

Fabrication of functional hollow carbon spheres with large hollow interior as active colloidal catalysts

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Abstract

In this study, we have established a facile method to synthesize functional hollow carbon spheres with large hollow interior, which can act as active colloidal catalysts. The method includes the following steps: first, hollow polymer spheres with large hollow interior were prepared using sodium oleate as the hollow core generator, and 2,4-dihydroxybenzoic acid and hexamethylene tetramine (HMT) as the polymer precursors under hydrothermal conditions; Fe^{3+} or Ag^+ cations were then introduced into the as-prepared hollow polymer spheres through the carboxyl groups; finally, the hollow polymer spheres can be pseudomorphically converted to hollow carbon spheres during pyrolysis process, meanwhile iron or silver nanoparticles can also be formed in the carbon shell simultaneously. The structures of the obtained functional hollow carbon spheres were characterized by TEM, XRD, and TG. As an example, Ag-doped hollow carbon spheres were used as colloid catalysts which showed high catalytic activity in 4-nitrophenol reduction reaction.

Key words

hollow carbon spheres; hydrothermal synthesis; ion-exchange; colloidal catalysts

1. Introduction

Nanosized noble metal particles often show high catalytic activity because a larger fraction of the atoms is available for the catalytic process [1]. However, these nanosized particles must be stabilized using capping agents to prevent their aggregation, which results in the decrease/loss of the catalytic activity because of the “better” protection of active surface sites [2]. Furthermore, they are difficult to separate and recover in a liquid-phase reaction. To address this issue, an possible option is to deposit noble metal nanoparticles in/on a colloidal supports which can then be separated via filtration or centrifuge step [1,3,4]. Colloid catalysts have been widely used for catalytic transformations, which combine the advantages of homogeneous and heterogeneous catalysis [5,6]. In recent years, various colloidal supports have been developed, such as carbon [3,7,8], silica [9], polymer [10], and metal oxides [11]. Among them, hollow carbon spheres are considered as suitable catalyst supports, duo to their superior physical and chemical properties, such as high specific surface area, large void space, low effective density, good chemical resistance to both alkaline and acidic media and excellent thermal

stability [8,12–21].

Very recently, we reported a novel synthesis for delivering of diverse, nanoscale and structurally stable hollow spheres, by utilizing the weak acid-base interaction ($-\text{COO}^-/\text{NH}_4^+/-\text{COO}^-$) induced assembly with oleic acid as the $-\text{COO}^-$ source and the soft template, ammonia as the base catalyst and dihydroxybenzoic acid (DA) and formaldehyde (F) as the precursors under hydrothermal conditions [8]. Herein, we describe a similar method to fabricate functional hollow carbon spheres characterized with large hollow interior. For example, after doped with Ag nanoparticles on the colloidal hollow carbon spheres, they show high catalytic activity in 4-nitrophenol reduction reaction.

2. Experimental

2.1. Chemicals

2,4-dihydroxybenzoic acid (DA) was obtained from Aldrich. Hexamethylene tetramine (HMT), sodium oleate, oleic acid, ammonia (25%), HCl (37%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AgNO_3 , 4-nitrophenol (4-NP), and NaBH_4 were obtained

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from Sinopharm Chemical Reagent Company. All chemicals were used as received without any further purification.

2.2. Synthesis of hollow polymer spheres (HPS)

In a typical procedure, 0.625 mmol HMT and 2.5 mmol DA were dissolved in 95 mL deionized water. 110 mg sodium oleate was dissolved in 5 mL deionized water. The two solutions were mixed under slow stirring (100 rpm), and then kept stirring for 30 min to yield a stable emulsion. Finally the mixture solution was transferred into an autoclave and hydrothermally treated at 160 °C for 4 h. The resulting sample (HPS-1) was retrieved by centrifugation (3000 rpm, 10 min), washed with deionized water and ethanol, and dried at 50 °C for 6 h. Sample of HPS-2 was synthesized using 56 μL oleic acid as surfactant, whilst the other reaction conditions were the same as those of HPS-1. For sample HPS-3, extra 90 μL ammonia was added to the hydrothermal system, whilst the other reaction conditions were the same as those of HPS-2.

2.3. Synthesis of hollow carbon spheres

Hollow carbon spheres (HCS) were obtained by heating HPS to 800 °C with a heating rate of 3 °C·min⁻¹ and being held at that temperature for 4 h under N₂ atmosphere. In order to obtain graphitized hollow spheres (HGS), HPS was first immersed in aqueous FeCl₃·6H₂O (0.24 M) overnight to introduce graphitization catalyst. Subsequently, the polymer was washed with deionized water and ethanol, dried at 50 °C for 6 h, and then pyrolyzed at 850 °C for 3 h under nitrogen flow. The obtained black powder was treated with concentrated HCl (37%) to remove the leachable Fe-based particles. Finally, the products were obtained after washing and drying.

2.4. Synthesis of Ag-doped hollow colloidal catalysts

HPS was first immersed in an aqueous AgNO₃ solution (0.24 M) overnight to load Ag⁺. Subsequently, the polymer was washed with deionized water and ethanol, dried at 50 °C for 6 h, and then pyrolyzed at 400 °C for 2 h under nitrogen flow to obtain the final HCS-Ag. For further application, the HCS-Ag catalyst was prepared as aqueous suspension, i.e. 20 mg HCS-Ag was homogeneously dispersed in 5 mL deionized water.

2.5. Catalytic reduction of 4-nitrophenol

Aqueous solutions of 4-nitrophenol (0.036 mL, 0.01 M) and NaBH₄ (0.24 mL, 0.5 M) were added to deionized water (2.25 mL) under constant stirring at room temperature. Subsequently, 0.015 mL of aqueous dispersion of the HCS-Ag catalyst was added to the above solution. The mixture was immediately transferred into a quartz cuvette with an optical path length of 1 cm, and UV-visible absorption spectra were recorded to monitor changes of the reaction mixture. The so-

lution was in situ measured every 3 min to obtain the successive information about the reaction.

2.6. Characterization

Transmission electron microscopy (TEM) analysis were carried out with a Tecnai G²20S-Twin equipment operating at 200 kV. The samples for TEM analysis were prepared by dropping an ethanol droplet of the products on carbon-coated copper grids and drying at room temperature. Scanning electron microscopy (SEM) investigations were carried out with a Hitachi S-4800 instrument. Nitrogen adsorption isotherms were measured with a Micromeritics ASAP2020 adsorption analyzer at 77 K. Before the measurements, all the samples were degassed at 200 °C for 6 h. The specific surface areas were calculated from the adsorption data in the relative pressure range of 0.05 to 0.3 using the Brunauer-Emmett-Teller (BET) method. The total pore volume was estimated from the amount adsorbed at a relative pressure of 0.97. Thermogravimetric analysis (TG) was conducted on a thermogravimetric analyzer STA 449 F3 with a heating rate of 10 °C·min⁻¹. The UV-vis spectra were recorded on a UV-vis spectrometer (Techcomp UV 2300) at 25 °C.

3. Results and discussions

3.1. Hollow polymer spheres with large hollow interior

In our previous work, a novel and generalizable hydrothermal synthesis for diverse hollow nanospheres was described, and these hollow nanospheres can be polymer, carbon, graphitic carbon, and metal doped carbon hollow nanospheres. The synthesis principle was based on the weak acid-base interaction ($-\text{COO}^-/\text{NH}_4^+/-\text{COO}^-$) induced assembly, which is created by dihydroxybenzoic acid, ammonium cations, and oleic acid [8]. So, the key point to fabricate hollow structure in the hydrothermal system is the presence of ammonium cations and carboxyl functional groups possessed by polymer precursor and hollow core generator. As we know, hexamethylene tetramine (HMT) can decompose into formaldehyde and ammonia under hydrothermal conditions [22]. In this study, in order to prepare hollow polymer spheres with large hollow interior, we found that this aim can be realized by modifying the synthesis conditions, such as using HMT to replace formaldehyde/ammonia, and sodium oleate to replace oleic acid. As shown in Figure 1(a), the hollow cavity size of sample HPS-1 is in the range of 150–400 nm, and the shell thickness is about 90 nm. Compared with the sample fabricated by the oleic acid/ammonia/DA&F system reported previously [8], HPS-1 sample possesses much larger hollow interior and wider sphere size distribution. This phenomenon may be attributed to the difference in the emulsion formation process. For oleic acid/ammonia/DA&F system, after mixing the oleic acid/ammonia solution and DA/F solution, the transparent mixture gradually transformed into emulsion solution because it needs time for inducing the weak acid-

base interaction, the reaction between ammonia and carboxyl-containing reagents. Therefore, the emulsion droplets are small and uniform in this system, which leads to the formation of uniform products with small hollow interior. For sodium oleate/HMT/DA system, after mixing the sodium oleate solution and HMT/DA solution, the emulsion formed immediately. The emulsion droplets obtained in this process are huge and non-uniform, which results in the formation of products with large hollow interior and broad size distribution. These results indicate that the formation process of emulsion can determine the structure of hollow sphere.

For comparison, oleic acid instead of sodium oleate was dispersed into the solution containing DA and HMT by ultrasonic treatment for 1 h to form an emulsion. Subsequently, the emulsion solution was transferred into an autoclave for

hydrothermal aging for 4 h at the temperature of 160 °C (denoted as HPS-2). As seen in Figure 1(b), the products consist of non-uniform hollow spheres with a wide size distribution (approximately ranging from 300 to 800 nm) and solid spheres with a diameter of ca. 100 nm. This indicates that oleic acid could not form uniform emulsion by ultrasonic treatment without any surfactant stabilization or ammonia neutralization at room temperature. HPS-3 was prepared under similar conditions as those of HPS-2, but oleic acid was dissolved in ammonia solution. As can be seen in Figure 1(c), sample HPS-3 consists of both hollow nanospheres with smaller size in the range of 100–200 nm and interconnected spheres. It is thus deduced that HMT cannot be used together with oleic acid to prepare hollow polymer spheres with good quality.

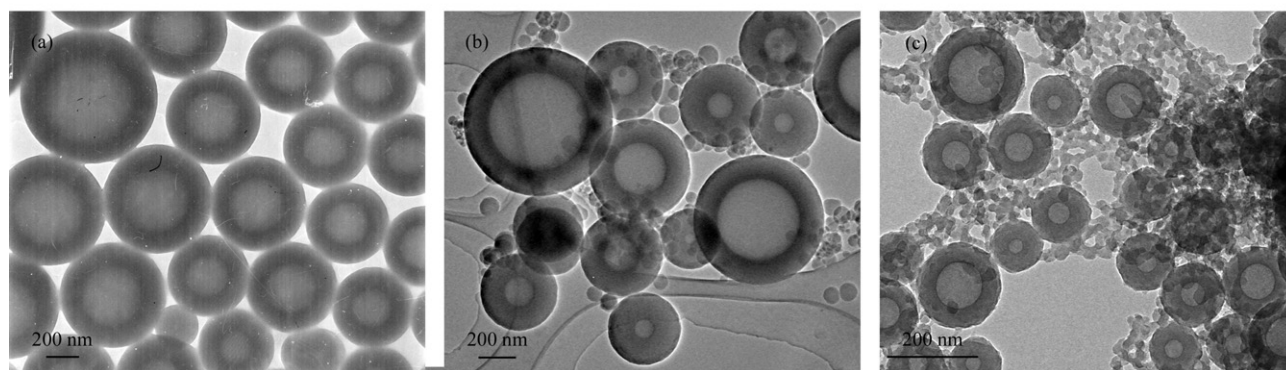


Figure 1. TEM images of (a) HPS-1, (b) HPS-2 and (c) HPS-3

3.2. Hollow carbonaceous spheres

Phenolic resins are usually employed as excellent precursors for the production of carbon products due to their excellent characteristics, such as high temperature resistance, thermal abrasiveness and high yield of carbon conversion [3,7,8,18,21,23]. The as-prepared hollow polymer spheres can be pseudomorphically converted to hollow carbon spheres through pyrolysis process. As shown in Figure 2(a) and (b), the TEM and SEM images of HCS-1 show remarkably larger hollow interior and a crack-free shell. Likewise, the HPS can be easily converted to hollow graphitized carbon spheres with Fe^{3+} cations ion-exchange, pyrolysis, and HCl washing processes [8,21,24]. As shown in Figure 2(c), sample of HGS-1 retained a perfect hollow core-shell structure. The high resolution transmission electron microscopy (HRTEM) observations (Figure 2d and e) reveal that the hollow spheres consist of well-developed nanosized turbostratic graphite structures and the average thickness of the graphitic sheet is estimated to be 5–10 nm. The graphitized nature of HGS-1 was also characterized by XRD. As shown in Figure 3(a), the patterns display the typical reflections of well developed graphitic carbon, and weak reflections of Fe and Fe_3C .

The porosities of the obtained HCS-1 and HGS-1 were analyzed by N_2 physisorption. The N_2 physisorption isotherm of HCS-1 (Figure 3b) belongs to type I curve, revealing pre-

dominantly microporous feature. The surface area and total pore volume of HCS-1 are $543 \text{ m}^2/\text{g}$ and $0.3 \text{ cm}^3/\text{g}$, respectively. Unlike HCS-1, sample of HGS-1 possesses type IV isotherm, indicating mesoporous feature. This phenomenon can be attributed to the structure collapse of carbon shell and movement of Fe-based particles in the graphitization process. The specific surface area and total pore volume of HGS-1 are $420 \text{ m}^2/\text{g}$ and $0.26 \text{ cm}^3/\text{g}$, respectively.

3.3. 4-nitrophenol reduction by Ag-doped hollow colloidal catalysts

Normally, various metal cations can be introduced into the HPS-1 via ion-exchange process which can then be engineered to colloidal catalysts with a high dispersion of nanoparticles as active species. Herein, as an example, Ag^+ was introduced into HPS-1 through an ion-exchange process. After pyrolysis, HCS-Ag was obtained. Figure 4(a) shows the TEM image of the products. Interestingly, a large number of Ag particles with diameters ranging from 10 to 15 nm are dispersed throughout the entire sample HCS-Ag. Figure 4(b) shows the XRD pattern of HCS-Ag. The main diffraction peaks at 38.1° , 44.3° , 64.4° , 77.3° , and 81.7° are indexed to (111), (200), (220), (311) and (222) reflections of silver, respectively (JCPDS File 04-0783). The weight content of Ag determined by TG is about 11.8% (Figure 4c).

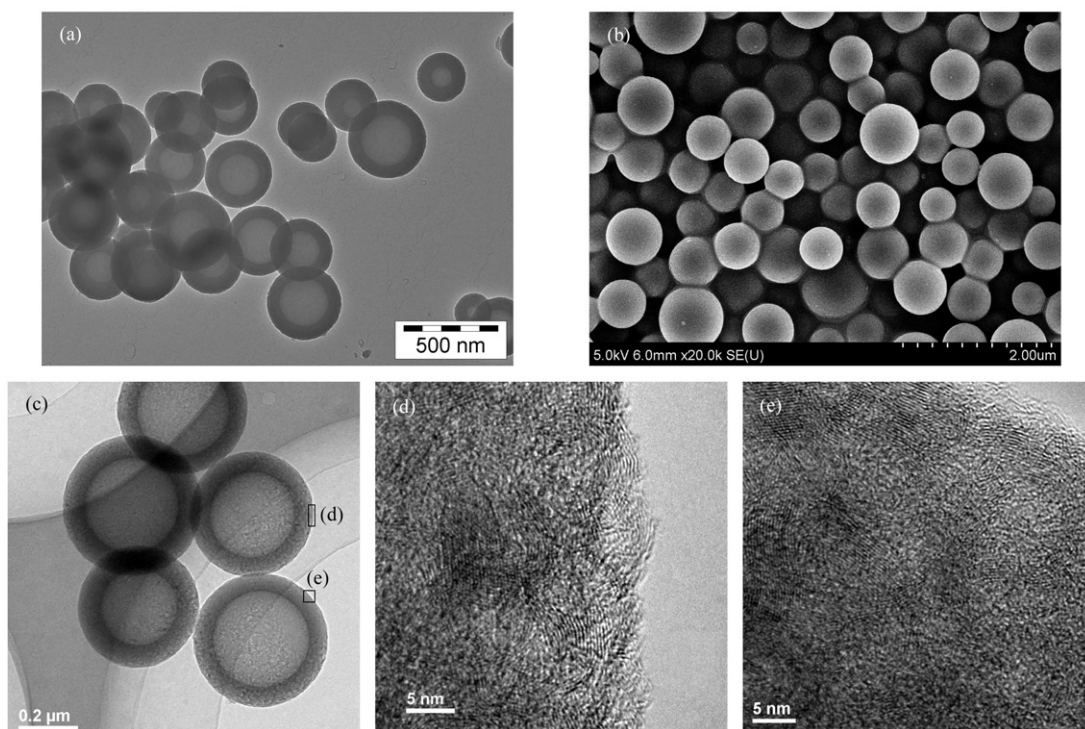


Figure 2. TEM (a) and SEM (b) images of HCS-1, TEM (c) and HRTEM images (d,e) of HGS-1

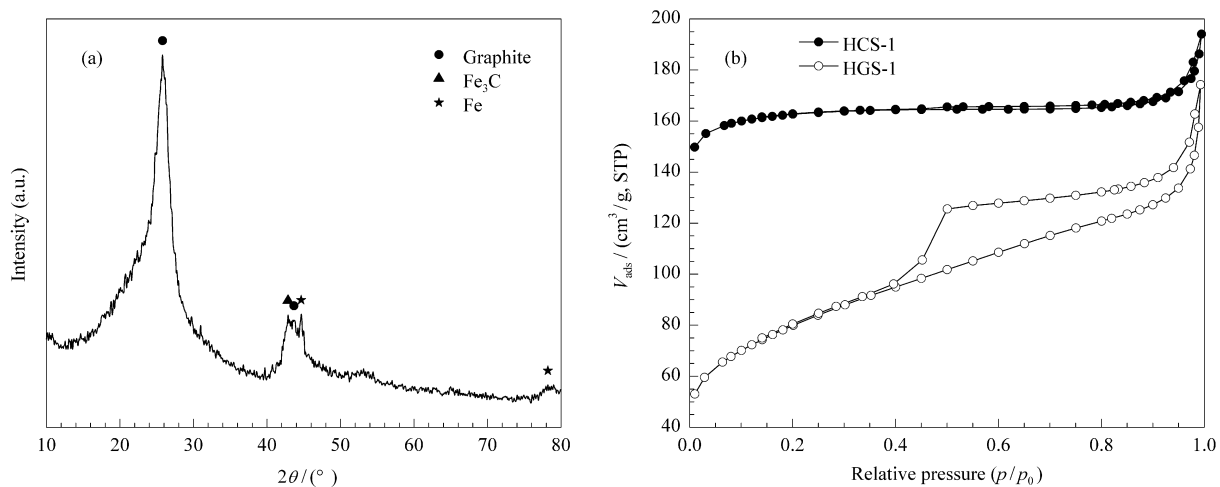


Figure 3. (a) XRD pattern of HGS-1, (b) N_2 physisorption isotherms of HCS-1 and HGS-1 (the isotherm of HGS-1 offset vertically by $50 \text{ cm}^3/\text{g}$, STP)

The reduction of 4-NP by sodium borohydride was chosen as a model reaction for studying the catalytic performances of hollow Ag-doped carbon spheres. As seen in Figure 4(d), the absorption maximum of the light yellow aqueous 4-NP solution is shown at $\sim 318 \text{ nm}$. After addition of sodium borohydride, the absorption maximum shifts to 400 nm and the light yellow color turns darker (Figure 4d) because of the formation of 4-nitrophenolate [25]. However, when a small amount of HCS-Ag (0.06 mg) composite was added, reduction commences and the time-dependent absorption spectra (Figure 4e) show a decrease in intensity of the absorption peak at 400 nm and concomitant development of a new peak

at 300 nm corresponding to 4-aminophenol (4-AP), i.e., the reduction product of 4-NP. The yellow color has completely disappeared after 9 min of reduction (inset Figure 4e). No reaction was observed in a control experiment using HCS-1, indicating that only Ag-doped composites play a catalytic role in the reduction of 4-NP. Considering that the reductant concentration is much higher than that of 4-NP, the reaction should be of first-order with regard to the reactant. A linear relationship between $\ln(C_t/C_0)$ and reaction time (t) was obtained for this reduction catalyzed by HCS-Ag (Figure 4f), wherein, the ratios of 4-NP concentrations (C_t at time t) to its initial value C_0 ($t = 0$) were directly given by the relative intensity of the

respective absorbance A_t/A_0 . This equation well matches the first-order reaction kinetics. The rate constant k was calculated to be 0.383 min^{-1} (or $106.4 \text{ s}^{-1} \cdot \text{g}^{-1}$) for this reaction. Compared with other substrate-supported Ag nanoparticles, the rate constant k of HCS-Ag composite is much higher than

previously reported ratios for silver nanoparticles supported on carbon spheres ($1.69 \text{ s}^{-1} \cdot \text{g}^{-1}$) [26]. This might be attributed to the high proportion of exposed Ag nanoparticles on hollow spheres than that of solid spheres, by a unit mass of catalysts.

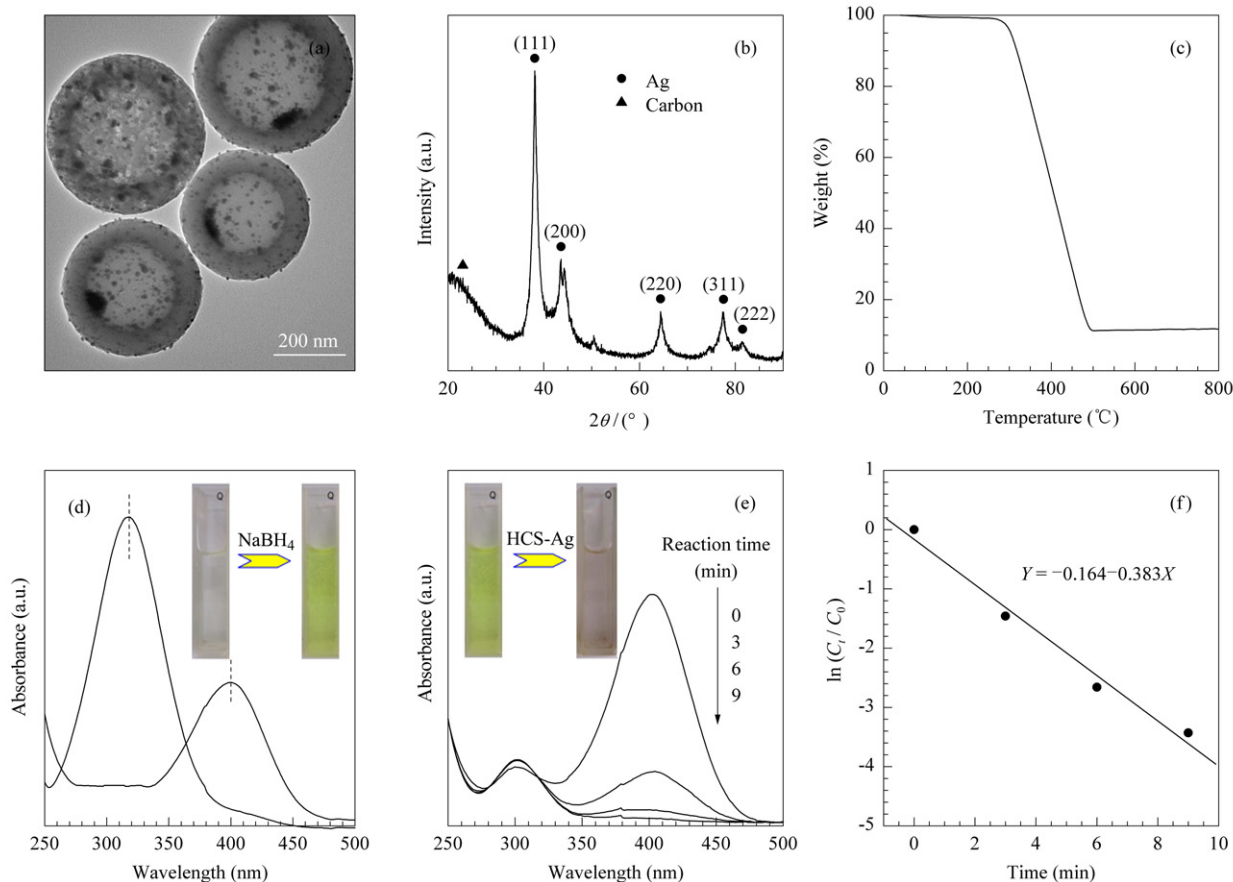


Figure 4. TEM image (a), XRD pattern (b), and TG curve (c) of HCS-Ag; UV-vis spectra and associated color changes (d) of 4-nitrophenol before and after adding NaBH_4 solution, and the reduction of 4-nitrophenol in aqueous solution recorded every 3 min using the HCS-Ag as a catalyst (e); the relationship between $\ln(C_t/C_0)$ and reaction time (f)

4. Conclusions

We have synthesized hollow polymer spheres with large hollow interior using sodium oleate as the hollow core generator, and hexamethylene tetramine and 2,4-dihydroxybenzoic acid as the polymer precursors under hydrothermal conditions. After introducing Fe^{3+} or Ag^+ into the polymer spheres via an ion-exchange process, finally, functional hollow carbon spheres with large hollow interior can be prepared. As an example, the high catalytic activity of Ag-doped colloidal catalysts has been demonstrated using a model reaction, 4-nitrophenol reduction reaction. We believe that this work provides a simple and generic recipe for the design of noble metal nanoparticles-doped hollow carbon spheres catalysts. This could offer new opportunities in the field of nanoengineering of targeted colloidal catalysts by taking the advantage of their excellent properties.

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