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Self-templating synthesis of hollow copper tungstate spheres as adsorbents for dye removal

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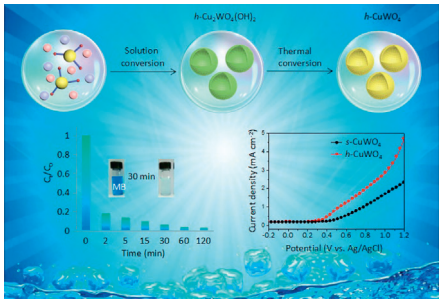
GRAPHICAL ABSTRACT



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ABSTRACT

In spite of recent progress in developing hollow micro/nanostructures, the synthesis of three-dimensional adsorbents with high adsorption efficiency and capability on the basis of these structures still remains a great challenge. Herein, we demonstrate a facile hydrothermal strategy to synthesize uniformly dispersed hollow $CuWO_4$ spheres. The as-prepared $CuWO_4$ spheres with unique mesoporous structure show favorable selective adsorption for cationic dyes and good recyclability. The adsorption capacity of hollow $CuWO_4$ towards methylene blue (MB) reaches 59.82 mg g^{-1}. Furthermore, the hollow $CuWO_4$ spheres present enhanced photoelectrochemical performance under visible light illumination. This strategy of acquiring specifically functionalized materials from smart design and simple chemical process has opened up wide opportunities on the fabrication of alternative absorbents and photoelectrodes based on $CuWO_4$ substrate.

1. Introduction

Developing high efficiency, low cost and environmental-friendly absorbents for increasingly serious worldwide water contamination has attracted more and more attentions [1–4]. During the last decade, porous materials with large specific surface area, high porosity, controlled structures and plentiful active sites, have highlighted a great potential on the removal of toxic heavy metal ions and organic pollutants from waste water [5–7]. Their intriguing structural characteristics permit their high adsorption efficiency and superior stability in water purification process. Accordingly, exploring well-defined and uniformly porous absorbents has been a long-pursed goal.

As a unique porous structure, hollow micro/nanostructures with controllable morphology have recently aroused significant interest because of their outstanding adsorption performance in application of removing toxic organics [8–11]. Especially the inorganic hollow spheres, which always show high specific pore

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volume, uniform pore size distribution and easy recyclability, have been considered as potential candidates with great application prospects for wastewater treatment [12–14]. Thus, many strategies have been applied to design and synthesize hollow spheres, including ion exchange method [15], hard-template method [16], soft-template method [17] and hydrothermal method [18]. However, most of the synthetic route are suffered from high cost, complicated procedures, unavoidable sacrifice of templates, and harsh experimental conditions even the undoubtedly collapse of the hollow structures. Therefore, the development of uniform and definite hollow nanostructures remains a formidable challenge.

Copper tungstate ($CuWO_4$), which is a well-known *n*-type semiconductor composed of two earth abundant metals [19,20], is always used as one of the most promising photoanode for water oxidation [21,22], photocatalysts for degradation of organic pollutants [23] and gas sensors [24] due to its reasonably narrow band gap (2.2–2.4 eV). However, most of the $CuWO_4$ products are irregular shaped or require complex seeding process during the synthetic journey. Herein, we present a one-pot, two-step method to prepare uniform hollow $CuWO_4$ spheres in a self-templating process, and intend to apply them as alternative absorbents for organic dyes removal based on the following considerations: firstly, the facial, non-toxic preparation procedure and abundance of corresponding metals allow the conceivably practical feasibility; secondly, the uniform morphology and definite hollow nanostructure guarantee the favorable efficiency as dye absorbents; last but not least, the chemical stability and easy regeneration enable the good durability. As expected, the prepared hollow $CuWO_4$ spheres exhibit impressive adsorptive properties and admirable recycling stability in the removal of cationic dyes, owing to the relatively large BET surface and the unique mesoporous structure. Furthermore, the greatly enhanced photoelectrochemical (PEC) activity under visible light irradiation compared to the solid $CuWO_4$ spheres is also observed.

2. Experimental section

2.1. Chemicals and materials

$CuCl_2{\cdot}2H_2O$ (AR), $Na_2WO_4{\cdot}2H_2O$ (AR), trisodium citrate dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, AR) and methylene blue (≥82.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Rhodamine B (≥99%) and methyl orange (≥99%) were purchased from Damao Chemical Reagent Factory (Tianjin, China). Malachite green (≥95%) was purchased from Aladdin Co., Ltd. (Shanghai, China). All materials were used as received.

2.2. Preparation of h- and s-$CuWO_4$

A facile self-templating method was used to fabricate $CuWO_4$ samples. The synthetic process of $CuWO_4$ samples was described in Scheme 1. Typically, 2 mmol $CuCl_2{\cdot}2H_2O$ and 2 mmol ($C_6H_5O_7Na_3{\cdot}2H_2O$) was dissolved in 40 mL deionized water, followed by the addition of 1 mmol $Na_2WO_4{\cdot}2H_2O$ under gentle magnetic stirring. Then, the homogeneous solution was transferred to a 50 mL Teflon-lined autoclave, which was sealed and maintained at 160 °C for 6 h and 48 h, respectively. After the autoclave was cooled to room temperature naturally, the green $CuWO_4(OH)_2$ precursor was collected by vacuum filtrating, washed by deionized water and ethanol for several times, and dried overnight. After calcination in air at 400 °C for 1 h and a mild acid treatment, the original appearance of the precursor can be maintained and the corresponding $CuWO_4$ spheres with hollow or solid structure can be obtained. The sample was designated as solid $CuWO_4$ spheres (*s*-$CuWO_4$) when the hydrothermal reaction time is 6 h. Meanwhile, the sample was named as hollow $CuWO_4$ spheres (*h*-$CuWO_4$) when the reaction time reached 48 h.

2.3. Characterization and measurements

The surface morphology and detailed microscopic structure of the samples were analyzed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F) and transmission electron microscopy (TEM, JEM2010-HR). The powder X-ray diffraction (XRD) measurements were conducted on a PANalytical PW3040/60 diffractometer equipped with monochromatic Cu K_α radiation (λ = 0.15418 nm). The chemical-state analysis of the products was measured with X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha). The optical properties of samples were observed over Hitachi UV-3010 spectrophotometer using $BaSO_4$ as a reference. The Fourier transform infrared spectrometer (FTIR) spectra were obtained with a Nicolet Nexus 470FTIR using powder-pressed KBr pellets. The surface area and the pore size distribution of the samples were calculated from the Brunauer–Emmett–Teller method (ASAP 2460 instrument).

2.4. Adsorption experiments

All adsorption experiments were carried out in dark condition to prevent photocatalytic reactions. The hollow $CuWO_4$ spheres (40 mg) were dispersed into 50 mL MB solution (20 mg L^{-1}) and sonicated for 30 min. After that, the adsorption was conducted under a gentle magnetic stirring at room temperature. At given time intervals, the analytic sample was taken out and centrifuged at 10,000 rpm for 10 min to remove sediments. The concentration of MB was determined by UV – vis spectroscopy (UV, Shimadzu UV-3150) monitored at 664 nm, from which the amount of MB adsorbed can be calculated. Adsorption equilibrium was established after stirring continuously for 30 min. As a contrast, the adsorption properties of the solid $CuWO_4$ spheres were monitored under the same condition. The amount of MB adsorbed at equilibrium Q_e (mg g^{-1}) was calculated from the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Q_e is the adsorption capacity (mg g^{-1}) of the adsorbent at equilibrium, C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the solute, V is the volume of the aqueous solution (L), and m is the mass of the adsorbent used (g) [25]. Each experiment has been carried out for three times, and the mean ± SD (standard deviation) has been considered for data analysis to confirm the representativeness. And the validity of a kinetics model can be tested *via* regression coefficients (R^2) and chi-square (χ^2) obtained from a kinetics model plot.

$$\chi^2 = \sum \frac{\left(Q_{e(exp)} - Q_{e(calc)}\right)^2}{Q_{e(calc)}^{\ 2}} \quad (2)$$

where $Q_{e(exp)}$ and $Q_{e(calc)}$ are the amount adsorbed per unit mass obtained from the experimental data and that calculated from the model, respectively [26].

2.5. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out on an electrochemical workstation (CHI 760D, China Chenhua), using an adjustable 350 W Xenon lamp irradiation with a UV-light cutoff filter (λ > 420 nm). In a complete test system, the as-prepared photoanode (effective area around 1.5 × 1.5 cm^2) was served as the working electrode with a platinum sheet as the counter electrode, and an Ag/AgCl electrode (saturated KCl) was employed as a refer-