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Full Length Article

Morphology controlled synthesis and photocatalytic study of novel CuS-$Bi_2O_2CO_3$ heterojunction system for chlorpyrifos degradation under visible light illumination

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ABSTRACT

In this study, $Bi_2O_2CO_3$ (BSC) nanoplates with high aspect ratio and hierarchical nanostructures were prepared by hydrothermal technique using urea/hexamethylenetetramine as hydrolysing agent and KCl as additive in different solvent systems. The relative molar proportion of urea and KCl was crucial for phase purity as well as thickness and planar dimension of the BSC plates. The BSC nanoplates were used as substrates to prepare CuS-$Bi_2O_2CO_3$ (CuS/BSC) direct z-scheme heterojunction systems. The heterojunction materials were characterized by FESEM, HRTEM, XRD, PL, FTIR and UV–Vis-DRS techniques. The presence of crystalline tetragonal BSC and hexagonal covellite CuS phase was inferred from XRD study. Morphologically, the CuS/BSC material contained CuS nanorods and BSC nanoplates. HRTEM study suggested microscopic close contact between the CuS nanorods and BSC nanoplates. Optical property study revealed improvement in visible light absorption and enhanced separation of excitons. The CuS/BSC materials were used as photocatalyst for chlorpyrifos pesticide degradation under visible light irradiation. The heterojunction materials were highly active achieving > 95% degradation within 3 h of reaction. The pathway and mechanism of CP degradation was elucidated using GCMS and radical scavenger experiments.

1. Introduction

In recent years, water pollution has been recognised as a potential global crisis which needs ongoing evaluation. Agricultural and industrial waste water contribute significantly to water pollution. The aqueous effluents from these sectors typically contain suspended solids, water pathogens, heavy metals and refractory organic compounds including pesticides, dyes and personal care products. Among different classes of recalcitrant organic pollutants, the pesticides have been recognised as potentially harmful due to their resistance to photolysis and formation of many carcinogenic and mutagenic by-products in environment [1–7]. The chlorpyrifos (CP) [O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate] is a widely used pesticide belonging to organophosphorothioate group which affect adversely the central nervous, endocrine and cardiovascular systems in human beings [3]. Therefore, the separation/mineralization of CP from aqueous streams has become a public concern. A variety of remediation strategies including physical, chemical and biological methods are practised for the separation/degradation of CP from aqueous system [4–8]. The Photocatalytic degradation method is one of the promising advance technologies for removal of pesticides from aqueous sources since it is economic and environmental friendly [9]. To our knowledge, very few studies are available towards photocatalytic degradation of chlorpyrifos mostly focusing on TiO_2 based photocatalyst under UV light irradiation. The TiO_2 based photocatalyst studied for CP degradation include nanocrystalline TiO_2 [10], $CoFe_2O_4$@TiO_2 decorated reduced graphene oxide [11] , V^{5+}, Mo^{6+}, Th^{4+} and Re^{3+} doped TiO_2 [12,13]. Although the developed photocatalytic protocols show good efficiency for CP degradation, their applicability is severely limited by the use of high energy UV radiation and complex processing steps. Thus development of novel photocatalytic materials which can efficiently degrade CP using visible light as energy source is highly desirable. With this objective, here in we have developed a novel CuS modified $Bi_2O_2CO_3$ heterojunction photocatalyst system for CP degradation under visible light illumination.

Among new generation of visible light active photocatalyst, the bismuth based semiconducting nanomaterials have acquired a special place due to their unique photo response activity. Several bismuth based nanostructured materials including $BiVO_4$, Bi_2O_3, BiOCl, BiOBr, $BiPO_4$, $Bi_2O_2CO_3$, Bi_2WO_6 and $Bi_2W_2O_9$ have been prepared and studied

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for their photocatalytic activity [14–21]. The $Bi_2O_2CO_3$ has been extensively used for degradation of organic dyes and hazardous organic pollutants [22–29]. The bismuth subcarbonate exhibits a typical band gap in the range 2.8–3.5 eV and display excellent UV light induced photocatalytic activity [23]. However, applicability of this material under visible light illumination is restricted due to higher band gap and poor separation of excitons. Recently, significant research focus has been directed towards preparation of $Bi_2O_2CO_3$ based visible light active photocatalyst by heterojunction formation [23–33], doping of elements [34–38], and metal deposition [39]. $Bi_2O_2CO_3$ based heterojunction materials with Ag_2O [23], Fe_3O_4 [24], BiOBr [25], BiOI [26], Ag_2CO_3 [27], Bi_2S_3/Bi_2O_3 [28], Co_3O_4 [29], β-Bi_2O_3 [30], Graphene [31,32] and $BiVO_4$ [33] show superior photocatalytic activity for decomposition of rhodamine B, methylene blue, methyl orange, phenol, formaldehyde and NO_x removal. Morphology controlled synthesis of $Bi_2O_2CO_3$ nanomaterials have also been performed using solvothermal method and mixed solvent systems [40–42]. Although there are reports on the photocatalytic application of $Bi_2O_2CO_3$ based nanoheterostructures, there is no report on the applicability of this important class of photocatalysts for degradation of pesticide molecules. In this work, we have synthesized copper sulfide (CuS) modified bismuth subcarbonate ($Bi_2O_2CO_3$) direct z-scheme heterojunction nanomaterials and studied their photocatalytic application for degradation of potentially harmful chlorpyrifos pesticide from aqueous solution. The direct z-scheme heterojunctions offer distinct advantages in terms of high redox ability and suppressed recombination of excitons compared to conventional type-II heterojunction systems [43–51]. In this study, $Bi_2O_2CO_3$ with different morphology were prepared by hydrothermal method using urea as a mild hydrolysing agent and KCl as additive at different molar proportions. Copper sulfides exist as monosulfides, mixed monosulpfides and disulfides (e.g. CuS, $Cu_{1.8}S$, Cu_2S) having low band gap values ranging from 1.2 to 2.2 eV which is appropriate for visible light absorption [52]. Moreover, both CuS and $Bi_2O_2CO_3$ have matching band gap potential for formation of direct z-scheme heterostructures with improved optical properties.

2. Experimental section

2.1. Materials and methods

Bismuth nitrate [$Bi(NO_3)_3{\cdot}5H_2O$], urea [N_2H_4CO], potassium chloride [KCl], and hexamethylene tetraamine were purchased from Hi Media Laboratories Pvt. Ltd. Copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$] and thiourea [N_2H_4CS] were procured from Merck Specialities Pvt. Ltd. All chemicals are of AR grade and used directly in the synthesis process.

2.2. Synthesis of $Bi_2O_2CO_3$ material (BSC)

The $Bi_2O_2CO_3$ (BSC) material with different morphology was prepared by using bismuth nitrate as precursor salt, urea/hetxmethylene tetraamine (HMTA) as hydrolysing agent and KCl as additive. Different reaction conditions such as simple precipitation, refluxing as well as hydrothermal condition were used to optimize the synthesis process. The bismuth nitrate:hydrolysing agent:additive molar ratio was varied in the range of 1:1:1–1:5:1. In a typical synthesis procedure, bismuth nitrate (1 mmol) and KCl (1 mmol) were dissolved in 100 ml of deionized water. To this solution, 5 mmol of urea in 70 ml water was added dropwise and stirred for 15 min followed by 10 min of sonication to ensure a homogeneous solution. The solution was transferred to a 250 ml stainless steel autoclave and treated hydrothermally at 160 °C for 24 h. The obtained solid residue was filtered, washed repeatedly with H_2O and EtOH (5 times) and kept in an oven at 90 °C for overnight to obtain the BSC material. The BSC materials are referred to as BSC-UxKy or BSC-HxKy where U, H and K represent urea, HMTA and KCl respectively. The x and y represent the molar quantity of Urea and KCl used during synthesis.

2.3. Synthesis of CuS/$Bi_2O_2CO_3$ heterojunction nanomaterials (CuS/BSC)

The as prepared BSC material was subsequently modified by CuS to prepare CuS/BSC heterojunction materials. In a typical process, required amount of copper nitrate and thiourea was dissolved in 170 ml water. One gram of BSC material was subsequently added to the solution. After stirring and sonication for 30 min each, the suspension was subjected to the hydrothermal treatment at 150 °C for 24 h in a 250 ml capacity stainless steel autoclave. The resulting material was separated by centrifugation and washed repeatedly with distilled water. The material was dried at 90 °C for 12 h to obtain the CuS/BSC material. Using the above procedure, CuS/BSC materials containing 5, 10 and 20 wt% of CuS was prepared. The heterojunctions are labelled as CuS5BSC, CuS10BSC, CuS20BSC, respectively, in the subsequent text.

2.4. Characterization methods

The XRD patterns of as synthesized pure CuS, BSC and CuS/BSC materials were recorded using a Rigaku, Ultima-IV multipurpose system fitted with a Ni filtered CuKα (λ = 1.5418 Å) X-ray source. The XRD profiles were obtained in 2θ range of 20–60° at an scan rate of 2°/min. The FTIR spectra of the solid samples were obtained as KBr pellets using a Perkin–Elmer spectrometer in the spectral range of 400–1600 cm^{-1}. The UV–Vis-DRS spectra were recorded using a Jasco V-650 spectrometer with $BaSO_4$ integration sphere. Solid-state Fluorescence (PL) spectra were obtained in the range of 350–600 nm (excitation wavelength 220 nm) using a Horiba Scientific Fluoromax-4 spectrometer. The morphology, size and structural properties of as synthesized nanomaterials were studied using FESEM (Nova NanoSEM microscope, 10 kV) and HRTEM (TECNAI 300 kV) techniques. The specific surface area of the heterojunction materials was evaluated by BET method by N_2 sorption study using a Quantachorme AUTOSORB 1 equipment. The XPS spectra of CuS10BSC-U5K1 material was recorded using a SPECS spectrophotometer (Germany) equipped with a 150 mm hemispherical analyser and Al Kα radiation (1486.74 eV) as the X-ray source. The binding energy corrections were made relative to the C1s peak at 284.6 eV.

2.5. Photocatalytic activity for chloropyrifos degradation

The CuS/BSC heterojunction materials were used as photocatalyst for aqueous phase degradation of chlorpyrifos pesticide (CP). The photocatalytic study was performed using a 150 ml capacity photoreactor fitted with a 150 W Xe lamp. Typically, to a 100 ml of 10 ppm CP solution, 25 mg of CuS/BSC photocatalyst was added and stirred for 30 min followed by 10 min of sonication under dark condition to achieve sorption equilibrium. To this aqueous suspension, 0.2 ml of H_2O_2 was added and exposed to the visible light source. At regular time interval, 3 ml of the reaction mixture was taken out and centrifuged to separate the catalyst. The supernatant was analyzed for CP concentration using UV-HPLC [Agilent semi preparative HPLC, G1322A, C-18 column] using reported procedure [53]. The photocatalytic degradation pathway was probed using GC-MS technique. The GC-MS analysis was performed using an Agilent GC–MS [Model 7890B/5977A] fitted with a DB-5MS column and a FID detector. The initial oven temperature was maintained at 50 °C for 5 min and programmed linearly at the rate of 5 °C/min until it reaches 250 °C where it is held for another 10 min. The injector and detector temperature was fixed at 270 °C and 280 °C, respectively.

3. Results and discussion

3.1. Morphology controlled synthesis of $Bi_2O_2CO_3$ materials

In this study, BSC materials with different morphologies were prepared by varying the hydrolysing agent (U/HMTA), KCl as additive and