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Facile preparation of sphere-like copper ferrite nanostructures and their enhanced visible-light-induced photocatalytic conversion of benzene

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ABSTRACT

Spinel copper ferrite nanospheres with diameters of about 116 nm were synthesized in high yield via a facile solvothermal route. The prepared nanospheres had cubic spinel structure and exhibited good size uniformity and regularity. The band-gap energy of $CuFe_2O_4$ nanospheres was calculated to be about 1.69 eV, indicating their potential visible-light-induced photocatalytic activity. The dramatically enhanced photocatalytic activity of the $CuFe_2O_4$ nanospheres was evaluated via the photocatalytic conversion of benzene under Xe lamp irradiation. By using the *in situ* FTIR technique, ethyl acetate, carboxylic acid and aldehyde could be regarded as the intermediate products, and CO_2 was produced as the final product during the reaction process. This study provided new insight into the design and preparation of functional nanomaterials with sphere structure in high yield, and the as-grown architectures demonstrated an excellent ability to remove organic pollutants in the atmosphere.

1. Introduction

Because of their attractive magnetic, electronic, thermal and catalytic properties, copper ferrites ($CuFe_2O_4$) have been widely investigated and used in variety of applications such as magnetic material [1,2], anode material [3], catalyst [2,4], and so on. Especially $CuFe_2O_4$ nanoparticles have long played an important role in various catalytic applications including thermal catalysis, photocatalytic degradation of pollutants and photocatalytic hydrogen production. Khedr et al. investigated the kinetics and mechanisms of CO_2 catalytic decomposition over freshly reduced nano-crystallite $CuFe_2O_4$ [4]. Nasrallah et al. fabricated the novel hetero-system $CuFe_2O_4$/CdS and studied its photocatalytic reduction of Cr(VI) [5]. Yang et al. reported photocatalytic activity evaluation of tetragonal $CuFe_2O_4$ nanoparticles for the H_2 evolution under visible light irradiation [6]. Faungnawakij and coworkers investigated the hydrogen reduction and metal dopant effects on catalytic hydrogen production from dimethyl ether over $CuFe_2O_4$ spinel-based composites [7].

Benzene is widely used as a solvent in industrial processes and is also one of the most abundant volatile aromatic hydrocarbons found in urban atmospheres. Many approachs were developed to remove benzene from the polluted environment because of its severe toxic effects on the human body [8]. Xu and coworkers reported the photocatalytic degradation of benzene using a carbon nanotubes (CNT)/TiO_2 nanocomposite photocatalyst prepared by a simple impregnation method [9]. Huang et al. synthesized a nanostructured $Cd_2Ge_2O_6$ photocatalyst, which showed enhanced photocatalytic activity for environmental purification of benzene in air [10]. Xue et al. obtained nanocrystalline $Sr_2Sb_2O_7$ via a facile hydrothermal method and found its high photocatalytic activity for benzene degradation [11]. The kinetic process of benzene photocatalytic degradation over visible-light-driven silver vanadates photocatalysts was investigated by Chen et al. [12]. Up to now, there are few reports about the photocatalytic conversion of benzene on sphere-like copper ferrite nanostructures irradiated with visible-light. In addition, as for the photocatalytic oxidation of benzene vapor, the reaction intermediates on the photocatalytic surfaces were often characterized through solvent extraction after the photoprocess [13], it may not reveal the real adsorbates formed on the surface of photocatalysts during the photoreactions. Therefore in the present study, visible-light-induced photocatalytic conversion of benzene

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over $CuFe_2O_4$ nanospheres was investigated using "in situ" measurements of infrared spectroscopy.

2. Experimental details

2.1. Preparation of materials

2.1.1. $CuFe_2O_4$ nanospheres

All chemicals in this work were analytical grade reagents and used as starting materials without further purification. $Cu(NO_3)_2{\cdot}3H_2O$ (5 mmol, 1.208 g) and $Fe(NO_3)_3{\cdot}9H_2O$ (10 mmol, 4.040 g) were dissolved in ethylene glycol (80 mL) to form a clear solution, followed by the addition of NaAc (7.2 g) and polyethylene glycol (2.0 g). The mixture was stirred vigorously for 90 min and then sealed in a Teflon lined stainless-steel autoclave (100 mL). The autoclave was heated and maintained at 200 °C for 22 h, and allowed to cool to room temperature. Subsequently, the black precipitates were collected and washed with ethanol followed by drying at 60 °C for 6 h. For the heat treatment, the samples were annealed at 650 °C for 2 h with a heating rate of 2 °C min^{-1}.

2.1.2. $CuFe_2O_4$ nanoparticles

The $CuFe_2O_4$ nanoparticles were prepared according to the reference [6]. The typical procedures are as follows: $Cu(CH_3COO)_2{\cdot}H_2O$ (5 mmol, 0.998 g) and $Fe(NO_3)_3{\cdot}9H_2O$ (10 mmol, 4.040 g) were dissolved together in 100 mL distilled deionized water to produce a clear solution. Then $NH_3{\cdot}H_2O$ (28%) was added into the solution drop by drop under vigorous stirring until the pH became around 9, and viscous precipitates were produced. The precipitates were then dried at 80 °C by using a water bath, and subsequently calcined at 850 °C for 3 h with a heating rate of 10 °C min^{-1}.

2.2. Characterization

The crystal structure of the $CuFe_2O_4$ nanospheres and nanoparticles was examined by X-ray diffraction (XRD, Rigaku D/max) with Cu Kα radiation (λ = 0.15418 nm). The morphology of the prepared samples was characterized by scanning electron microscopy (SEM, JSM-5600 LV) and transmission electron microscopy (TEM, Hitachi 800 system at 200 kV). Energy dispersive X-ray analysis (EDX, Horiba 7593 H) was performed to determine the elemental concentration distribution on the sample. X-ray photoelectron spectroscopy (XPS, PHI 5600 mode) was performed to examine the surface properties and composition of the samples. All the binding energies were calibrated by using the contaminant carbon (C 1s) 284.6 eV as a reference. Fourier transform infrared (FTIR, BRUKER VERTEX 70) spectrum was recorded in the range 4000–450 cm^{-1} with 4 cm^{-1} resolution. The light absorption property was measured using UV–Vis absorption spectrophotometer (JASCO, UV-550) with a wavelength range of 200–800 nm. Thermogravimetric and differential thermal analysis (TG/DTA, Seiko SII 6300) were performed at a heating rate of 10 °C/min under air atmosphere.

2.3. Photocatalytic activity evaluation

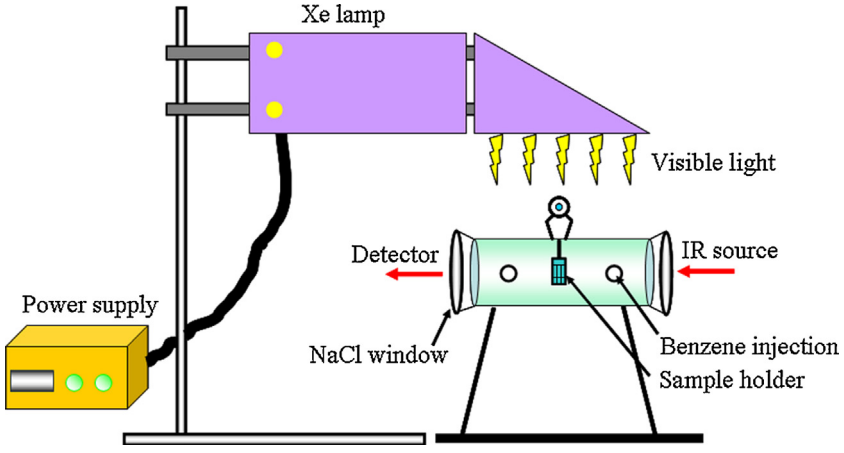
Photocatalytic activities of the catalysts were determined using the photocatalytic conversion of benzene under visible-light irradiation in a self-made *in situ* quartz IR photoreaction cell. The cell (diameter, 4 cm; length, 10 cm) consisted of two NaCl windows and a sample holder (diameter, 13 mm) for the catalyst wafer (0.05 g). After the catalyst was placed in the sample holder, a small amount of benzene was injected into the reactor with a microsyringe. The benzene vapor was allowed to reach adsorption equilibrium in the reactor prior to irradiation. The analysis of the benzene concentration in the reactor was conducted with a GC-FID (Agilent 7890A). The initial concentration of benzene after adsorption equilibrium was controlled at about 280 mg/m^3. The Xenon lamp (XQ-500 W) (λ > 400 nm) with the light intensity of about 50 mW cm^{-2} was turned on to allow the photocatalytic reaction to proceed under batch conditions. The IR spectra were continuously collected on the VERTEX 70-FTIR with a resolution of 1 cm^{-1} and 20 scans in the region of 4000–600 cm^{-1} during the course of reaction. Scheme 1 showed the schematic illustration of the photocatalytic reaction setup.

3. Results and discussion

3.1. XRD analysis

The phases of the synthesized nano-sphere-like $CuFe_2O_4$ and $CuFe_2O_4$ nanoparticles are identified by XRD characterization (Fig. 1). The diffraction peaks of the $CuFe_2O_4$ nanospheres are in good agreement with the standard diffraction pattern of the spinel $CuFe_2O_4$ (JCPDS 25-0283). Obviously, all the diffraction peaks can be indexed to (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (5 1 1) and (4 4 0) crystallographic planes. The lack of diffraction peaks from impurities suggests the high phase purity of nano-sphere-like $CuFe_2O_4$. However the diffraction peaks of $CuFe_2O_4$ nanoparticles prepared using co-precipitation method can be readily indexed to tetragonal-type $CuFe_2O_4$ (JCPDS 34-0425).

The average crystallite sizes of nano-sphere-like $CuFe_2O_4$ are determined from the broadening of the peak corresponding to the



Scheme 1. Schematic illustration of the photocatalytic reactor system setup.