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Facile and low temperature route to synthesis of CuS nanostructure in mesoporous material by solvothermal method

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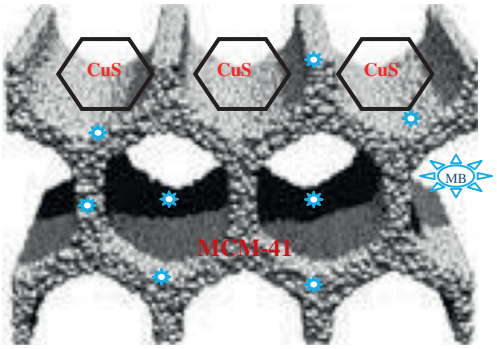
HIGHLIGHTS

- We used *solvothermal method* for synthesis of *CuS/MCM-41* nanocomposite.
- CuS material has *different phases.* The synthesis only one phase of CuS is very hard.
- We synthesized one phase of CuS nanostructure by *solvothermal method in ethylene glycol.*
- It is observed different phases for CuS by solvothermal method in water solvent.
- For characterization of heterogeneous catalysts we need to *novel experimental* techniques.

GRAPHICAL ABSTRACT



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ABSTRACT

The synthesis of CuS nanomaterial in MCM-41 matrix has been realized by chemical synthesis between MCM-41, copper sulfate pentahydrate and thiourea via a solvothermal method in ethylene glycol and water, separately. X-ray diffraction analysis (XRD), diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fourier transform infrared (FT-IR) were used to characterize the products. At synthesized CuS/MCM-41 sample in ethylene glycol, X-ray diffraction and diffuse reflectance spectroscopy showed pure covellite phase of copper sulfide with high crystality. But prepared CuS/MCM-41 sample in water shows the covellite, chalcocite and the djurleite phase of copper sulfide nanostructures. The formation of CuS nanostructures was confirmed by FT-IR. Photocatalytic activity of CuS/MCM-41 nanocomposites was studied for degradation of Methylene Blue (MB) under visible light. The CuS/MCM-41 nanocomposite is more effective nanocatalyst than synthesized CuS/MCM-41 sample in water for degradation of methylene blue. Several parameters were examined, catalyst amount (0.1–1 g L^{-1}), pH (1–13) and initial concentration of MB (0.96–10 ppm). The extent of degradation was estimated from the residual concentration by spectrophotometrically. The support size was obtained in the range 60–145 nm by TEM. In the same way, the average size of copper sulfide in CuSMCM-41E and CuS/MCM-41W nanostructures were obtained about 10 nm and 16 nm, respectively.

Introduction

Synthetic dyestuffs used by several industries such as textile, dyeing and printing industries are a major source of water pollution which is visible even in a low concentration of dyes. Removing color from wastewaters is often more important than other colorless organic substances because of their considerable effects on the environmental water [1–4]. Heterogeneous photocatalysis has already been investigated and successfully applied to the degradation of different organic pollutants. Among the various methods, a great deal of attention has paid to the advanced

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oxidation process (AOP) for the treatment of air and water streams [5]. AOP can generate free radicals, such as hydroxyl radicals ($OH^{\cdot}$) which are strong and nonselective oxidant species that react with the majority of organic pollutants. Free radicals such as $HO_2^{\cdot}$ and $O_2^{\cdot}$ may also be involved in the degradation process, but these radicals are less effective than the hydroxyl radicals [6]. Up to date, remarkable progresses have been made in the photodegradation of dye pollutants under ultraviolet (UV) light, while less efforts have been paid to the visible light. Therefore, effective utilization of visible light to degrade different organic pollutants using the solar energy has been an attractive attempt in recent years [7,8].

Nano-scale semiconductor particles possess higher surface area to volume ratio than their bulk counter parts, and thus allow for greater photon adsorption on the photocatalyst surface [9–11]. As a result, such materials offer potential uses in catalysis, electronics, sensors, light transmission and solar cells applications [12–16]. Many of the current studies are focused on the synthesis of different nanostructured materials and their various applications.

CuS is a transparent *p*-type semiconductor with a band gap 1.27 eV for bulk form. The top of the valence band is primarily composed of well-hybridized states of Cu 3d and S 3p states, while the bottom of the conduction band consists mainly of Cu 4s state. The band gap of CuS was found to be a direct-allowed transition type through the analysis of the symmetry of these states. It was also found that the dispersion of the valence band is relatively large due to the considerable hybridization of Cu 3d and S 3p states. This dispersed valence band is responsible for the emergence of *p*-type electrical conduction in this material. On the other hand, the dispersion of the conduction band is rather small, probably because of the layered structure, in comparison with typical *n*-type conducting materials. This small dispersion of the conduction band leads to the wide band gap and high stability of exactions in CuS [17]. Copper sulfides are a particularly interesting class of metal sulfides due to their ability to form with various stoichiometries. The copper–sulfur system can exist in the chalcocite (Cu_2S) and covellite (CuS) phases, with several stable and metastable phases of various stoichiometries between the two ideal ones [17]. Copper sulfide is found to exist into two forms at room temperature as "Copper-rich" and "Copper-poor." Copper-rich phases exist as anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.94}S$) and chalcocite (Cu_2S). The Copper-poor phase exists as covellite (CuS). Covellite has been known to exist in two forms, brown CuS and green CuS.

Recent studies showed that doping a semiconductor onto a suitable support has several advantages in photocatalysis processes. (1) increases the activity of the semiconductor (2) decreases the high turbidity (3) increases the adsorption of pollutants (4) minimize electron/hole recombination (5) prevent uncontrollable growth of particles (6) prevent particle aggregation (7) controls particle size [18,19]. In this context, molecular sieves due to their unique properties including ion exchange, size, charge and shape electivity, are good candidates to support a semiconductor onto them [20–22]. Incorporated and photocatalysis of copper sulfide in different matrix has not been extensively studied. Thus the development of facile, low temperature and surfactant-free approach for the controlled synthesis of CuS nanostructure in matrix is very imperative to explore different structural aspects of materials.

In this work, the photo-efficiency of the CuS incorporated into MCM-41 was studied in the degradation of an aqueous solution containing Methylene Blue (MB). Methylene blue is a widely used colored compound in dyeing and printing textiles. CuS/MCM-41 nanocomposite has been prepared by solvothermal method in water and ethylene glycol (EG) (polyol method), separately. CuSO4 and thiourea were as a source of Cu and S ions, respectively and ethylene glycol as a solvent. Efficiency of two nanocomposite was compared in the degradation of aqueous solution of MB. After the selection of CuS/MCM-41 by polyol method as more effective catalyst with respect to other nanocomposite by solvothermal method, some experiments were performed to investigate the effects of various experimental parameters including catalyst loading, pH of the solution and initial dye concentration on the efficiency of photodegradation process.

Experimental

Materials

All the chemical reagents and solvents used in the present work, including copper sulfate, thiourea, ethylene glycol, ethanol, tetraethylorthosilicate (TEOS), HcL, NaOH and hexadecyltrimethylammonium bromide are analytical grade reagents (Merck) and were used as received without further purification. Hydrochloric acid and sodium hydroxide were applied for variation of PH of sample solutions. The dye of methylene blue (C.I. name: Basic Blue 9, $C_{16}H_{18}ClN_3S{:}3H_2O$) (Scheme 1) was purchased from Fluka company.

Preparation of MCM-41 matrix

The MCM-41 material was synthesized by a room temperature method with some modification in the described procedure in the literature [23]. We used tetraethylorthosilicate (TEOS: Merck, 800658) as a source of silicon and hexadecyltrimethylammonium bromide (HDTMABr; BOH, 103912) as a surfactant template for preparation of the mesoporous material. The molar composition of the reactant mixture is as follows:

$$SiO_2 : \ 1.6EA : \ 0.215HDTMABr : \ 325H_2O$$

where EA stand for ethylamine. The MCM-41 prepared was calcined at 550 °C for 5 h to decompose the surfactant and obtain the white powder. This powder was used for loading the CuS nanostructures.

Preparation of CuS/MCM-41 catalysts

Preparation of CuS/MCM-41 by polyol method

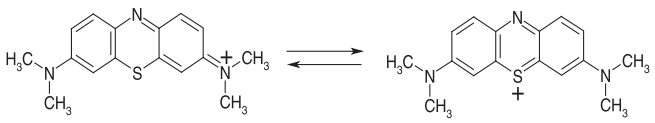
In a typical synthesis, 1 mmol $CuSO_4{\cdot}5H_2O$ (0.31 g) was dissolved in 50 mL ethylene glycol and a green solution was formed. Then 2 mmol thiourea (Tu, $SC(NH_2)_2$, 0.19 g) was added into the above mentioned solution under vigorous stirring for 30 min. After that, MCM-41 matrix was treated in above solution for 2 h. Adsorption of sulfate thiourea complex of copper $[Cu(SC(NH_2)_2)_2SO_4]$ from aqueous solution on the MCM-41 matrix followed by thermal decomposition of the adsorbed complex at 250 °C with formation of finely dispersed copper sulfides and elimination of gaseous products (Eq. (1)):

$$[Cu(SC(NH_2)_2)_2SO_4] \overset{250\,^{\circ}C\ air}{\rightarrow} CuS + 2N_2\uparrow + 2HcL\uparrow + H_2S\uparrow + 2CO_2\uparrow + 2H_2O\uparrow$$

The black product (CuS) was collected and washed repeatedly with deionized water and ethanol several times to remove the impurities and by products. Finally the product was dried in oven at 70 °C for 4 h. The prepared sample is called CuS/MCM-41E.

Preparation of CuS/MCM-41 by solvothermal method in water

In this method, CuS nanostructures synthesis was carried out as mentioned above under same conditions only water was used



Scheme 1. Structure of methylene blue.