aid of the reactive vinyl groups on the surface of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds.

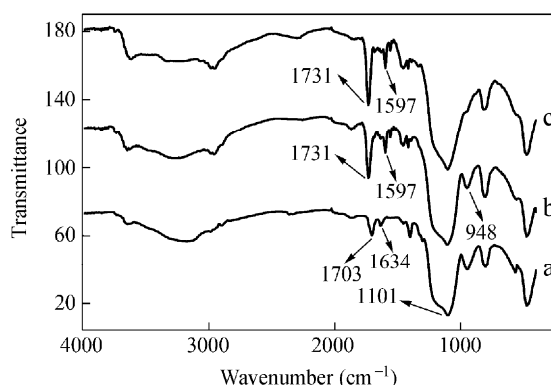


Fig. 2 FT-IR spectra: (a) MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds, (b) tri-layer $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres and (c) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$

Preparation of Magnetic Polymer Microsphere Stabilized Gold Nanocolloids

In our previous work, pyridyl functionalized $\text{P}(\text{EGDMA-co-VPy})$ microspheres were used to stabilize gold nanocolloids and prevent mutual aggregation with the aid of the interaction between pyridyl groups and Au atoms^[23, 26]. Consequently, tri-layer magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres with pyridyl groups on the outer polymer shell-layer were utilized for the *in situ* synthesis of magnetic polymer microsphere stabilized gold metallic nanocolloids through the reduction of HAuCl_4 with NaBH_4 as reductant. TEM has been proven to be a powerful technique for the determination the size and morphology of the polymer microsphere stabilized gold metallic nanocolloids in our previous works^[23–26]. Here, TEM micrograph of magnetic polymer microsphere stabilized gold nanocolloids was shown in Fig. 1(c), which demonstrated the absence of aggregation of the gold nanoparticles during the *in situ* reduction of HAuCl_4 in presence of the pyridyl group functionalized magnetic polymer microspheres as stabilizers. Nanometer size gold particles with

number average diameter of 5.2 nm was clearly observed on the surface of the pyridyl functionalized magnetic inorganic/polymer tri-layer microspheres as shown in Fig. 1(c). Careful inspection of the microsphere-stabilized gold nanocolloids in Fig. 1(c) indicated that some gold nanocolloids were buried under the surface layer of the polymer shell-layer, which may be due to the efficient stabilization effect of the pyridyl groups on the gel-layer of the magnetic polymer microspheres formed by the two-stage distillation precipitation polymerization. This was much similar to the results in our previous works^[23–26], which implied that the functional groups both on the surface and the soft gel-layer of the resultant polymer shell-layer were highly accessible with effective stabilization for gold metallic nanocolloids.

The extremely rapid formation of homogeneous gold metallic nanocolloids on the gel and surface of pyridyl functionalized polymer shell-layer for the tri-layer magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres upon addition of NaBH_4 as reductant without agglomeration demonstrated that the pyridyl groups were highly effective for the stabilization for gold metallic nanocolloids through the efficient interaction between pyridyl groups and Au atoms.

The Magnetization Property of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@Au$

The magnetic properties of the particles containing magnetic components were studied by using a VSM spectrometer at room temperature. Figure 3 shows the magnetization curve of MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds, tri-layer magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres, and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@Au$, respectively. Obviously, all of the three kinds of microspheres exhibited superparamagnetic properties originating from the magnetic Fe_3O_4 cores in the center of the microspheres at room temperature. In other words, little remanence existed when the magnetic field was removed. In addition, the saturation magnetization of the composite microspheres decreased with coating of functional polymer shell-layer and gold metallic nanocolloids, which was due to the decrease in the effective mass ratio of the magnetic cores in these microspheres. The magnetic polymer microsphere stabilized gold metallic nanocolloids with strong magnetization property provided them possible as a facilely recoverable catalyst in an external magnetic field.

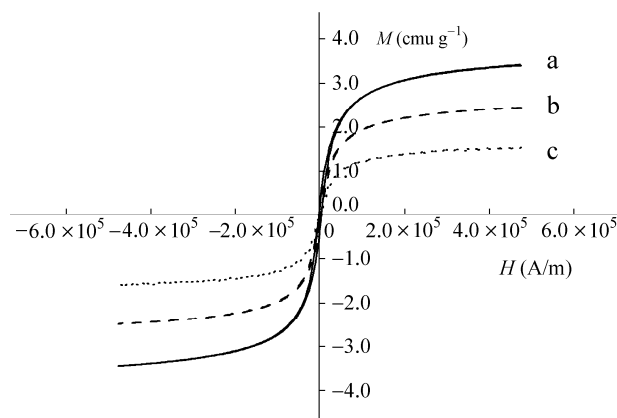


Fig. 3 Hysteresis loops for samples at room temperature: (a) MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds, (b) tri-layer $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres and (c) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@Au$

Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol in Aqueous Medium

To study the catalytic activity of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@Au$, the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AnP) in aqueous medium with NaBH_4 as reductant was selected as a model reaction. In this reaction, the reactant and product could be facilely detected by UV-spectroscopic method without formation of any by-product. An aqueous solution of 4-NP has a distinct UV-Vis spectral profile with absorption peak at 399 nm, while 4-AnP has a characteristic peak at 295 nm in UV-Vis absorption. In the present work, addition of aqueous NaBH_4 solution to 4-NP aqueous solution in the presence of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@Au$ as

catalyst resulted in a significant decrease of the absorption peak at 399 nm corresponding to 4-NP. During the reaction, the yellow color faded with the simultaneous formation of a new absorption peak at 295 nm assigning to 4-AnP as shown in Fig. 4. The complete disappearance of UV-Vis absorption peak at 399 nm corresponding to 4-NP occurred at 30 min. In other words, the reaction time of complete reduction of 4-NP to 4-AnP with $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ as catalyst was 30 min in the present work. However, the reduction of 4-NP does not proceed under the condition of large amount of NaBH_4 in absence of the magnetic polymer microsphere-stabilized gold metallic nanocolloids, which is proven by the unchanged UV-Vis absorption peak at 399 nm. Therefore, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ acted as an efficient catalyst to transfer the electrons from BH_4^- to 4-NP for the reduction of 4-AnP in aqueous medium.

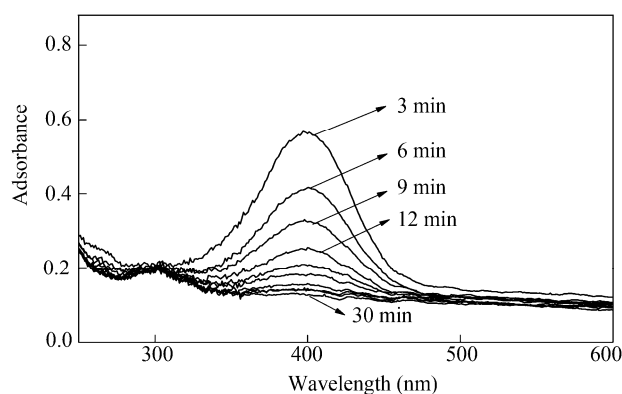


Fig. 4 UV-Vis spectra of the catalytic reduction of 4-NP to 4-AnP developed with different reaction time

On account of the magnetization property as discussed above, such magnetic polymer microsphere stabilized gold metallic nanocolloids were conveniently harvested or directed to a specific location with the aid of external magnetic field, which were clearly observed as shown in Fig. 5. Figure 5(a) was a light yellow mixture of 4-NP and NaBH_4 aqueous solution without addition of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$, while Fig. 5(b) showed the magnetic separation of these inorganic/polymer microsphere stabilized gold metallic nanocolloids after the catalytic reduction of 4-NP when an external magnetic field was applied after several minutes. The results indicated that such magnetic microsphere stabilized gold nanocolloids were directed along the external magnetic field and the reaction mixture became transparent and colorless, implying the complete catalytic reaction and facile separation of the gold nanocolloids for recovery.

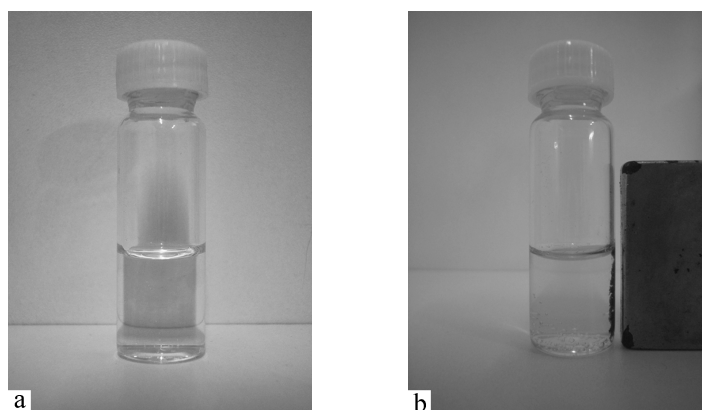


Fig. 5 Digital photos of catalytic system: (a) 4-NP and NaBH_4 solution before adding $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$, (b) after the catalytic reaction with $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ and recovery of the catalyst in an external magnetic field

To compare the catalytic property of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ catalyst with neat gold nano-colloids, sodium citrate stabilized Au nanoparticles with diameter of 23 nm were chosen as the comparative catalyst. It should be pointed out that the total surface area of the sodium citrate stabilized gold particles in the catalytic reaction approximately equals to that of Au nanoparticles of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ catalyst used above. Three parallel reactions were processed and the average reaction time was 340 s, which indicated that the catalytic activity of the sodium citrate stabilized 23 nm gold nano-colloids is much better than that (30 min) of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ catalyst in the first catalytic cycle of the reduction. Despite of this, the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ catalyst still can be facily separated from the reaction system by outer magnetic field, while the neat gold nano-colloids can hardly be recovered. The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ catalyst also showed better recycle-catalytic property after several reaction times as discussed in the following, whereas the neat gold nano-colloids would severely aggregate after one time of catalytic reaction according to the results from Yin's group^[22]. Such aggregation would cause sharp decrease of the catalytic property.

The recycling catalytic property of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$ was quantitatively determined by the reaction time for the complete disappearance of UV-Vis absorption peak at 399 nm corresponding to 4-NP as plotted in Fig. 6. The concentrations of the reactant and catalyst were increased by 20 times comparing to the above typical reduction. Therefore, the catalytic reduction could be completed within about 10 min. The results demonstrated that the catalytic property decreased slightly after each recycling with the aid of an external magnetic field in this work. After several times of recycling, the magnetic polymer microsphere stabilized gold nanocolloids tended to agglomerate during the catalytic reaction, which led to the decrease of catalytic activity of the magnetic microsphere stabilized gold nanocolloids. This may be due to the competitive coordination of the amino groups in 4-AnP products with Au nanocolloids, which decreased the stabilization effect of the pyridyl groups on the surface and gel-layer of the polymer shell-layer of the tri-layer magnetic microsphere. However, comparing with the carboxylic acid groupstabilized gold metallic nanocolloids in our previous work^[24], the decrease of the catalytic activity of the magnetic polymer microsphere stabilized gold metallic nanocolloids in this work was slight, which indicated that the protection of the pyridyl group for gold metallic nanocolloids was more effective than that of carboxylic acid group. This result was in good agreement with our previous conclusion^[25].

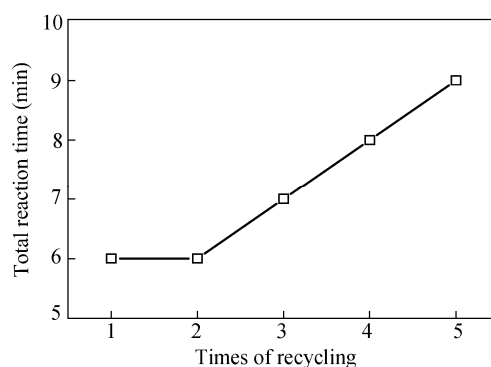


Fig. 6 The times of recycling versus total reaction time during the recycling catalytic reactions

CONCLUSIONS

Magnetic polymer microsphere stabilized gold metallic nanocolloids with number average diameter of 5.2 nm was *in situ* synthesized by the reduction of HAuCl_4 with NaBH_4 as reductant in presence of tri-layer magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})$ microspheres as stabilizer, prepared by the distillation precipitation polymerization of EGDMA crosslinker and VPy functional monomer in acetonitrile with MPS-modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ seeds which played a key role during the polymerization procedure to afford a tri-layer magnetic

inorganic/polymer microsphere having a pyridyl functionalized polymer outer shell-layer. The magnetic polymer microsphere stabilized gold metallic nanocolloids ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{P}(\text{EGDMA-co-VPy})@\text{Au}$) exhibiting high catalytic activity for the reduction of 4-NP to 4-AnP in aqueous system were facilely separated and recycled with the aid of an external magnetic field. The competitive coordination effect of amino groups in 4-AnP products with gold metallic nanocolloids led to the slight decrease of catalytic activity of gold nanocolloids after several catalytic reaction cycles. The composite nanocolloids behaved superparamagnetic property originating from the magnetic Fe_3O_4 core, which can be applied further in many industrial fields.

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