Multifunctional Amphiphilic Carbonaceous Microcapsules Catalyze Water/Oil Biphasic reactions

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Supporting Information

1. Preparation of porous hollow carbonaceous spheres (PHCSs)
2. Preparation of metal and Fe3O4 coated PHCSs
3. Assemble of Pickering emulsion
4. Zininc reduction
5. The reduction of p-nitroanisole with NaBH4
6. Characterization
7. Optical microscopy images of PHCSs stabilized Pickering emulsion
8. Conductivity of the Pickering emulsions as a function of the volume fraction of water
9. Optical microscopy images of the pH-sensitive behavior of the PHCSs
10. Hydrolysis of α,α,α-Trichlorotoluene
11. Synthesis of benzoic anhydride from benzoyl chloride and sodium benzoate
12. PHCSs coated with palladium
13. PHCSs coated with silver
14. PHCSs coated with both palladium and silver
15. PHCSs coated with both magnet and palladium

1. Preparation of porous hollow carbonaceous spheres (PHCSs)

In a typical experimental procedure, S. cerevisiae cells (3-4 g, purchased from Angel Yeast Co., Ltd., China) are dispersed in deionized water and acetone with rapid stirring for 8 h respectively. Then the slurry is transferred into a 50 mL Teflon-sealed autoclave which is filled with 40 ml deionized water and 2.0 g NaCl and maintained at 180-200 °C for 8 h. The puce solid products were separated by filtration, then washed by three cycles with deionized water and alcohol, and oven-dried at 80°C for 4 h.

2. Preparation of metal and Fe3O4 coated PHCSs

The reaction is conducted in a 50 ml 3-neck-flask with a reflux condenser. 0.2 g PHCSs are dispersed in 15 ml deionized water with 10 ml corresponding metallic salt solution (10mM HAuCl₄, 10mM PdCl₂ or 0.1M AgNO₃), the PH is adjusted at about 2. The flask is heated and maintained boiling for 1 h. The product is obtained by filtration and washed with deionized water and alcohol. The bimetallic coated PHCSs is obtained in a similar way but react the PHCSs with 0.1M AgNO₃ and 10mM Pd(NO₃)₂ in sequence. For Fe₃O₄ coated PHCSs: 1.0 g PHCSs as well as 0.3 g FeCl₃·6H₂O are mixed in ethylene glycol (20 mL), followed by adding 0.5 g NaAc as dispersing agent. The mixture was stirred vigorously for 40 min and then sealed in a Teflon-lined stainless-steel autoclave (50 ml capacity). The autoclave was heated and maintained at 180 °C for 10 h. The crude products are washed with ethanol for several times. The Fe₃O₄ coated PHCSs can be further modified with metals by the method depicted above.
3-Assemble of Pickering emulsion

0.1 g PHCSs are dispersed in toluene and added with a certain amount of water, adjust the oil-to-water volume ratio from 2:8 to 8:2 and keep the total volume at 40 ml. Ultrasonic stir the system until an obvious layer of emulsion forms. The prepared Pickering emulsion is observed under the optical microscope. The Pickering emulsion which the oil-to-water volume ratio is 4:6 is assembled with toluene and hydrochloric acid solution. The system is then adjusted to alkaline by adding solid sodium hydroxide and magnetic stirs the emulsion for 10 h. After that, the system is readjusted back to acidic by replacing a part of water phase with hydrochloric acid solution and magnetic stirs the emulsion for 10 h.

4-Zinin reduction

The reaction is conducted in a 100 ml 3-neck-flask with a reflux condenser, by taking 0.005 mol p-nitroanisole in 20 ml toluene with 0.015 mol (0.03 mol) of Na₂S in 30 ml water, and a certain amount of catalyst (0.2 g (0.5 wt%) PHCSs or 2.5 × 10⁻⁵ mol·ml⁻¹ TBAB or 1.25 × 10⁻⁴ mol·ml⁻¹ TBAB or 0.2 g (0.5 wt%) PS-PEG) at 80°C under magnetic stirring. The reaction is monitored by a gas chromatography (SP-2100) with the KB-5 chromatographic column (Kromat Corporation). The used PHCSs are separated by separating funnel and filtration, and washed by three cycles with deionized water and alcohol.

5-The reduction of p-nitroanisole with NaBH₄

The reaction is conducted in a 100 ml 3-neck-flask with a reflux condenser, by taking 2.5 mmol p-nitroanisole in 20 ml toluene with 0.05 mol of NaBH₄ in 30 ml water, 0.2 g (0.5 wt%) PHCSs are added as catalyst at room temperature with magnetic stirring. The used PHCSs are separated by separating funnel and filtration, then washed by three cycles with deionized water and alcohol.

6-Characterization

Emulsions were observed with optical microscopy using a COIC XSN-HS7 biological microscope. The conductivity of the emulsion is determined by lei-ci DDS-307 conductivity meter using lei-ci DJS-1C Pt black electrodes. Conductivity measurements were made immediately after emulsification. Powder XRD was performed with monochromatized Cu Kα radiation (λ=1.5418 Å). Scanning electron microscopy (SEM) measurements were performed with a Hitachi S-5500 FE-SEM microscope.

7-Optical microscopy images of PHCSs stabilized Pickering emulsion
Figure S1. Optical microscopy images of PHCSs stabilized Pickering emulsion which the oil-to-water ratio is from 2:8 to 8:2.

8-Conductivity of the Pickering emulsions as a function of the volume fraction of water

Conductivity/µS cm⁻¹

Figure S2. Conductivity of the Pickering emulsions as a function of the volume fraction of water.
9- Optical microscopy images of the pH-sensitive behavior of the PHCSs

![Optical microscopy images](image)

**Figure S3.** (a) Optical microscopy image of acidic treated Pickering emulsion. (b) Optical microscopy image of alkaline treated Pickering emulsion. (c) Optical microscopy image of recovery of the Pickering emulsion when readjusted to acidic after alkaline treatment.

10- Hydrolysis of α,α,α-Trichlorotoluene

α,α,α-Trichlorotoluene (4.1 g, 21 mmol) in 20 ml toluene was mechanical stirred with 30 ml of 20% aqueous NaOH at 80 °C. Runs catalyzed by 0.40 g (0.5wt%) PHCSs. A kinetic profile of the reaction is shown below.

![Kinetic profile](image)

**Figure S4** Kinetic profiles of the hydrolysis of α,α,α-Trichlorotoluene. ■ blank test, ▲ catalyzed by 0.40 g PHCSs.

11- Synthesis of benzoic anhydride from benzoyl chloride and sodium benzoate

Typical experiments were conducted by taking 0.025 mol of benzoyl chloride in toluene (25 ml), 0.04 mol of sodium benzoate in water (25 ml), and 0.4 g (0.5wt%) PHCSs maintained at 30 °C. A
kinetic profile of the reaction is shown below.

![Kinetic profile of the Synthesis of benzoic anhydride.](image)

**Figure S5** Kinetic profiles of the Synthesis of benzoic anhydride. ■ blank test, ▲ catalyzed by 0.40 g PHCSs.

12-PHCSs coated with palladium

![SEM image of the Pd-PHCSs. BSE-SEM image of the Pd-PHCSs. XRD pattern of the Pd-PHCSs. Energy dispersive X-ray spectroscopy measurements of Pd-PHCSs. The size distribution of palladium nanoparticles on the Pd-PHCSs.](image)

**Figure S6.** (a) SEM image of the Pd-PHCSs. (b) BSE-SEM image of the Pd-PHCSs. (c) XRD pattern of the Pd-PHCSs. (d) Energy dispersive X-ray spectroscopy measurements of Pd-PHCSs. (e) The size distribution of palladium nanoparticles on the Pd-PHCSs.
13-PHCSs coated with silver

Figure S7. (a) SEM image of the Ag-PHCSs. (b) BSE-SEM image of the Ag-PHCSs. (c) XRD pattern of the Ag-PHCSs. (d) Energy dispersive X-ray spectroscopy measurements of Ag-PHCSs. (e) The size distribution of silver nanoparticles on the Ag-PHCSs.

14-PHCSs coated with both palladium and silver
**Figure S8.** (a) SEM image of the Ag-Pd-PHCSs. (b) BSE-SEM image of the Ag-Pd-PHCSs. (c) XRD pattern of the Ag-Pd-PHCSs. (d) Energy dispersive X-ray spectroscopy measurements of the Ag-Pd-PHCSs.

15-PHCSs coated with both magnet and palladium

**Figure S9.** (a) SEM image of the magnetic Pd-PHCSs. (b) BSE-SEM image of the magnetic Pd-PHCSs. (c) XRD pattern of the magnetic Pd-PHCSs. (d) Energy dispersive X-ray spectroscopy measurements of the magnetic Pd-PHCSs.