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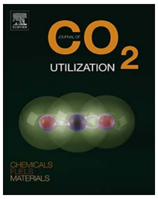

Cu_2ZnSnS_4 (CZTS)-ZnO: A noble metal-free hybrid Z-scheme photocatalyst for enhanced solar-spectrum photocatalytic conversion of CO_2 to CH_4

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ABSTRACT

Development of photocatalytic materials for achieving the aspects of cost-effectiveness, improved performance and high stability is a subject of enormous interest among the photocatalysis research society. With the aim of achieving above mentioned features, herein we report a noble metal free, solar-light active, efficient and highly stable hybrid Cu_2ZnSnS_4 (CZTS)-ZnO photocatalyst, synthesized by a simple two-step process. The morphological, crystalline, band alignment, optical and electronic properties of the prepared samples are intensively investigated. Photocatalytic performance is evaluated by measuring, under the simulated solar light, the ability of the photocatalyst to convert CO_2 into hydrocarbon fuels, primarily CH_4. Our optimum CZTS-ZnO photocatalyst sample exhibits a CH_4 yield of 138.90 ppm $g^{-1} h^{-1}$, a factor of ≈ 31 times greater than the un-sensitized ZnO nanorods, and ≈ 22 times greater than the CZTS nanoparticles; with excellent stability yielding similar CH_4 production up to five test-cycles. The enhanced performance of the hybrid, noble metal-free photocatalyst can be attributed to improved light absorption and efficient separation of the photogenerated charge due to the Z-scheme heterojunction interface.

1. Introduction

Photocatalytic materials are of great scientific interest, with a range of applications that includes degradation of organic pollutants [1,2], environmental remediation [3], solar cells [4], photocatalytic water splitting [5], and CO_2 conversion to useful chemicals and fuels [6]. However while a great many semiconductor photocatalysts have been investigated, limited stability, cost-effectiveness, and photoconversion efficiency have limited translation from laboratory to commercial application. Among the various semiconductor photocatalysts, Zinc oxide (ZnO), a n-type direct band gap semiconductor ($E_g \approx 3.3$ eV), offers several advantages including low cost, non-toxicity, and high photosensitivity [7]. Despite its encouraging properties a significant amount of work is still needed to enhance the photocatalytic performance of ZnO. Key factors restricting ZnO performance include limited visible light absorption, and rapid electron-hole recombination. Efforts to overcome these challenges include non-metal (e.g. C, N and S) doping aimed towards narrowing the ZnO band gap and extending light absorption to longer wavelengths [8], noble metal (e.g. Pt, Au, Cu) loading [9] for efficient separation of photogenerated charges, and heterojunction formation by coupling two different semiconductor materials [10,11]. The doping strategy is an effective option that lowers the band gap, in turn extending the light absorption. However dopant-induced defects lower the mobility of photogenerated charges, increasing electron-hole recombination [12,13]. While noble metal loading typically improves charge separation, in turn enhancing photocatalytic performance, overall material costs are higher and there are unsolved issues associated with catalyst-poisoning [14]. Heterojunction photocatalysts are currently of considerable interest due to the prospect of obtaining broad spectrum light absorption with improved charge separation [15,16]. Z-scheme photocatalysts are particularly intriguing as they offer stronger redox capacity [17], resulting in significantly improved photocatalytic performance [18] without the loss of photocorrosion stability [19].

In general, a Z-scheme photocatalyst is composed of two different semiconductors, with one semiconductor (SC1) having a conduction band in between the valence band and conduction band of the other semiconductor (SC2) [20]. The photogenerated electrons from the conduction band of SC1 neutralize the holes of the valance band of SC2, whereas the holes of SC1 are filled by reducing agents and SC2 electrons are donated to oxidizing species. Charge transfer between the coupled semiconductors can proceed with or without the presence of a

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charge mediator, by which Z-scheme systems are, respectively, classified as direct or indirect [21], with direct Z-scheme photocatalysts generally more preferred as they are less complex and thus better suited for application [22,23].

A thorough survey of the literature show reports on ZnO based Z-scheme photocatalysts like ZnO/CdS [24], N-doped ZnO/g-C_3N_4 [25], CdS/Au/ZnO [26], ZnO-CdS/reduced graphene oxide [27], g-C_3N_4/ZnO [28], ZnO-Au-SnO_2 [21], and ZnO-Au@CdS core-shell nanorods arrays [29] for a variety of photocatalytic applications such as photocatalytic water splitting, Rhodamine B dye degradation, decomposition of aromatic compounds, and CO_2 photoreduction. The diverse studies show enhanced photocatalytic efficacy with stable performance in their respective applications. During the past few years Cu_2ZnSnS_4 (CZTS), a non-toxic, *p*-type, direct band gap ($E_g \approx$ 1.4-1.5 eV as dependent upon synthesis method) [30], earth abundant and visible light absorbing compound semiconductor has been studied for use in photovoltaics [31], optoelectronics [32], photocatalysis [33], and environmental remediation [34]. Specific to CO_2 photoreduction, our interest, there exist but few reports employing CZTS, which include studies on a CZTS/TiO_2 composite [35], CZTS electrodes modified with CdS and In_2S_3 buffer layers [36], and CZTS photocathodes modified with ruthenium complex polymer [30]. Herein we report on a new class of hybrid ZnO-based Z-scheme photocatalyst synthesized by a facile two-step synthesis methodology and employed for CO_2 photoreduction to hydrocarbon fuels. ZnO nanorods (NRs) loaded with Cu_2ZnSnS_4 (CZTS), using two-step synthesis approach comprised of: (i) solution phase synthesis of ZnO NRs, and (ii) loading of the ZnO NRs with different amounts of CZTS nanoparticles. A schematic of the adopted synthesis approach is shown in Fig. 1. The photocatalytic activity of our CZTS-ZnO photocatalyst is evaluated with respect to its ability to promote the photocatalytic conversion of CO_2 to hydrocarbons (methane is primarily obtained), under simulated solar light (AM 1.5G). Considering the hazards of catastrophic global heating [37], the ability to use sunlight to convert CO_2 back into a fuel is extremely compelling.

To the best of our knowledge this report is the first on synthesis and application of a Z-scheme CZTS-ZnO photocatalyst to CO_2 photoreduction. The photocatalyst manifests significantly enhanced photocatalytic CO_2 conversion, 138.90 ppm g^{-1} h^{-1}, a factor of ≈ 31 times greater than the un-sensitized ZnO nanorods, and ≈ 22 times greater than the pure CZTS nanoparticles. The excellent performance of our Z-scheme CZTS-ZnO photocatalyst is attributed to broad spectrum light absorption and efficient separation of the photogenerated charge. We suggest our study may help lead to further improved materials in the future.

2. Experimental section

2.1. Materials and reagents

For the synthesis of ZnO nanorods, CZTS nanoparticles and hybrid CZTS-ZnO photocatalyst, copper(II) nitrate trihydrate (Puriss, 99–104%), zinc chloride (ACS reagent, ≥ 97%), tin(II) chloride (reagent grade, 98%) and sodium sulphide (99.98%) are purchased from Sigma-Aldrich. Sodium hydroxide (94%) and methanol (> 95%) were purchased from Duksan Reagents (Republic of Korea). All chemicals were used without any further purification.

2.2. Synthesis of ZnO nanorods

For the synthesis of the ZnO nanorods, 10.0 g of sodium hydroxide (NaOH) is dissolved in 35.0 ml of deionized (DI) water, and heated to 70 °C. Zinc chloride solution (6.1 g dissolved in 15.0 ml DI water) is added dropwise to the NaOH solution under continuous stirring; the stirring is continued for 7 h at 70 °C. The obtained white mixture is cooled, washed and centrifuged several times with DI water until the pH becomes neutral (pH ~ 7–8). The white centrifuged powder is then vacuum dried at 80 °C for approximately 12 h, followed by calcination at 400 °C for 2 h.

2.3. Synthesis of CZTS nanoparticles

CZTS nanoparticles are synthesized using a previously reported hydrothermal technique [38]. Briefly, copper(II) nitrate trihydrate (0.144 g) is dissolved in 20.0 ml of DI water. To this solution zinc chloride (0.042 g) and tin(II) chloride (0.057 g) are added while stirring followed by sonication for 10 min to form the homogeneous mixture. After that sodium sulphide (0.186 g) is added, resulting in a black-colored solution which is stirred for another 5 min. The blackish mixture is placed within a Teflon-lined hydrothermal autoclave of 29.0 ml capacity and heated at 180 °C for 18 h in a box furnace, after which the autoclave is allowed to cool naturally to room temperature. Finally, the black CZTS powder is collected and washed with DI water several times, followed by vacuum drying at 70 °C for 12 h.

2.4. Synthesis of hybrid CZTS-ZnO (CZ) photocatalysts

A fixed amount of ZnO nanorods (0.1 g) are added to a variable amount of CZTS precursor, vigorously stirred for 30 min, and then subjected to a hydrothermal treatment similar to that as used for the synthesis of the pure CZTS nanoparticles. The amount of CZTS loading (weight percent, wt%) is varied by varying the stoichiometric amounts of CZTS precursors with respect to a fixed amount of ZnO (0.1 g) in 20.0 ml of DI water to get 10%, 20%, 30% and 40% CZTS loaded ZnO

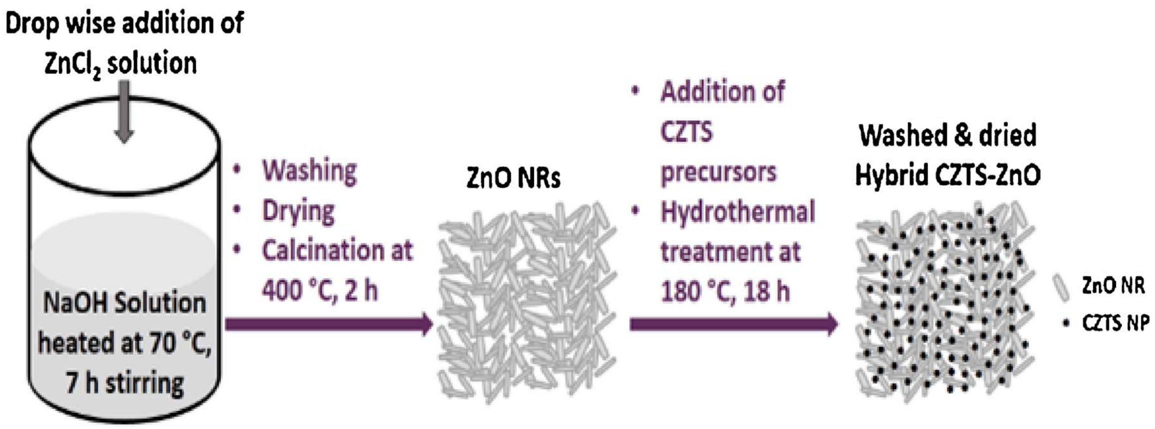

Fig. 1. Schematic view for the synthesis procedure of hybrid CZTS-ZnO photocatalysts.