

Research Note

Encapsulation of nanosized catalysts in the hollow core of a mesoporous carbon capsule

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Abstract

We present a novel synthetic method for the fabrication of encapsulated nanosized catalysts that have a core/shell structure consisting of numerous inorganic nanoparticles confined within the hollow core of a mesoporous carbon capsule. Specifically, we applied this synthetic strategy to CoFe_2O_4 nanoparticles (size ~ 10 nm), which were encapsulated within inner core of porous carbon capsules of ca. 350 nm diameter. We examined the catalytic activity of this core/shell catalytic composite toward H_2O_2 decomposition (Fenton reaction) and found that decomposition rates measured for this material were considerably higher than those for the unsupported nanoparticles and other nanocatalysts reported in the literature. The synthetic strategy described here could be extended to the preparation of other catalysts with similar core/shell structures.

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1. Introduction

Heterogeneous catalysts usually consist of nanoparticles exhibiting catalytic activity supported on high-surface area solids. In such catalysts, the overall rate of the catalytic process is determined not only by the intrinsic properties of the catalyst, but also by mass transfer pathways that are dependent on the physical properties of the support. Catalytic activity can be enhanced by improving the dispersion of the catalytic nanoparticles over the support and minimizing diffusional resistance. The use of unsupported catalytic nanoparticles instead of supported ones is an attractive way to improve catalytic activity, because it allows minimization of the mass transfer resistance typical of supported catalysts. Recently, much attention has been given to the synthesis of nanoparticles (e.g., metals, oxides) and the study of their catalytic activity [1–4]. Unfortunately, nanosized catalysts tend to aggregate due to surface interactions, greatly reducing their activity [5]. To ensure good catalytic performance, it is important that they be prevented from coalescing. This objective can be achieved by coating the

catalytic nanoparticles with such substances as organic ligands (polymers) [6], dendrimers [7], porous carbon shells [8,9], or inorganic layers [10]. The techniques usually used to protect the nanosized catalytic particles are rather complex, involving a multistep process. Herein we report a novel and simple approach to preparing nanoparticulate catalysts that are protected against coalescence. The synthetic method involves confining the catalytic nanoparticles within the macroporous core of a mesoporous carbon capsule of ~ 350 nm diameter with a porous, ~ 40 – 50 nm thick shell. This methodology has two important advantages: (a) The core of the carbon capsule can be almost completely filled with numerous nanoparticles rather than by only one [8–10] or a few nanoparticles, and (b) the mesopores (size ~ 2 – 3 nm) of the carbon shell ensure rapid diffusion of the reactant and products. In the present work, we have exemplified this synthetic strategy by preparing cobalt ferrite (CoFe_2O_4) nanoparticles, which were confined within the core of a mesoporous carbon capsule. We evaluated the catalytic performance of this system for the decomposition of H_2O_2 in liquid phase (Fenton reaction) and demonstrated the effectiveness of this core/shell catalyst by comparing the results with those derived from nonencapsulated CoFe_2O_4 nanoparticles.

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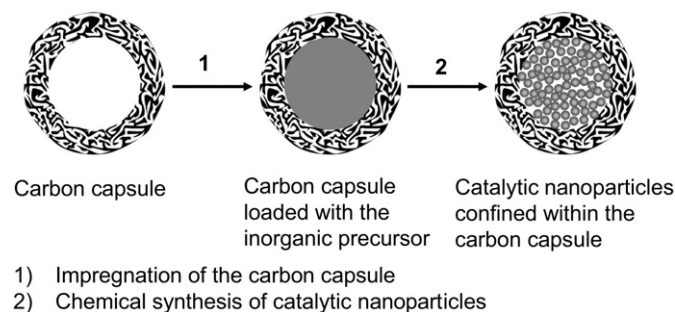


Fig. 1. Synthetic scheme for the preparation of encapsulated nanocatalysts.

2. Experimental

The carbon capsules with a hollow core and a mesoporous shell were prepared using submicrometric solid core/mesoporous shell silica spheres [11] as sacrificial templates following the procedure reported by Hyeon et al. [12]. To incorporate the CoFe_2O_4 nanoparticles in the hollow core, the carbon capsules were impregnated with a solution of hydrated metal nitrates in ethanol in the stoichiometric proportion (Co/Fe atomic ratio of 0.5). The solution was added dropwise up to incipient wetness, and then the impregnated sample was dried at 80°C . This process was repeated several times until the desired amount of inorganic precursor was attained ($\sim 50\%$ wt of CoFe_2O_4). To convert the impregnated inorganic precursor into CoFe_2O_4 nanoparticles, we used a method recently reported by our group [13]. In brief, the impregnated sample was first exposed in a closed vessel to propionic acid vapors at 80°C for 15 h and then thermally treated under N_2 at 280°C for 2 h. The general synthetic strategy used to prepare these core/shell catalytic composites is illustrated in Fig. 1.

Nonencapsulated CoFe_2O_4 nanoparticles were synthesized following a nanocasting route, using a silica gel as a sacrificial template. The experimental details of the procedure used for the synthesis of this material are given elsewhere [14,15].

X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA, using $\text{CuK}\alpha$ radiation. The morphology of the powders was examined by scanning electron microscopy (SEM), using a Zeiss DSM 942 microscope, and transmission electron microscopy (TEM), using a JEOL-2000 FXII microscope. Nitrogen adsorption and desorption isotherms were performed at -196°C in a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was deduced from the isotherm analysis in the relative pressure range of 0.04–0.20. The total pore volume was calculated from the amount adsorbed at a relative pressure of 0.99. The PSD was calculated by means of the Kruk–Jaroniec–Sayari method [16].

Hydrogen peroxide decomposition experiments were performed in mechanically stirred batch conditions (orbital stirrer). Experiments were carried out at two initial $[\text{H}_2\text{O}_2]_0$ concentrations, 5 mM and 0.2 M. Experiments performed at $[\text{H}_2\text{O}_2]_0 = 5$ mM were conducted in a 50-ml flask using 32 mg of CS- CoFe_2O_4 (~ 15 mg of active phase) or 15 mg of CoFe_2O_4 nanoparticles. Experiments performed at $[\text{H}_2\text{O}_2]_0 = 0.2$ M were conducted over 25 ml of solution, using 15 mg of CS-

CoFe_2O_4 (~ 7 mg of active phase) or 7 mg of CoFe_2O_4 nanoparticles. The decomposition reaction was followed by measurement of the formation of gaseous oxygen in a volumetric system.

3. Results and discussion

The structural properties of this nanocomposite, designated CS- CoFe_2O_4 , were investigated by SEM, TEM, X-ray diffraction (XRD) analysis, and gas adsorption measurements. The SEM image of the CS- CoFe_2O_4 particles show that they are uniform and have a spherical morphology with a diameter of around 350 nm (Fig. 2a). Some of these particles appear to be deformed, which is a consequence of their hollow structure. The TEM images obtained for these materials clearly reveal their core/shell structure (Figs. 2b, 2c, and 2d). Indeed, the hollow core (diameter ~ 250 nm) of the carbon capsules is almost completely filled with cobalt ferrite nanoparticles (Figs. 2b and 2c). The encapsulated inorganic phase consists of agglomerated nanoparticles. It can be seen that these nanoparticles are surrounded by a porous carbon layer (Fig. 2c), which has a thickness of ~ 40 – 50 nm (Fig. 2d). What is more, the porous carbon shell hardly contains any inorganic nanoparticles, as clearly evidenced by the TEM image displayed in Fig. 2d. This reveals that a significant fraction of the porosity of the carbon shell is preserved, which is important for guaranteeing the fast transfer of matter between the confined catalyst and the external environment (reactants).

More detailed information about the porous characteristics of the carbon shell was obtained by nitrogen physisorption analysis. Fig. 3 shows the nitrogen sorption isotherm and the pore size distribution (inset) obtained for CS- CoFe_2O_4 . This sample exhibits a BET surface area of $690\text{ m}^2\text{ g}^{-1}$ and a pore volume of $0.55\text{ cm}^3\text{ g}^{-1}$. The pore size distribution shows that the porous carbon shell of this composite contains a porosity composed of mesopores with size centered at ~ 2.5 nm (see Fig. 3, inset).

These results indicate that encapsulation of cobalt ferrite nanoparticles within the carbon capsule causes a reduction in porosity. Thus, the BET surface area and pore volume values expressed on a carbon mass basis (normalized to carbon content) are $1380\text{ m}^2\text{ g}^{-1}\text{ C}$ and $1.1\text{ cm}^3\text{ g}^{-1}\text{ C}$, considerably lower than those obtained for the carbon capsules ($1870\text{ m}^2\text{ g}^{-1}$ and $2.0\text{ cm}^3\text{ g}^{-1}$). This reduction is associated with the fact that a small amount of inorganic nanoparticles are inserted in the carbon shell. The foregoing results indicate that although the textural properties of the carbon shell in the CS- CoFe_2O_4 sample are reduced by the presence of nanoparticles, the shell still retains a widely accessible porosity.

Evidence of the formation of the cobalt ferrite spinel was obtained by XRD analysis. The XRD pattern shown in Fig. 4 reveals that the encapsulated CoFe_2O_4 nanoparticles are well crystallized. The size of the crystallites deduced by applying Scherrer's equation to the (311) peak of the XRD pattern is about 10 nm. The size of the cobalt ferrite nanoparticles deduced by means of XRD is in agreement with that obtained by TEM inspection (see Figs. 2c and 2d).

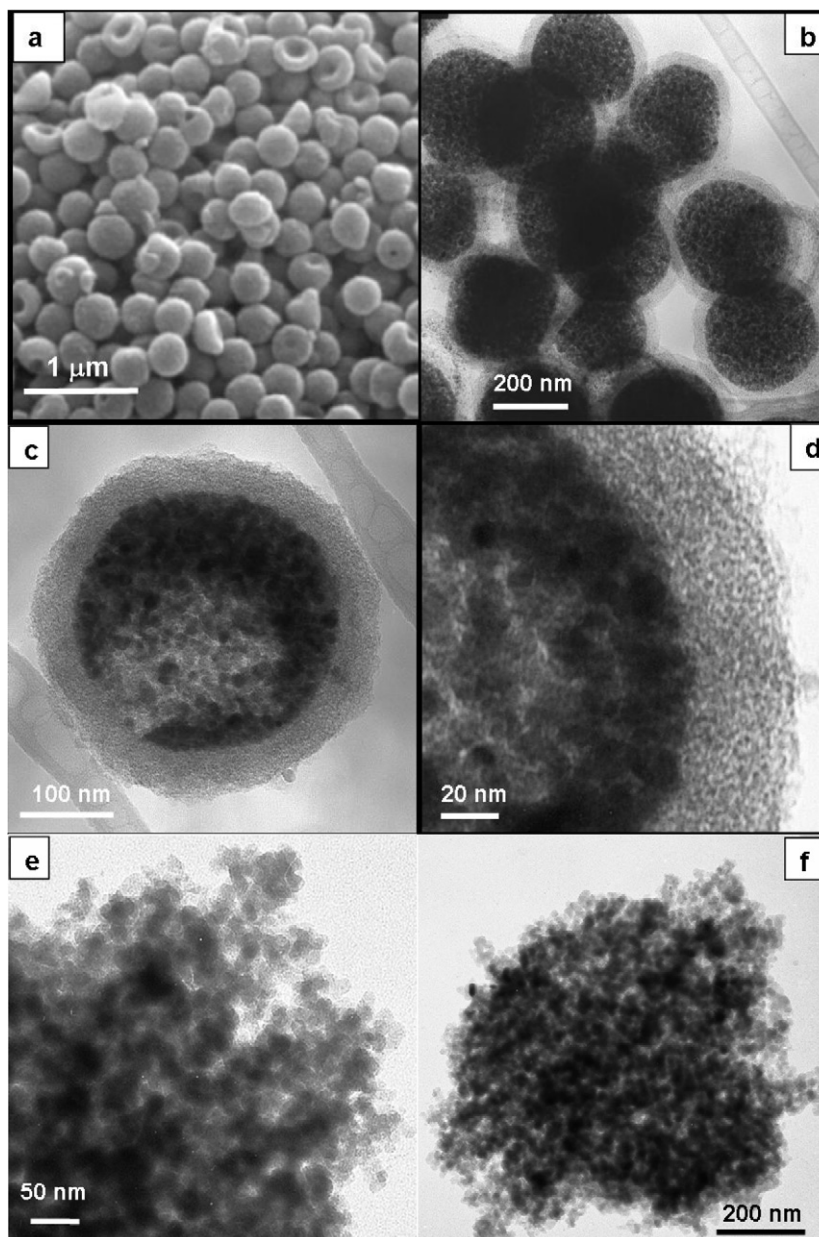


Fig. 2. (a)–(d) SEM and TEM images for the core/shell CS-CoFe₂O₄ nanocomposite. (e, f) TEM images for the nonencapsulated CoFe₂O₄ nanoparticles.

One of the most important reactions investigated over ferrite catalysts is the heterogeneous Fenton process ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+}$), which involves the *in situ* generation of hydroxyl radicals ($\bullet\text{OH}$) that allow the oxidation and mineralization of organic pollutants dispersed in an aqueous medium [17–20]. To accelerate the reaction rate, the Fenton process usually combines the use of specific catalysts with UV irradiation [18, 21,22]. However, there is great interest in the development of highly active catalysts that do not require the use of UV light. This can be achieved by using nanosized catalysts, the high external surface area of which ensures high activity. Accordingly, in this work we investigated the use of high-surface area CoFe₂O₄ nanoparticles confined within a mesoporous carbon capsule (CS-CoFe₂O₄ sample) as a heterogeneous Fenton catalyst. For comparison purposes, we also examined the

catalytic activity of nonencapsulated CoFe₂O₄ nanoparticles. These nanoparticles have a size of ~ 10 nm and an external surface area of $117 \text{ m}^2/\text{g}$ [14]. However, due to the high superficial energy inherent to the nanoparticles and to the magnetic properties of cobalt ferrite, the nonencapsulated CoFe₂O₄ nanoparticles (see Fig. 2e) tend to coalesce and form large (up to $1 \mu\text{m}$) aggregates, as evidenced by the TEM image shown in Fig. 2f. Fig. 5 shows the variations of the decomposed H_2O_2 with time for both types of catalysts, that is, encapsulated and nonencapsulated CoFe₂O₄ nanoparticles at two different initial H_2O_2 concentrations. It is clear that remarkable activity is achieved by the encapsulated catalyst (CS-CoFe₂O₄) regardless of the initial concentration. Thus, the decomposition of H_2O_2 is completed after <35 min for $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$ and after <10 min for $[\text{H}_2\text{O}_2]_0 = 0.2 \text{ M}$, whereas for nonencapsu-

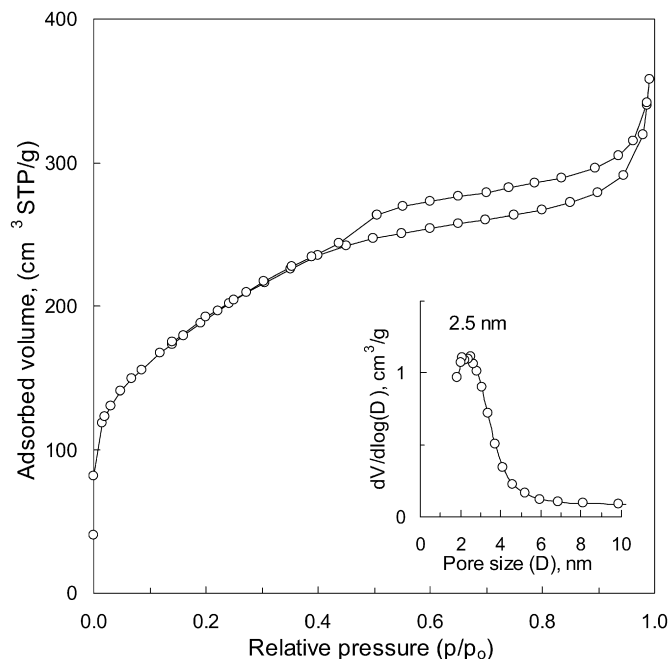


Fig. 3. Nitrogen sorption isotherm and pore size distribution (inset) of CS-CoFe₂O₄.

lated CoFe₂O₄ nanoparticles, completing the reaction requires ~ 75 min for $[\text{H}_2\text{O}_2]_0 = 5$ mM and ~ 50 min for $[\text{H}_2\text{O}_2]_0 = 0.2$ M. We believe that the formation of large agglomerates in the case of nonencapsulated CoFe₂O₄ nanoparticles induces an increase in mass transfer resistance, which is responsible for its lower catalytic activity in relation to the encapsulated catalytic system. The rate constants deduced for H₂O₂ decomposition ($[\text{H}_2\text{O}_2]_0 = 5$ mM) by assuming a first-order reaction are 0.111 min^{-1} for CS-CoFe₂O₄ nanoparticles and 0.041 min^{-1} for CoFe₂O₄ nanoparticles. These values for the rate constant are considerably larger than that recently reported by Hyeon et al. for an iron oxide–alumina–silica (FeAlSi) composite Fenton catalyst, which was ca. $7.82 \times 10^{-4} \text{ min}^{-1}$ under similar experimental conditions [23]. We examined the catalytic activity of nonimpregnated carbon capsules and observed that it is more than three orders of magnitude lower in relation to that measured for the CS-CoFe₂O₄ sample.

The foregoing results clearly show that the activity of a catalytic system formed by unsupported nanosized particles can be greatly enhanced if the aggregation of nanoparticles is prevented. An important characteristic of the CS-CoFe₂O₄ catalytic system is that it can be easily recovered from the reaction media by applying an external magnetic field. Thus, it was experimentally observed that the CS-CoFe₂O₄ particles dispersed in water are rapidly attracted (< 1 min) by a conventional magnet placed close to the reaction vessel (Fig. 5, inset), demonstrating the efficacy of magnetic separation.

4. Conclusion

In summary, we have presented a synthetic method for the fabrication of a novel catalytic system composed of numer-

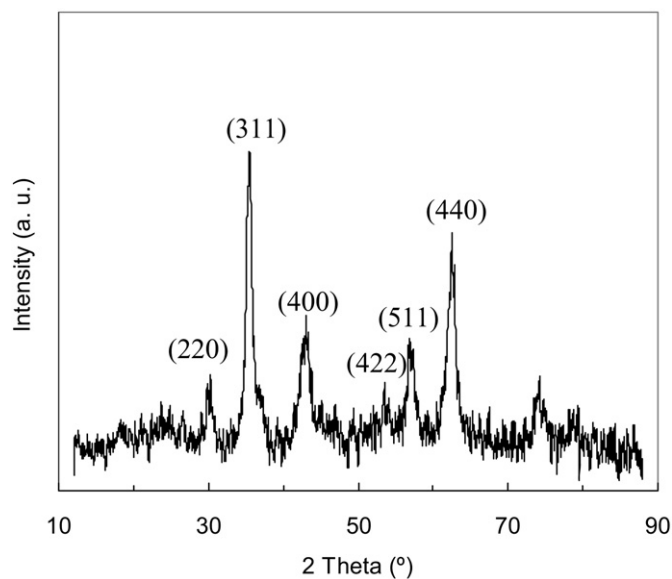


Fig. 4. X-ray diffraction pattern of CS-CoFe₂O₄.

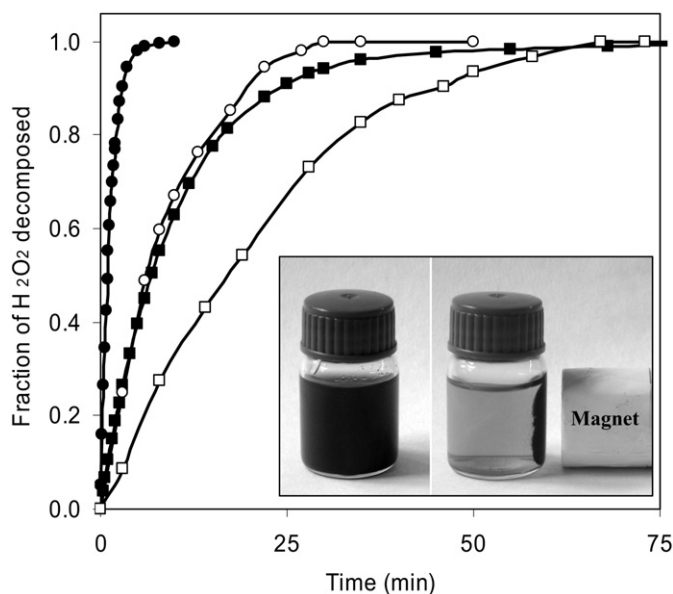


Fig. 5. Modification of the fraction of H₂O₂ decomposed with the time for CS-CoFe₂O₄ (circles) and CoFe₂O₄ nanoparticles (squares). Empty symbols: $[\text{H}_2\text{O}_2]_0 = 5$ mM. Solid symbols: $[\text{H}_2\text{O}_2]_0 = 0.2$ M. Inset: Illustration of the magnetic separation of the CS-CoFe₂O₄ nanocomposite from the liquid media.

ous unsupported nanoparticles confined within the hollow core of a porous carbon capsule. This synthetic strategy was exemplified using a heterogeneous Fenton catalyst consisting of CoFe₂O₄ nanoparticles encapsulated within porous carbon capsules of ca. 350 nm diameter. The composite exhibited very high catalytic activity for the decomposition of H₂O₂, exceeding that of similar nonencapsulated CoFe₂O₄ nanoparticles and other heterogeneous Fenton catalysts reported in the literature. The methodology presented here constitutes a general synthetic route that could be applied to the preparation of other catalytic systems with a similar core/shell architecture.

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