Catalysis Today xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Interparticle double charge transfer mechanism of heterojunction α-Fe_2O_3/Cu_2O mixed oxide catalysts and its visible light photocatalytic activity

Sandeep Kumar Lakhera[a], Aakash Watts[b], Hafeez Yusuf Hafeez[b], Bernaurdshaw Neppolian[b],*

[a] *Department of Physics and Nanotechnology, SRM University, Kattankulathur, Chennai 603203, Tamil Nadu, India*
[b] *SRM Research Institute, SRM University, Kattankulathur, Chennai 603203, Tamil Nadu, India*

ARTICLE INFO

Article history:
Received 28 September 2016
Received in revised form 5 February 2017
Accepted 15 March 2017
Available online xxx

Keywords:
Mixed metal oxide
Photocatalysis
Heterojunction
Hydrogen
Photodegradation

ABSTRACT

α-Fe_2O_3/Cu_2O mixed oxide photocatalysts were prepared by one step facile hydrothermal method. During the synthesis, the growth of phase pure and highly crystalline polyhedral Cu_2O crystals occurred and simultaneously a heterojunction formed between α-Fe_2O_3 and Cu_2O particles. The optical band gap of bare Cu_2O was found to be 1.8 eV which was less than the reported values and incorporation of 5 wt% α-Fe_2O_3 further reduced the band gap of Cu_2O to 1.75 eV, indicating an enhanced absorption of visible light by the binary photocatalysts. More importantly, the loading of α-Fe_2O_3 on Cu_2O augmented the charge carriers separation and transfer at the interface, which was evident by the reduced photoluminescence intensity of α-Fe_2O_3/Cu_2O photocatalysts. The influence of different loading amounts of iron oxide (1–10 wt%) on Cu_2O was evaluated. Among them, 5 wt% α-Fe_2O_3 loaded Cu_2O showed the enhanced photodegradation activity due to the formation of an effective *p-n* heterojunction and exhibited nearly 30% and 95% increase in the photodegradation rate of methyl orange (MO) compare to bare Cu_2O and α-Fe_2O_3, respectively. The photo generated superoxide radicals were found to be the main reactive species responsible for the degradation of MO. The excellent photodegradation activity of α-Fe_2O_3/Cu_2O photocatalyst is mainly attributed to the enhanced visible light absorption, efficient charge carriers separation and transfer. Based on the experimental results, a double charge transfer mechanism was proposed for the separation and transfer of photogenerated charge carriers in the photocatalysts.

1. Introduction

Generally, wide band gap semiconductor photocatalysts such as, TiO_2, ZnO, SnO_2, ZrO_2 have been extensively used for the photodegradation of organic pollutants under UV light irradiation [1–5]. However, the solar spectrum constitutes only 3–5% of UV light [6]; thus, limiting the efficiency and commercial viability of the wide band gap photocatalysts. Visible light constitutes nearly 43% of the solar spectrum [7]; therefore, much work has been carried out to activate the wide band semiconductor in the visible region of light by loading of transition metals or incorporation of low band gap semiconductors as a sensitizer [8–12]. Another major issue responsible for limiting the efficiency of metal oxide photocatalysts is the fast recombination rate of the charge carriers, which can be largely circumvented by designing a hetero or homojunction between the metal oxides. Therefore, providing a superior charge transfer efficiency and activity compared to a single metal oxide semiconductor [13].

Diverse mixed metal oxides, such as $BiVO_4$/TiO_2 [14], NiO-TiO_2 [15], TiO_2/Bi_2O_3 [16], $ZnCo_2O_4$ [17], Cu_2O/TaON [18], α-Fe_2O_3/$ZnFe_2O_4$ [19], $CaIn_2S_4$/g-C_3N_4 [20], Bi_2O_3/$BaTiO_3$ [21], In_2S_3/TiO_2 [22], WO_3/BiOCl [23], Cu_2O/TiO_2 [24] etc., have been prepared for effective utilization of solar light for various applications, namely hydrogen production [25], CO_2 reduction [26], photocatalytic degradation of organic pollutants [27] and wastewater remediation [28]. For example, enhanced photocatalytic degradation of 4-chlorophenol was observed by Neppolian et al., due to the efficient transfer of electrons from the high band ZrO_2 to low band TiO_2 through sub-states of ZrO_2 [29]. Giridhar and coworkers reported a highly efficient WO_3-ZnO mixed oxide photocatalysts for the photodegradation of cationic methylene blue and anionic orange G dyes [30]. Ganeshbabu et al. prepared Cu_2O/TiO_2 with rGO (reduced graphene oxide) support for the effi-

---

* Corresponding author.
E-mail addresses: neppolian.b@res.srmuniv.ac.in, b_neppolian@yahoo.com (B. Neppolian).

http://dx.doi.org/10.1016/j.cattod.2017.03.020

cient production of hydrogen [31] and CuO/TiO_2 with rGO as a potential photocatalyst for complete degradation of organic pollutants under diffused light along with ultrasound [32]. Kamat et al. observed a synergistic photoelectrochemical activity for transparent $WO_3/BiVO_4$ heterojunction electrode [33].

Last few years, particularly, iron oxide and copper oxide in the form of mixed metal oxides has gained considerable attention for various applications due to their narrow band gaps, suitable band edge potentials, earthly abundant and non-toxicity [34,35]. Li et al. reported that α-Fe_2O_3/Cu_2O nanotubes exhibited efficient conversion of CO_2 into methanol [36]. Mirtchev et al. synthesized γ-Fe_2O_3/Cu_2O by solution phase seed growth method [37]. Tian et al. discussed the efficient photocatalytic degradation of RhB by ternary composite α-$Fe_2O_3/SnO_2/Cu_2O$ [38]. Ti-loaded α-Fe_2O_3/Cu_2O heterojunction thin film electrodes has reported to shown efficient hydrogen production under visible light [39]. However, to our best knowledge, binary α-Fe_2O_3/Cu_2O mixed metal oxide photocatalysts have not been reported for the degradation of organic pollutants under visible light irradiation.

Although various synthesis approaches have been used to prepare Cu_2O based polyhedron nanostructures, most of these methods such as wet chemical reduction, microemulsion, solvothermal, electrodeposition and sonochemical reactions involve a multi-step preparation method, use of organic solvents or surfactants to control the structure and morphology [40–49]. Herein, we prepared an efficient α-Fe_2O_3/Cu_2O binary mixed metal oxide photocatalysts through a facile and low cost hydrothermal method. Compare to other preparation methods, this non toxic and environmental friendly method can produce Cu_2O polyhedron without any use of surfactants, organic solvents and additives. The *p-n* heterojunction photocatalyst formed by this process was further optimized by varying the wt% of α-Fe_2O_3, and Methyl Orange was used as a model pollutant to study its photocatalytic activity under visible light irradiation.

2. Material and methods

2.1. Materials and charecterization

Analytical grade copper acetate monohydrate [$Cu(CH_3COO)_2{\cdot}H_2O$] and Methyl orange dye were purchased from Sigma-Aldrich and iron oxide powder (α-Fe2O3) was obtained from SRL Chemicals, India. Milli-Q water was used in all experiments and the other reagents were used as received without any further purification.

The composition and phase purity of the prepared catalysts were analyzed by X-ray diffraction (PANaltical X'pert powder diffractometer) using Cu Kα radiation ($\lambda = 1.5406$ Å) at room temperature. The particle size and surface morphology of the as-prepared samples were probed by field emission scanning electron microscopy (FEI Quanta FEG 200 HR-SEM). UV–vis absorption spectra and diffuse reflectance spectra (DRS mode) were recorded using UV-2600 spectrophotometer (Shimadzu). Fourier transform infrared spectroscopy (FTIR) was obtained using Perkin Elmer-USA. X-ray photoelectron spectroscopy (XPS) was recorded on a Kratos Axis 165. The surface area, pore size and pore volume measurement were carried out based on Brunauer–Emmett–Teller method using the nitrogen adsorption and desorption isotherms (BET, Quantachrome Nova-1000 surface analyzer).

2.2. Synthesis of α-Fe_2O_3/Cu_2O photocatalyst

2.2.1. Preparation of α-Fe_2O_3

3.0 g of α-Fe_2O_3 powder was dispersed in 100 ml of ethanol and ball milled for 4 h at 400 rpm, followed by quick drying of ethanol at 80 °C. After drying, the ball milled sample was immediately used to prepare α-Fe_2O_3/Cu_2O catalyst.

Table 1
The nomenclature and compositions of different samples prepared by the facile hydrothermal method.

Nominal composition	Sample names					
	CF-1	CF-3	CF-5	CF-8	CF-10	CF-5AN
Cu_2O (wt%)	99	97	95	92	90	95
α-Fe_2O_3 (wt%)	1	3	5	8	10	5

2.2.2. Preparation of α-Fe_2O_3/Cu_2O

α-Fe_2O_3/Cu_2O was prepared by facile hydrothermal method [50], in detail, 0.233 M copper acetate monohydrate was dissolved in 70 ml deionized water and ultrasonicated for 5 min. Afterward, different wt% of ball milled α-Fe_2O_3 (1, 3, 5, 8 and 10%) was added to the solution and the reaction mixture was ultrasonicated for 5 min, followed by vigorous stirring for 1 h. The mixed reddish suspension was transferred into a 100 ml Teflon-lined autoclave and kept at 200 °C for 12 h. After cooling, the reddish product of α-Fe_2O_3/Cu_2O (CF) photocatalysts was collected by centrifugation, washed with deionized water and ethanol several times and dried at 60 °C for 24 h. Similarly, bare Cu_2O was also synthesized without adding α-Fe_2O_3. The dried samples were named as Cu_2O (C), CF-1, CF-3, CF-5, CF-8 and CF-10, as shown in Table 1. For comparing the effects of ball milling, a similar hydrothermal method was adopted to prepare the binary photocatalyst α-Fe_2O_3/Cu_2O by using iron nitrate nonahydrate and copper acetate monohydrate as salt precursors for α-Fe_2O_3 and Cu_2O, respectively and the sample is named as CF-5AN (Experimental details, SI†).

2.3. Photocatalytic activity

In order to examine the photocatalytic degradation ability of the photocatalysts, methyl orange (MO) was selected as a model pollutant. The required amount of the photocatalyst powder (30 mg) was suspended in 30 ml of aqueous dye solution (10 mg/L of MO), in a 100 ml borosilicate reactor. The mixture of photocatalyst and the pollutant suspension was kept under stirring condition in dark for 30 min to achieve the adsorption–desorption equilibrium, followed by irradiation with Xenon lamp with cut off filter ($\lambda > 400$ nm) (250 W, Oriel instruments, USA), under constant stirring at room temperature. At regular time intervals, 3 ml of aliquot of the sample was collected, centrifuged and the% photodegradation of the dye samples was analyzed by using UV–vis spectrophotometer. The total organic carbon (TOC) analysis of the photodegraded dye was conducted using TOC analyzer (Shimadzu, TOC-L, Japan).

For hydrogen evolution reaction, 5 mg of the α-Fe_2O_3/Cu_2O photocatalyst was dispersed in 50 ml of 5 vol% of the glycerol-water solution in a glass borosilicate reactor. The reactor was sealed with airtight rubber septum and stirred magnetically for 30 min, followed by 30 min nitrogen gas purging to create an inert environment in the reactor. The solution was magnetic stirrered throughout the experiment to ensure homogeneity of the suspension during light irradiation. The reactor was illuminated by 250 W Xenon lamp with cut-off filter ($\lambda > 400$ nm) and the generated gas was collected at every hour and injected into an off-line gas chromatograph with a TCD detector (Shimadzu GC-2014 with Molecular Sieve/5 Å column) using nitrogen as a carrier gas.

Please cite this article in press as: S.K. Lakhera, et al., Interparticle double charge transfer mechanism of heterojunction α-Fe_2O_3/Cu_2O mixed oxide catalysts and its visible light photocatalytic activity, Catal. Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.03.020