Shape Controlled Synthesis of Cu_2Se Nanostructures and Their Effect on the Performance of Photocatalytic Dye Degradation of Nitrobenzene under Visible Light Illumination

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Abstract

Cu_2Se nanostructure have been synthesized by hydrothermal method using different hydroxide solutions to control the morphology. The bare NaOH and mixed NaOH + KOH solutions resulted Cu_2Se nanoplates and Cu_2Se nanowires respectively. The synthesized Cu_2Se nanostructures have been characterized by XRD and SEM. The XRD patterns reveal the pure cubic phase of Cu_2Se. SEM micrographs exhibited nanoplate and nanowire like structures for bare and mixed hydroxide solutions respectively. Photocatalytic performance of Cu_2Se nanowire is observed to be higher the Cu_2Se nanoplates under visible light irradiation over nitrobenzene.

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1. Introduction

As a p-type semiconductors, copper selenides have numerous components viz., CuSe, Cu_2Se and Cu_3Se_2 with different crystal structures, which makes them promising for numerous potential applications including thermo-electric [1], opto-electric [2], gas sensors [3], solar cells [4], photocatalysis [5], photochemical water splitting [6] and hydrogen generation [7]. Among the copper selenides, Cu_2Se has been considered as one of the most investigated materials owing to its unique properties. Recent reports reveal that Cu_2Se nanostructures with different morphologies including nanowires [6], nano-cauliflower [8], nanoplates [9], nanosheets [5, 10], and thin films [11] have been fabricated using various methods.

The recent literature revealed that low cost, high electrical conductivity and environmentally friendly nature of Cu_2Se makes it suitable for various fields of applications

including electrochemical photoreactions like degradations of organic dyes and hydrogen production. Zhao et al., reported the highly efficient hydrogen production (>98%) of Cu_2Se/Co_3Se_4 multivalent hetero-nanocrystals at low working potentials (1.11 V) without any O_2 or CO_2 emission, which demonstrates the minimization of power consumption and pure H_2 production [12]. Huang et al., reported that the highly flexible Cu_2Se thin films displayed more than 97% of its electrical conductivity after 800 cycles and the fabricated device showed good stability with the maximum power density of 580.70 mWm^{-2} [1]. Raju et al., reported the high specific capacitance (1925 F/g) of Cu_2Se nano-cauliflower. However, Cu_2Se/CuS 3D/2D nanocomposite exhibited superior specific capacitance of 2727 F/g, which is 41.66% higher than that of pure Cu_2Se [8]. Yue et al., reported the in-situ synthesis of Cu_2Se nanosheets for high stability sodium ion battery and they found that Cu_2Se nanosheets showed high specific capacity of 293 mAh/g at 1 A/g, which indicates that Cu_2Se nanosheets can be used as hifh stability anode materials for sodium storage [10].

In the present study focused on hydrothermal synthesis of Cu_2Se nanostructures for photocatalytic degradation of nitrobenzene. The synthesized nanostructures were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) for phase identification and morphology study.

2.Materials and Methods

2.1. Materials: Copper acetate (Cu (CH_3COO)-99.4%) selenium dioxide (SeO_2-99.4%) -Alfa Aesar andNaOH, KOH, hydrazine hydrate (N_2H_4 50-60%)– Sigma Aldrich were used to synthesize Cu_2Se nano structures were used without further purification.NB was selected for photocatalytic degradation as organic pollutant which is procured from Aldrich. Distilled water was used for all catalyst syntheses and to prepare NB and MG solution

2.2. Catalyst preparation and characterization

Copper selenide (Cu_2Se) nanostructures were prepared using hydrothermal method with the assistance of hydroxide solution and mixed hydroxide solutions. For Cu_2Se nanowires mixed hydroxides (NaOH & KOH) and nano plates NaOH has been used by keeping same total weight of hydroxides. Initially, uniform mixed hydroxide solution has been prepared using NaOH and KOH with Na/K ratio of 52:48 by taking total weight of 3 g. Under continuous stirring of the mixed hydroxide solution, 1 m mol of copper acetate ($Cu(CH_3COO)_2$)and 0.5 m mol of selenium dioxide (SeO_2)and 2 mL of hydrazine hydrate as reducing agent were added. The total solution was transferred to the 25 mL Teflon-coated auto clave and kept for 30 min in ultra-sonication and then the vessel was tightly sealed moved into the preheated furnace with a temperature of 200 ^oC.The autoclave kept in furnace for 24 hr by maintaining same temperature and then taken out after reaching room temperature naturally. The final black colored product was centrifuged and washed several times with ethanol and D.I water and finally dried in a vacuum oven at 60^oC.X-ray diffraction patterns of the as-synthesized Cu_2Se nanostructures was recorded using Rigaku O/MAX-RC (Cu Kα, λ = 1.5406 Å)) with scanning rate of 4 degree per min from 20-70° degrees. The surface morphology of the prepared Cu_2Se nanostructured catalysts was acquired using scanning electron spectroscopy (SEM, TOPCON DS -130C).

2.3. Photocatalytic degradation of nitrobenzene using Cu_2Se nanostructured catalysts

In order to ensure the photo catalytic degradation of nitrobenzene using nanostructured copper selenide catalysts, an adsorption/desorption equilibrium has been established in between dye and prepared catalysts. The solution of organic pollutant of nitrobenzene 250 mL was prepared with the concentration of 10 mg/L, then the prepared catalysts with an amount of 100 mg was mixed under continuous stirring at room temperature

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in 500 mL conical flask, which is covered with aluminum foil and kept in dark to avoid the reaction with light. Before and after illuminations, these solutions were maintained under air equilibrate conditions. In order to explore the efficiency of photo catalyst degradation of organic pollutant using Cu_2Se nanostructured catalysts, the decomposition of nitrobenzene under visible light (λ> 450 nm) has been evaluated. A high-pressure 400-W mercury vapor lamp with a 450-nm cutoff filter was used during illumination to ensure the desired visible light irradiation. To estimate the change in concentration of nitrobenzene, at a given intervals of illumination time, using Millipore syringe 5 mL of the sample solution was withdrawn from the test solution. After centrifugation of sample solution their absorbance spectra was measured using UV-Vis spectrophotometer using distilled water as reference. To assess the concentration of nitrobenzene was estimated using ratio of C/C_0 at each specific intervals of illumination, here C and C_0 are the value of absorbance at specific interval of time t and initial concentration before degradation.

3.Results and Discussion

3.1. XRD analysis

The XRD patterns of Cu_2Se nanostructures is depicted in Fig. 1.The diffraction peaks are centered at 26.78, 31.15, 44.34, 52.87 and 65.29, which are corresponding to the crystal planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 0 0) of Cu_2Se respectively. It is clearly observed that the intensity of diffraction peaks of nanowires is higher than that of nanoplates, which indicates the high crystallinity and orientation of lattice plane in Cu_2Se nanowires. There are no noticeable diffraction peaks detected in both the XRD patterns, with indicates the high crystalline nature of Cu_2Se. All the diffraction peaks are indexed to the cubic phase of Cu_2Se with lattice cell parameters a = 0.5789 nm which is in line with the JCPDS file no: 88 – 2044.

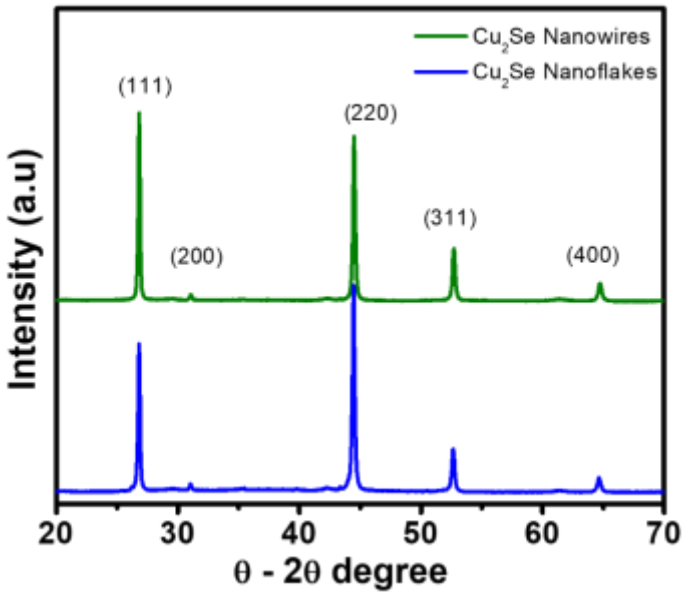

Fig. 1 X-ray diffraction patterns of Cu_2Se nanostructures

3.

2. Morphology study

The SEM micrographs of hydrothermally synthesized Cu_2Se nanostructures using bare (NaOH) and mixed (NaOH + KOH) hydroxide solution are shown in Fig. 2. The bare NaOH solution results non

uniformly distributed nanoplates as displayed in Fig. 2(a). Whereas the mixed hydroxide solution results the clear nanowires as depicted in Fig. 2(b).It is clearly suggesting that the mixed hydroxide solution leads for the better crystal orientation.

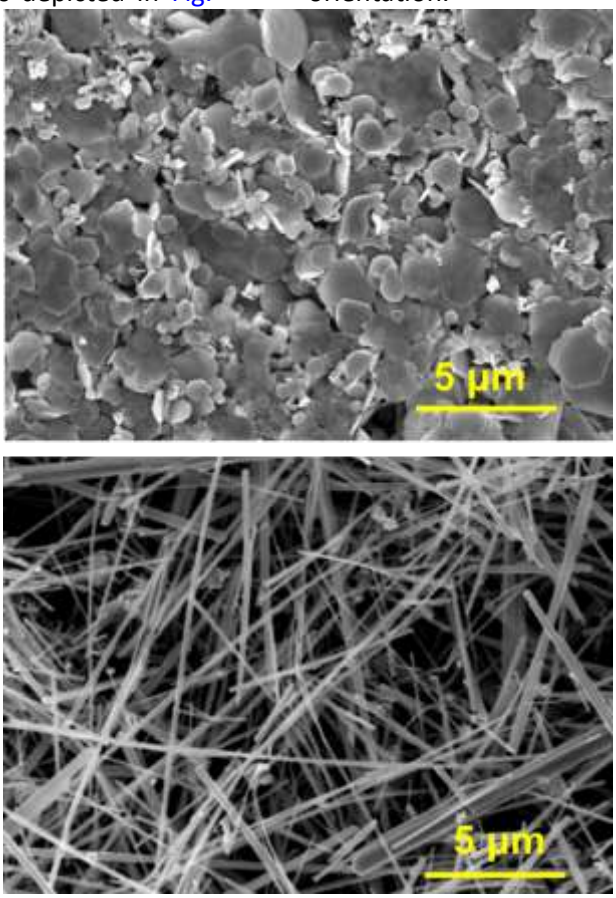

Fig. 2 SEM micrograph of (a) Cu_2Se nanoplates and (b) Cu_2Se nanowires

3.3. Photocatalytic activity

UV–vis absorptionspectroscopy was used toexaminethe photodegradation efficiency of the synthesized Cu_2Se nanostructures asshownin Fig. 3(a, b), which reveals that theCu_2Senanostructures have strongUV–visible lightharvestingcapabilityinthewavelengthrange of200 -500nm. It is clearly observed that thecatalytic activity of Cu_2Se nanostructures against nitrobenzene isgreatlyimprovedundervisiblelight irradiation. Fig. 3(c) showsthephotocatalyticdegradation activityofCu_2Se film nanostructures. The Cu_2Se nanowires exhibited higher photodegradation efficiency over Cu_2Se nanoplates, which may be attributed to the better crystalline nature of Cu_2Se nanowires. The kinetic rate constant of Cu_2Se nanowires is higher than that of Cu_2Se nanoplates indicating the better photocatalytic performance of Cu_2Se nanowires as shown in Fig. 3(d).

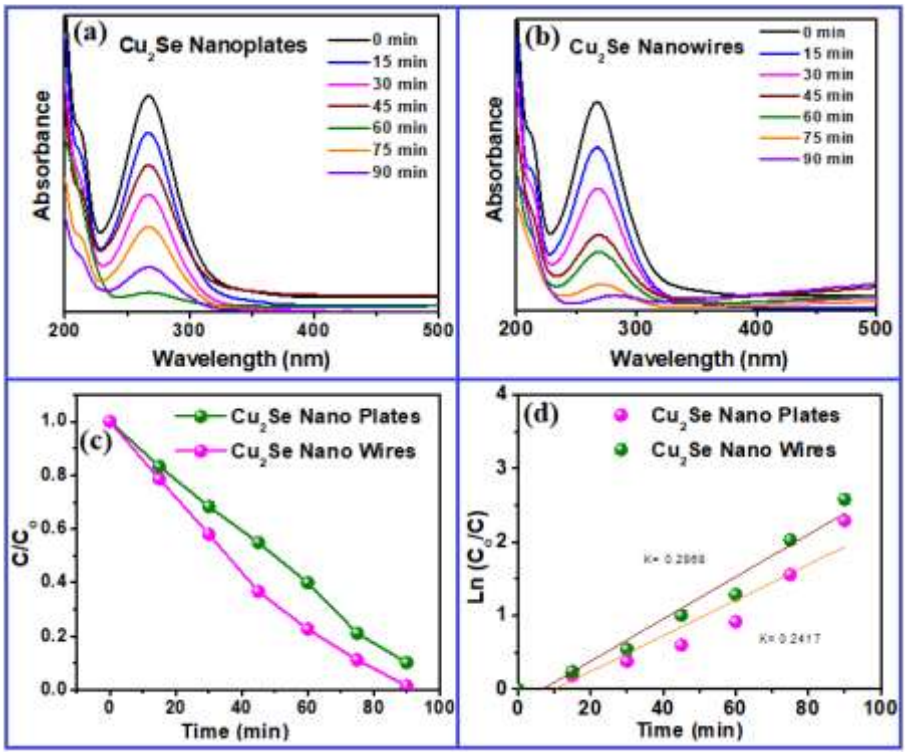

Fig. 3 Photocatalytic activity of Cu_2Se nanostructures over nitrobenzene

Conclusion

Cu_2Se nanostructures were fabricated utilizing a hydrothermal technique and several hydroxide solutions to control the morphology. Cu_2Se nanoplates and nanowires were formed from bare NaOH and mixed NaOH + KOH solutions, respectively. XRD and SEM were used to characterize the synthesized Cu_2Se nanostructures. The XRD patterns show that Cu_2Se is in its pure cubic phase. SEM micrographs of Cu_2Se nanostructures derived from bare and mixed hydroxide solutions revealed nanoplate and nanowire-like morphology. Under visible light irradiation, the photocatalytic performance of Cu_2Se nanowires is found to be superior to that of Cu_2Se nanoplates.

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