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Template-free synthesis of inorganic hollow spheres at water/“water-brother” interfaces as Fenton-like reagents for water treatment

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A B S T R A C T

This paper reports a template-free method to synthesize a series of inorganic hollow spheres (IHSs) including Cu-1, Cu-2, Ni-1, Ni-2 based on mineralization reactions at water/“water-brother” interfaces. “Water-brother” was defined as a solvent which is miscible with water, such as ethanol and acetone. The water/“water-brother” interfaces are very different from water/oil interfaces. The “water-brother” solvent will usually form a homogenous phase with water. Interestingly, in our method, these interfaces can be formed, observed and utilized to synthesize hollow spheres. Utilizing the unique porous properties of the spheres, their potential application in water treatment was demonstrated by using Cu-1 IHSs as Fenton-like reagents for adsorption and decomposition of Congo Red from aqueous solution. The final adsorption equilibrium was achieved after 30 min with the maximum adsorption capacity of 86.1 mg/g, and 97.3% removal of the dye in 80 min after adsorption equilibrium. The IHSs can be reused as least 5 times after treatment by NaOH. This method is facile and suitable for large-scale production, and shows great potential for watertreatment.

Introduction

Inorganic hollow spheres (IHSs) have attracted many scientists' attention due to their diverse applications such as catalysis (Chen et al., 2015; Zhu et al., 2013), energy storage (Li et al., 2013; Yang et al., 2013), supercapacitors (Cao et al., 2011; Ma et al., 2012), nanoreactors (Z. Chen et al., 2010; Fang et al., 2012), chemical sensors (Cheng et al., 2015; Li et al., 2015), watertreatment (Fei et al., 2008; Wang et al., 2012), and drug delivery (Su et al., 2015; Zhao et al., 2008). During the past several years, many methods have been developed to fabricate IHSs, using templates or template-free methods. The soft templates include emulsions (Guo et al., 2010), micelles (Sasidharan et al., 2011), vesicles (Xu and Wang, 2007), bubbles (Sun et al., 2013), and droplets (Jiang et al., 2004). Micelles of poly(styrene-b-acrylic acid-b-ethyleneoxide) and bubble templates were utilized to fabricate hollow titania nanospheres (Sasidharan et al., 2011) for rechargeable lithium-ion batteries and bismuth vanadate hollow spheres (Sun et al., 2013) for photocatalysis, respectively. The hard templates include latex cages (Yang et al., 2005), carbon spheres (Zhang et al., 2014), silica spheres (Y. Chen et al., 2010), hydrated metal sulfate spheres (Lu et al., 2011) and hematite spheres (Zhao et al., 2009) *etc*. For example, carbon spheres were used to prepare

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$Fe_3O_4@SiO_2$ hollow mesoporous spheres (Zhu et al., 2010) for drug delivery, and silica spheres were used as templates to synthesize hollow mesoporous aluminosilica spheres (Fang et al., 2012) for catalytic nanoreactors. Self-templating methods are a special case in hard-templating methods. The templates in self-templating methods (Fang et al., 2013; Ma et al., 2015) initially act as templates but gradually form the outer shells of the final IHSs. Fe_3O_4 hollow spheres (Ma et al., 2015) and hollow mesoporous silica (Fang et al., 2013) were synthesized using a self-templating strategy. Template-free methods have also been extensively used as an effective way to prepare hollow materials based on self-assembly (Mo et al., 2005; Zhou et al., 2015) and Ostwald ripening (Xu et al., 2014; Yec and Zeng, 2014). Hollow $ZnFe_2O_4$ microspheres (Zhou et al., 2015) were fabricated by self-assembly as acetone sensor. Li_2FeSiO_4 hollow spheres (Xu et al., 2014) as cathode materials for lithium-ion batteries were synthesized by Ostwald ripening.

Water is the most important and essential resource for life. Water pollution has become a serious issue all over the world. Some pollutants with high toxicity and carcinogenicity can seriously affect human health. Many metal oxide materials as potential adsorbents have been reported to effectively remove toxic heavy metal ions and organic pollutants from wastewater. These oxide materials include urchin-like α-FeOOH (Wang et al., 2012), hollow SnO_2 spheres (Shi and Lin, 2010), zeolite membranes (Kazemimoghadam, 2010), nanocrystalline copper/nickel oxide (Carnes et al., 2002), and 3D flowerlike ceria micro/nanocomposite (Zhong et al., 2007). Urchin-like α-FeOOH hollow spheres (Wang et al., 2012) were used for water treatment by absorption of As(V), Pb(II) and Congo Red. 3D flowerlike ceria micro/nanocomposites (Zhong et al., 2007) were used for removing As(V) and Cr(VI). Fenton/Fenton-like reactions are also common processes to deal with water pollution (Zbiljic et al., 2015). Through Fenton/Fenton-like reactions, many organic pollutants such as phenol (Babuponnusami and Muthukumar, 2012), aniline (Anotai et al., 2010), imidacloprid (Guzsvany et al., 2010), Methylene Blue (Dutta et al., 2001) and Congo Red (Zhang and Nan, 2014) can be oxidized by Fe^{2+} (Wang, 2008), Fe^{3+} (Chu et al., 2005) and Cu^{2+} (Ruan et al., 2010). Fenton/Fenton-like reactions have also been used effectively in water treatment.

Herein we synthesized Cu-1 (Ni-1) and Cu-2 (Ni-2) IHSs using a crystallization – dissolution – interface mineralization (CDIM) method with water/“water-brother” (acetone, ethanol) interfaces respectively. A “water-brother” is a polar solvent which is miscible with water, such as acetone and ethanol. In the special method CDIM, water/“water-brother” interfaces can be formed, observed and utilized to synthesize IHSs. Cu-1 IHSs were proved to absorb and degrade Congo Red effectively, which gives these inorganic hollow spheres great potential in water treatment.

1. Materials and methods

1.1. Chemicals and reagents

Sodium hydroxide and hydrogen peroxide were purchased from Xilong Chemical (China). Cupric sulfate and nickel sulfate hexahydrate were purchased from Sinopharm Chemicals (China). Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$) was purchased from Tianjin Basifu Chemicals (China). Ethanol was purchased from Tianjin Tianli chemicals (China). Acetone was purchased from Tianjin Fuyu Fine Chemical (China). The solutions were prepared with ultrapure water (18.2 MΩ·cm^{-1}).

1.2. Preparation of IHSs

The crystal clusters of $CuSO_4$ and $NiSO_4$ were synthesized by injecting 250 μL saturated $CuSO_4$ (1.28 mol/L at 20°C) and $NiSO_4$ (1.79 mol/L at 20°C) aqueous solution into 25 mL acetone/ethanol under magnetic stirring (1400 r/min) for 3 hr. IHSs were formed by mixing together 1 mL crystals suspended in acetone/ethanol with a certain amount of NaOH water solution. The reaction lasted 3 min. The precipitates were washed by centrifuging with ultrapure water 3 times. Table 1 details the reactants, solvents, and amounts of NaOH used to prepare IHSs.

1.3. Observation of IHSs formation process under microscope

The processes for forming IHSs were observed by microscope. 25 μL crystal clusters in suspension and 25 μL or 50 μL of a certain concentration of NaOH solution were injected into a sealed cell in the proper order.

1.4. Adsorption and decomposition experiments for Congo Red

In absorption experiments, Congo Red (20 mL, 0.07 mg/mL), ultrapure water (19 mL) and Cu-1 IHSs (1 mL, 15.7 mg/mL) were mixed together. At certain time intervals, 3 mL of the mixture was taken out and centrifuged. The supernatant (2 mL) was measured by a UV–Vis spectrometer to calculate the concentration of Congo Red in solution according to the calibration curve shown in Appendix A Fig. S2. The adsorption kinetics curves were then obtained.

To optimize the concentration of H_2O_2, a mixture of Congo Red (1.5 mL, 0.14 mg/mL), ultrapure water (1.325 mL) and Cu-1 IHSs (75 μL, 15.7 mg/mL) was maintained for 40 min to reach absorption equilibrium. Then a certain concentration H_2O_2 (100 μL) was added into the mixture to obtain final concentrations of H_2O_2 of 0.16, 0.65, 1.13, 1.61, 3.22, 16.12 and 32.26 mmol/L. Similarly, 3 mL of the mixture was taken out after 80 min and centrifuged. The supernatant (2 mL) was measured by a UV–Vis spectrometer to calculate the concentration of Congo Red in solution to optimize the H_2O_2 concentration.

The following procedure was carried out to determine the dynamics of the Fenton-like reaction. A mixture of Congo Red (20 mL, 0.14 mg/mL), ultrapure water (19 mL) and Cu-1 IHSs

Table 1 – The reactants, solvents and amounts of NaOH for IHSs (inorganic hollow spheres) synthesis.

	Reactant	“Water-brother” phase	Amount of NaOH
Cu-1 IHSs	$CuSO_4$	Acetone	2 mL 0.03 mol/L
Ni-1 IHSs	$NiSO_4$	Acetone	1 mL 0.13 mol/L
Cu-2 IHSs	$CuSO_4$	Ethanol	1 mL 0.06 mol/L
Ni-2 IHSs	$NiSO_4$	Ethanol	2 mL 0.15 mol/L