

ZnO-CdS-Ag₂S double S-scheme heterojunctions with significant hydrogen evolution reaction and dye degradation properties

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ABSTRACT

Here in, we report a new methodology for the fabrication of free template ternary ZnO-CdS-Ag₂S nanohybrids with superior photocatalyst properties for the hydrogen evolution reaction (HER) and dye degradation. Firstly, ZnO nanorods (NRs) were synthesized using a solvothermal method and used as a seed template for the growth of CdS-Ag₂S QDs. The CdS-Ag₂S QDs were grown using two different methods of microwave irradiation and photochemical treatment using thioglycolic acid (TGA) as both capping agent and digestive reactant. Structural characterizations proved the formation of the ternary structure with both methods of synthesis. XPS analyses revealed that photochemical approach results in the formation of a ternary composite with higher ZnO nanoparticles concentration. Electrochemical studies inferred that samples prepared using photochemical treatment have the least of charge transfer resistance, large surface area of 132 m²/g, large electrochemical surface area and higher electrochemical performance. Linear sweep voltammetry obtained current densities of magnitude of 100 mA cm⁻² at bias -0.475 V vs. RHE, onset potential of -0.238 V, and Tafel slope of 45 mV/dec. Moreover, samples prepared using photochemical approach showed also high cyclic HER stability and reproducibility of the same results from the same ink after storing for six months. This method of synthesis can be applied for the synthesis of multi-functional ternary metal oxide-QD-QD nanocomposites for energy conversion applications. A S-scheme band diagram is suggested to infer the internal charge separation mechanism and high HER and photocatalyst activities of the ternary compound.

1. Introduction

The race in research and development of hydrogen generation and CO₂ capture has been the subject of tremendous studies in the last decade [1–5]. Despite of successful synthesis and application of the single junction two-dimensional (2D) metal dichalcogenides for high relatively catalytic properties in hydrogen generation [6–8], their commercial application is still controversial, due to their low cyclic stability and scarcity of heavy metal sources such as Mo, Te, W elements [9–11]. From the energy point of view, the challenging issue is an appropriate band diagram (either band gap or fermi level in the case of alloys), and work function alignment. In addition to that, the correspondence of the band diagram with the reduction-oxidation reaction

energies of the known liquid medium such as water, ethanol, and methanol, for the aforementioned compounds should be evaluated according to the fundamental perspectives of the electrochemical reactions [12,13]. Therefore, to boost the photocatalyst activity of materials, the band gap of targeted compounds should be in the favorable range of the UV/Vis/NIR energy of the solar spectrum (350–750 nm) with conduction or valance band close to redox/oxidation energies of liquid medium and with an efficient rate of electron-hole separation/extraction [14]. From the electrochemical theory, to fulfill hydrogen evolution reaction (HER), this compound needs to possess a high effective surface area, high rate of charge transfer/extraction, proper work function alignment, and abundant active sites for the completion of Tafel/Volmer and Volmer/Heyrovsky reactions [15].

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Moreover, it must be also chemically and structurally stable in continuous cyclic reaction chains. In this view, novel heterojunction nanocomposites have been studied with a varieties of materials involved such as TiO₂ nanotube/AgIn₅Se₈ quantum dots [16], ultrathin 2D/2D WO₃/g-C₃N₄ [17], porous Ni₅P₄ [18], Bi₂O₃/Bi₂MoO₆ [19], In₂Se₃/CdS [20], Ce doped ZnO/Carbon nanotubes [21], ZnO/SrTiO₃ [22], 0D/1D ZnBi₂O₄/ZnO [23], SiP/TiO₂ [24], self-assembled CdS@Boron Nitride core-shells [25], Ni₂P/Bi₃O₄Br-OVs heterojunction [26], ZnCdS/CoSP [27], PdO/GdFeO₃ [28], ZnIn₂S₄/FePO₄ [29] CoO QDs/Bi₂MoO₆ monolayer [30], etc. The purpose of the synthesis of heterostructured nanomaterials is to take advantage of varieties of band gaps, conduction and valence band positions as well as efficient charge separation using the choice of materials that lead to appropriate band alignment [5,31]. These novel heterogeneous catalysts were explained via a step-scheme (S-scheme) to justify the mechanism of charge transfer and photocatalytic hydrogen production in heterostructured material [22,31–37] such as Cu₂V₂O₇/α-Fe₂O₃ [38], Bi₂WO₆/AgInS₂ [39], Cu₃P/TiO₂ [40], Co₉Se₈/TiO₂ [41] and Ag₂Mo₂O₇/CoMoO₄ [42]. In the S-scheme model, when two different n-type semiconductors that are in contact with each other, are exposed to external light or electric field, the electrons that are excited to the conduction band (CB) of high Fermi energy material recombine with the holes in the valence band (VB) of low Fermi energy semiconductor, building an electric field at the interface as driving force in the opposite direction from the low Fermi energy (LFE) semiconductor to the higher Fermi energy (HFE) one, causing accumulation of electrons in CB of LFE semiconductor for reduction and segregation of holes in HFE for oxidation [5,31,32,43]. Song et al. have fabricated a novel through-holes heterojunction that suggests the photogenerated charge relocation mechanism of g-C₃N₄/BiOBr for efficient catalytic dye degradation [44]. Recently, Zheng et al. suggested the formation of S-scheme at the heterojunction of amorphous Co₃O₄ and crystalline CuBr with efficient hydrogen generation and stability after cyclic HER activities [35]. More interestingly, a new mechanism of double S-scheme for charge separation and H₂ production has been reported in novel triple nanostructures [31,45] with a high yield of H₂ generation such as CdSe/WS₂/g-C₃N₄ [46], Co₃O₄/NiCo₂O₄/NiO [47], Bi₂S₃/MoO₃/C₃N₄ [48], CdS/g-C₃N₄/graphene [37], NiCuInS₂:In₂S₃/g-C₃N₄ [49], Mn_{0.2}Cd_{0.8}S@ZnO hetero/nanostructures [50], and Ga₂O₃/ZnO/WO₃ triple compound [51]. As an example, via a dual S-scheme mechanism, hierarchical nanostructured Co₉S₈-MoS₂-Ni₂P obtained a photocatalytic hydrogen evolution rate of 5.69 mmol g⁻¹ h⁻¹ [52]. ZnO nanomaterials have been studied widely due to their superior photocatalyst properties as reported elsewhere [53–55]. For instance, ZnO@ZnIn₂S₄ heterojunction were fabricated using the hydrothermal growth of ZnIn₂S₄ nanomaterials on ZnO rod shape with boosted active sites for catalytic reduction of CO₂ [56]. CdS materials have been also investigated as photocatalysts [57] either in a single in compound or combination with other materials such as ZnO [58], or TiO₂ [59], and also as core/shells [60–62]. CdS/Ag₂S nanocomposites as one of the heterogeneous combinations have significant features such as different optical properties [63] and superior photocatalyst activity and their hierarchical forms have been employed also for hydrogen generation [64]. One of the important keys for efficient charge transfer/separation under light exposure is interface formation as has been reported by Shi et al. [14]. They have used an in-situ sulfurization to form four types of interfaces which their formation led to efficient charge transfer and a significant hydrogen evolution rate of 44.70 mmol h⁻¹ g⁻¹ in the triple heterojunctions of ZnS/CdS/ZnO [14]. Controlling the formation of interfaces, and appropriate band alignment is highly dependent on the method of synthesis and the control of parameters in the synthesis process [21]. Ahmad et al. have investigated the role of the synthesis method in the hydrogen evolution activity of the prepared nanocomposites by comparing hydrothermal and sol/gel synthesis methods and they have shown efficient charge transfer by showing a significant reduction of arc radius in the corresponding measured Nyquist plots [21]. Therefore, considering the significance of the synthesis approach

and the processes entailed, Xiaoyu Xie et al. reported a synthesis of ZnO nanorod/CdS/Ag₂S core-shells assembled on a substrate with enhanced photoelectrochemical properties due to its dual-channel charge extraction. They utilized a sputtering technique for CdS growth and then they used a cation exchange for Ag₂S formation. They have reported a current density of ~6.82 mA cm⁻² for HER efficiency at an external bias of 1.23 V vs. reversible hydrogen electrode (RHE) [65]. In another report, Chen et al., in 2016 studied the synthesis of the ternary composition of ZnO/CdS/Ag₂S with enhanced visible light photo dye degradation properties [66]. They have grown CdS/Ag₂S structure using the ionic successive deposition (SILAR) method on ZnO nanowires with a length of the micrometer.

Here, we report a template-free synthesis of ZnO/CdS/Ag₂S ternary nanocomposites via dual chemical routes and we have compared the effect of the synthesis route on the photocatalyst and HER activity by means of different characterizations. First, ZnO nanorods were synthesized and their morphology and size were optimized by a hydrothermal method, thereafter CdS/Ag₂S quantum dots were grown on them with two different routes of simple photochemical treatment and microwave irradiation. Also, we have compared the effect of CdS/Ag₂S growth techniques of microwave irradiation and photochemical treatment to conclude the effectiveness of the method of fabrication for obtaining highly efficient dye degradation photocatalyst and electro-photocatalytic hydrogen generation, simultaneously. Besides the novel synthesis methods of ZnO/CdS/Ag₂S nanocomposites that have been utilized in this study, thioglycolic acid (TGA) was also used as a double-functional agent to provide a digestive effect for ZnO NRs as the core of the ternary compound as well as playing also as the capping agent for the rate and size control of CdS/Ag₂S QDs. Moreover, A S-scheme model was also suggested to justify the efficient charge separation for observed high HER activity of the ternary compounds.

2. Experimental methods

2.1. Synthesis of ZnO/CdS/Ag₂S nanocomposites

2.1.1. Optimizing ZnO nanorods synthesis

In Table S1 (please see the supporting information file) the synthesis parameters are tabulated. To optimize the quantities of precursors, three different routes with their corresponding references are examined to obtain high-quality, uniform ZnO NRs as the basis structure for the growth of QDs. In the synthesis method of ZnO-3, simply 1.48 g Zinc nitrate (Zn(NO₃)₂, 99 %) and 4 g Sodium hydroxide (NaOH) were dissolved in 50 ml and 5 ml DI water, respectively, and mixed and stirred for 10 min, then 3.5 ml of ethylenediamine (C₂H₈N₂) and 27.5 ml of ethanol (96 %) were injected to 30 ml of it and sonicated for 20 min. Thereafter, the solution was transferred to a Teflon-lined autoclave and placed in the oven at 180 °C for 12 h. After that, it was allowed to cool down to room temperature and the slurry solution was washed with DI water. The resultant precipitate was dried at 50 °C for 1 h. The dried powder was placed in a furnace and annealed at 500 °C for 1 h to crystallize the ZnO NRs.

2.1.2. Synthesis of CdS/Ag₂S quantum dots on ZnO NRs by microwave irradiation

Table S2 shows the synthesis parameters and values of ZnO-CdS-Ag₂S nanocomposites and Figs. S1–a (supporting information file) demonstrates the schematic of the synthesis procedure that has been developed in this study. Firstly, Sodium thiosulfate (Na₂S₂O₃) and Cadmium Acetate dihydrate (Cd(CH₃COO)₂) precursor solutions were prepared and mixed, and Thioglycolic acid (C₂H₄O₂S) known as TGA was injected in the solution and stirred for 5 min and pH was adjusted to 8 by dropwise injecting of Ammonia (NH₄OH) solution. Thereafter, 20 mg of the prepared ZnO NR powder was dispersed in DI water using a probe sonicator, then the two solutions were mixed and stirred in a beaker for 5 min then it was placed in the microwave for 2 min. After

obtaining a yellow-orange colour solution, the Silver nitrate (AgNO_3 , 99.8 %) precursor solution was prepared by simply dissolving AgNO_3 in DI, and it was added to the yellow-orange colour solution and the final solution was exposed to microwave irradiation again up to 16 min to obtain a uniform dark brown solution as indicated in Figs. S1–a. The resultant dark solution was then centrifuged and simply dried at room temperature. The samples prepared by this method are addressed to M1, M2, and M3 in the remainder of the text.

2.1.3. Synthesis of $\text{CdS}/\text{Ag}_2\text{S}$ quantum dots on ZnO NRs by photochemical reactions

The growth of $\text{CdS}/\text{Ag}_2\text{S}$ QDs in this method is quite similar to the microwave method, except the reactions take place under a UV lamp at room temperature as shown in Figs. S1–b. To begin, the preparation of $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Cd}(\text{CH}_3\text{COO})_2$ precursor solutions is the same as the microwave irradiation method as mentioned in the previous section. Thereafter, 20 mg of the prepared ZnO NR powder was dispersed in DI water using a horn sonicator, then the two solutions were mixed and exposed to UV irradiation for 2 min to initiate the growth of CdS QDs. After that, the AgNO_3 precursor solution was added to it and placed under a UV lamp for 40 min to obtain a dark brown solution. The obtained solution was centrifuged, and the black powder was dried for further analysis. The samples synthesized with this method are labeled as P1 and P2.

2.1.4. Dye degradation sampling

200 mg/L of $\text{ZnO}/\text{CdS}/\text{Ag}_2\text{S}$ powder was dispersed using a bath sonicator into the 2.5 mL of 100 mg/L methylene blue (MB) solution and it was placed in the dark for half an hour. Then the mixture of dye and nanocomposite solution was positioned at a fixed distance of 10 cm from the mercury lamp with filter (250 W, 254 nm). The absorption spectra were recorded in the range between 200 and 800 nm by 10 min intervals of UV irradiation.

2.2. Characterization methods

X-ray diffraction (XRD) measurements were conducted by D8-Advance Bruker X-ray diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was performed on a Bestec system considering the resolution of 0.1 eV, by using $\text{Al K}\alpha$ X-ray emission as the photon source (Thermo Fisher Scientific Company of the United States) and data were calibrated using C 1s peak at binding energy of 284.8 eV. Energy dispersive x-ray spectroscopy and Field Emission Scanning Electron Microscopy (EDX-FESEM) were employed using a Zeiss (Gemini 1550) microscope having a field emission (FE) electron source and an in-lens detector for secondary electrons and elemental mapping for morphological study. Optical Photoluminescence (PL) and absorption spectra were obtained using an Avantes spectrometer model of AvaSpec-2048 TEC. The exciting wavelength was 254 nm. Transmission electron microscope (TEM) images were recorded by a LEO912 AB electron microscope with an accelerating beam voltage of 200 kV. Fourier Transform InfraRed (FTIR) spectroscopy was carried out using Hamamatsu C15511-01. Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis were performed using an automated gas sorption analyser (BELSORP mini I, Made in Japan).

2.2.1. Electrochemical characterization methods

The working electrode preparation was performed using deposition of 10 μL of a slurry solution on pre-cleaned Glassy carbon (2 mm diameter) electrodes the solution was prepared using 2 mg/ml of nanocomposite in DI water together with the injection of 1 μL of Nafion as binder. The electrochemical measurements were carried out using three electrode Autolab PGSTAT 204 workstation equipped by NOVA 2.1 software. Electrochemical measurement is based on an electrochemical cell including three electrodes: the working electrode based on

glassy carbon (GC) and Pt as counter electrode and reference electrode using Ag/AgCl in 3.5 M KCl electrolyte. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were used to evaluate the hydrogen evolution reaction (HER) activities of the nanocomposites. LSV measurement was performed in 0.5 M H_2SO_4 electrolyte with a constant scan rate of 5 mV/s, from the positive to negative potential to investigate the HER activity of the samples. IR compensation was applied during each measurement. CV measurement was performed in a mixture solution of 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, and 1 M KCl as electrolyte by different scan rates [67–69] and also in 0.5 M H_2SO_4 for determination of capacitance and electrochemical active surface area (ECSA). Electrochemical impedance spectroscopy (EIS) was conducted at a bias voltage of 0.35 V also in the standard ferrocyanide solution to infer charge transfer properties of the modified electrodes. The transient photo-current response (Light off-on) experiment was performed using a 254 nm UV lamp with power output of 16 W, exposing the modified electrodes in 0.5 M H_2SO_4 electrolyte to it and recording amperometry measurements by 10 s intervals of light on and off.

3. Results and discussion

3.1. Structural properties of $\text{ZnO}/\text{CdS}/\text{Ag}_2\text{S}$ nanocomposites

ZnO NR morphology and crystallinity are very critical from both experimental and physics point of view: the ZnO morphology and size highly changes the growth of CdS and Ag_2S QDs and also band alignment and charge transfer is also dependent on the ZnO crystal growth as the underlying structure. Thus, as it has been explained in section 2.1.1, firstly different ZnO nanorods were synthesized and a careful track of morphology was performed as it has been shown in Fig. S2. It is evident that thick nanorods (with several hundred nanometers diameter) or branched rods (Fig. S2-a,b & c,d) are not suitable for such a purpose. Thus, the nanorods in Fig S2-e,f were chosen as the template for the growth of CdS and Ag_2S QDs. Fig. S3 is the corresponding XRD pattern of Fig. S2-e,f which is in good agreement with the ZnO Wurtzite crystal structure from the previous reports [54,70]. Figs. S4–a shows the XRD patterns of all samples in Table S2. The ZnO crystal phase is the dominant phase in all the patterns, as it was the basis of $\text{CdS}/\text{Ag}_2\text{S}$ growth. There are also peaks at $2\theta = 24.8^\circ$, 26.5° , 43.8° and 47.7° corresponding to atomic planes of (100), (002), (110), and (103) of CdS Wurtzite [71]. (013) and (221) atomic planes of the Ag_2S monoclinic phase are overlapping with ZnO atomic planes. Only the (042) atomic plane of Ag_2S is indicated clearly for sample P2 in Figs. S4–b. To elucidate precisely the formation of CdS and Ag_2S structures, detailed XPS was performed for M3 and P2 samples. Fig. S5-a&b shows the survey scan of M3 and P2, respectively. XPS orbital scans of Zn, Cd, and Ag elements were performed for both samples as depicted in Fig. 1 and a summary of statistical comparison of atomic concentrations, binding energy, and peaks' width are tabulated in Table S3. The relative atomic percentages of the elements indicate the relative concentration of Zn, Cd, and Ag elements. A quick grasp of Fig. S5, Fig. 1, and Table S3 indicates the presence of all elements as the indication of ZnO Wurtzite, CdS Wurtzite phase, and Ag_2S Acanthite phase reported elsewhere [72–74]. Moreover, Table S3 indicates the ionizing states of Cd^{+2} and Ag^{+1} and there is no segregation or by-product phase formation in both microwave irradiation and photochemical synthesis routes that confirms $\text{ZnO}/\text{CdS}/\text{Ag}_2\text{S}$ ternary compound has been successfully synthesized with both methods. In addition to that, it also shows P2 sample has higher Zn and Ag concentrations as can be inferred from the XRD patterns of Figs. S4–b. Because ZnO Bragg peaks have clearly higher intensity, and also (042) atomic plane of Ag_2S is also observable. It is worth mentioning that in Table S3, Cd and Ag elements of P2 have significantly less FWHM than those of M3. The broadening of XPS peaks indicates the atomic dislocation and bond dissociation in the crystal structure. Thus, it can be interpreted that Ag_2S and CdS grow on ZnO with more crystallinity in the photochemical approach compared to the

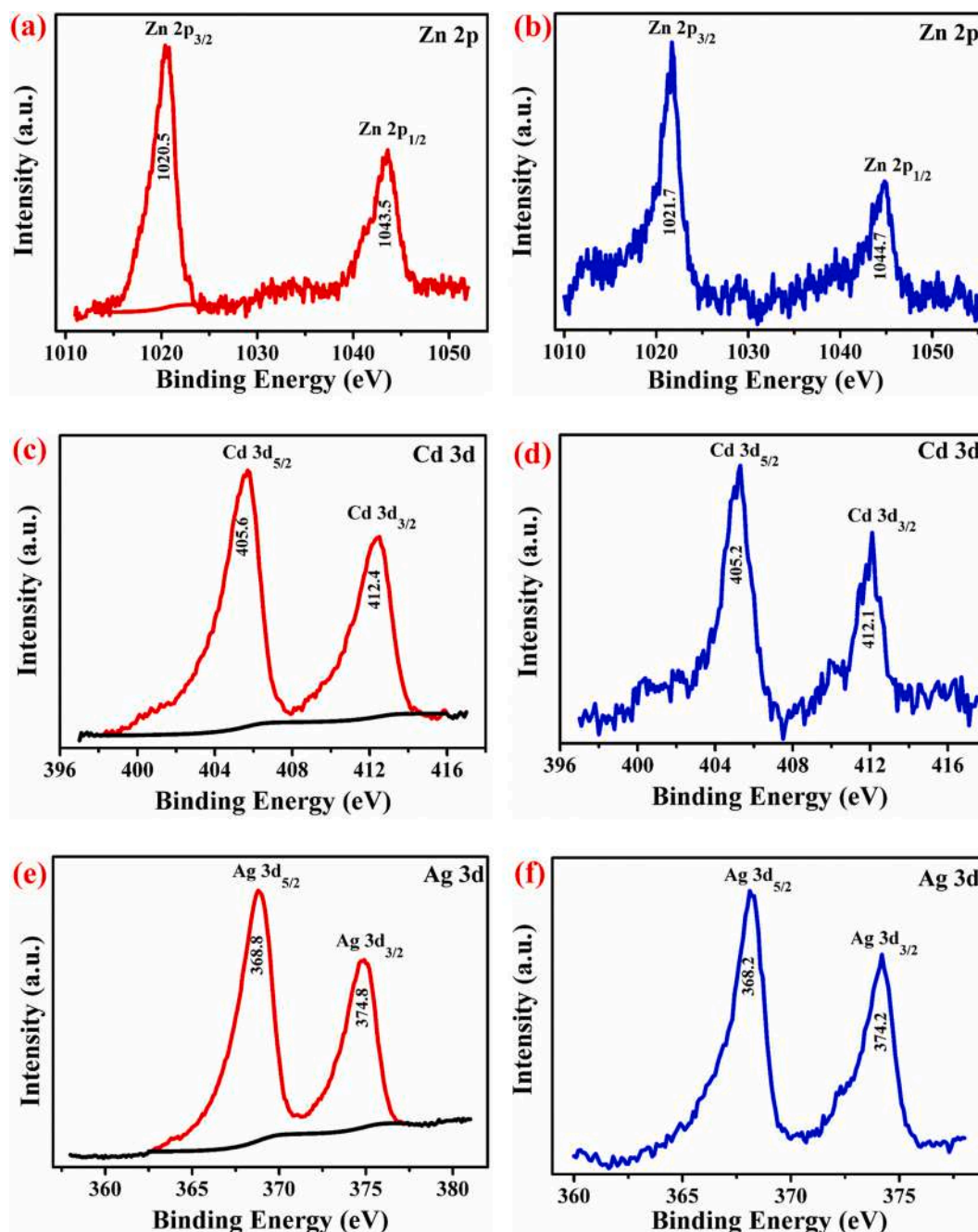


Fig. 1. XPS orbital scans of (a) Zn 2p (c) Cd 3d and (e) Ag 3d of sample M3, and (b) Zn 2p (d) Cd 3d, and (f) Ag 3d orbital scans of sample P2.

microwave method. The FWHM values of O1s XPS scan (Fig.S5-e,f) show that both P2 and M3 samples have the same oxygen ionization of O^{2-} that belongs to Zn-O bonding. Moreover, S 2p and S 2s orbital scans (Fig. S5-g,h & i,j) reveal the S^{2-} ionization state. Besides, the S 2p orbital scan of sample P2 has an extra peak which is related to SO_3^{2-} due to the slow dissociation of $Na_2S_2O_3$ in photochemical synthesis compatible with our previous reports [63,75]. From the discussion above, it can be inferred that the P2 sample has a more crystalline structure of resultant ZnO-CdS-Ag₂S compared to M3. Moreover, it has also a higher Zn concentration than the M3 sample which was expected to be the same as in the synthesis, since initially both samples had entirely the same amount of ZnO NRs, Cd and Ag precursors (Table S2). The reason lies in the chemistry of these synthesis routes and the delicate role of TGA as a capping agent for the growth control of QDs. Here, it has also a digestive (corrosive) effect on the ZnO nanorods. Since TGA is an acid, it releases

its H proton in the chemical reactions reversibly and thus can etch ZnO nanorods gradually during the synthesis process of CdS/Ag₂S QDs. In the case of photochemical reaction, it has less digestive effect since the reaction is taking place at room temperature and after adding TGA to ZnO solution, TGA molecules initially release their H^+ proton and lead to a low rate of ZnO digestion. In contrast, during Microwave irradiation, TGA molecules are activated with both electromagnetic radiation and thermal convection which consequently yield a higher rate of ZnO digestion. Hence, the M3 sample preserves less ZnO NRs as the basis for the growth of CdS-Ag₂S QDs than P2. To examine the aforementioned hypothesis, FESEM and TEM images of both samples are shown in Fig. 2. FESEM images of Photochemical (P2) and microwave (M3) samples show that the microstructure of the samples are very similar up to tens of nanometer scale and are very uniform with spherical shape as indicated by yellow circles in the images. On the other hand, TEM images of M3

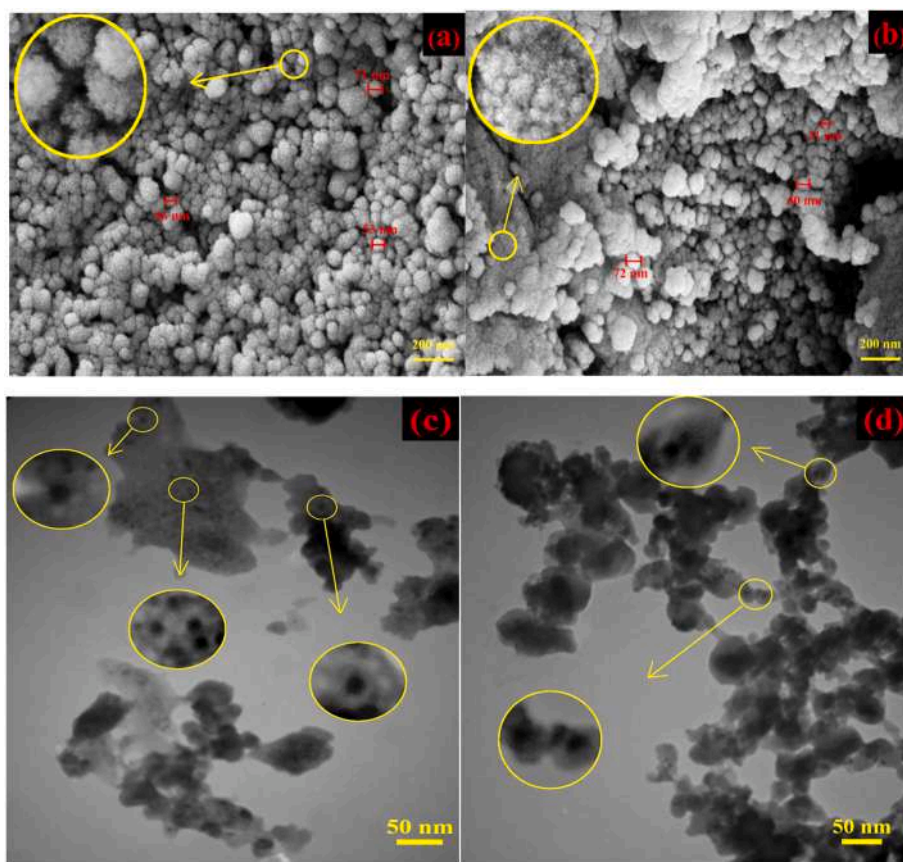


Fig. 2. SEM images of samples synthesized by Microwave irradiation method: (a) M3, and (b) P2, and TEM images of (c) P2, and (d) M3. The arrows indicate enlarged areas and yellow circles are the corresponding high resolution image of the magnified area. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

and P2 in Fig. 2 reveal that there are small spherical nanoparticles embedded in the network of grown CdS/Ag₂S QDs as they have been magnified by yellow circles and arrows. This circular shape is an indication of digestion of the ZnO NRs since their morphology was elongated in a preferred direction. Moreover, the number of these core particles are higher for sample P2 in Fig. 2-c compared to M3 in Fig. 2-d. This is an indication of higher content of ZnO nanoparticles as the core structure embedded in the CdS/Ag₂S QD network.

3.2. Dye-degradation photocatalyst study

Fig. S6 shows the UV/Vis absorption spectra for different samples dispersed in water. They clearly show similar absorption with an extended tail in the visible range due to the absorption of Ag₂S. It is worth noticing that sample P2 shows a higher absorption value in the visible/NIR range which can be due to the higher growth of Ag₂S as it was also conceived from XPS analyses. Fig. S7-a-e show the MB absorption under UV exposure spanning time for the different samples. Therefore, deduced from their spectra, Fig. 3-a&b show the photocatalyst activity of the samples in MB degradation over time. The statistics have been summarized in Table S4. It can be observed that P2 has the highest rate of degradation and M3 is the next best sample. CdS/Ag₂S sample as control which was synthesized using a photochemical approach showed a low rate of degradation and ZnO NRs didn't have any photodegradation effect as shown in Fig. 3-c. Fig. 3-d depicts the FTIR spectra of the samples, that indicating well attachment of TGA molecule to the surface of ZnO for the growth of CdS/Ag₂S as its vibrational mode of COOH⁻ group has been shown which is indicating of its attachment to the surface of ZnO and CdS/Ag₂S QDs, according to the previous reports [60,62,63,70]. Moreover, the Zn-O vibration mode

appears in the ZnO sample as well as samples P2 and M3 that infer the presence of ZnO compounds in the final composites. Hence, both methods of synthesis show enhancement of the photocatalyst effect of ternary nanocomposites, and photochemically synthesized samples have superior photodegradation properties than microwave synthesized samples. The role of degradation species is very crucial in determining the mechanism of degradation and therefore, the general scheme for the band diagram and electron/hole separation [19,23,47]. Hence, tertiary butanol (t-BuOH), *p*-benzoquinone (BQ) and ethylenediaminetetraacetic acid (EDTA) were employed as scavengers to study the trapping agents of •OH, •O²⁻ and h⁺, respectively [47]. The MB degradations that were reached 95.2 %, using P2, were obtained 43.1 %, 79.5 %, and 16 %, for •OH, •O²⁻ and h⁺, respectively. It reveals the important role of h⁺ and •OH, respectively, which is also an indication of efficient charge separation in the ternary compound. It should be noted that h⁺ plays a major role in dye degradation in reverse order compared to the report of Bahadoran et al. [23].

3.3. Electrochemical study

In the preceding section, ternary nanocomposites were found to be the efficient photocatalysts for MB degradation under UV illumination, thus according to the previous reports and suggested band diagrams [65, 66], there should be an efficient charge transfer through ZnO/CdS/Ag₂S structures. To examine this hypothesis, Impedance spectroscopy and cyclic voltammetry of the different nanocomposites-modified GC electrodes were performed in a standard solution of ferrocyanide (20 mL of 5 mM K₃[Fe(CN)₆], K₄[Fe(CN)₆] and 1 M KCl.). Fig. S8-a&b illustrate CV measurements and Fig. S8-c&d show the Nyquist plots for samples prepared with microwave irradiation and photochemical treatment,

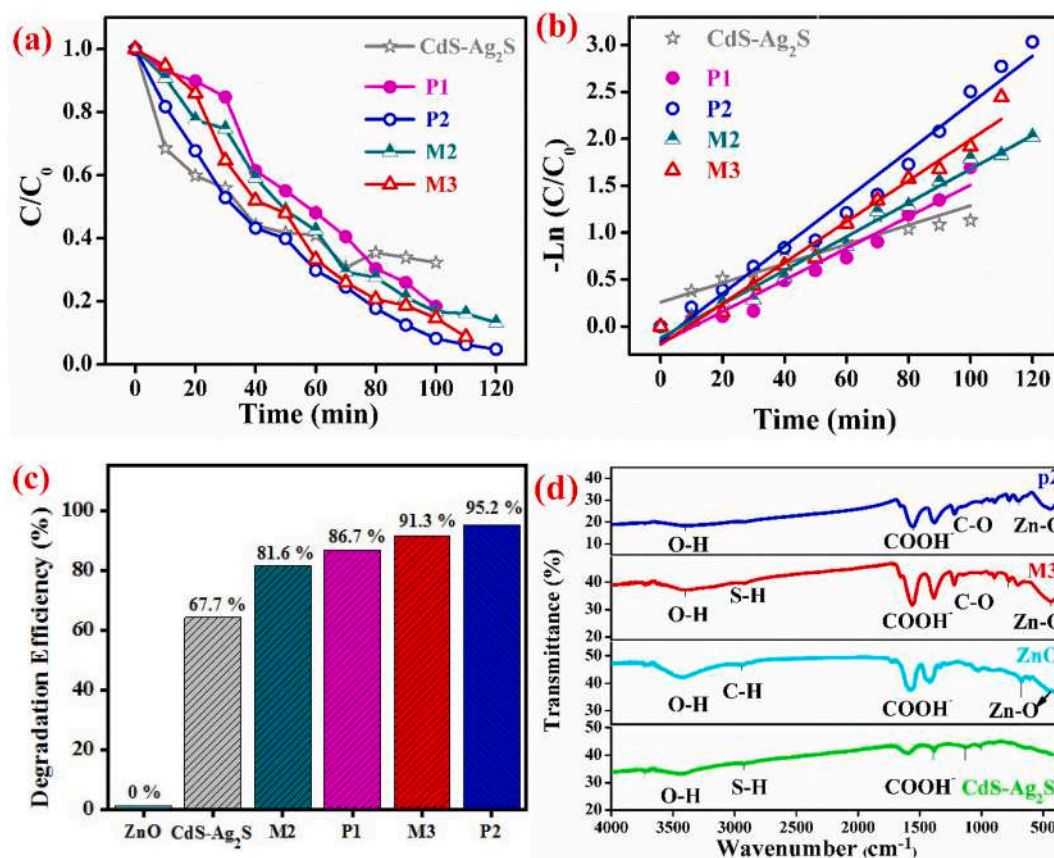


Fig. 3. (a) Time evolution of the change for relative concentration of MB, (b) Logarithm of relative concentration of MB Vs. time for determination of degradation rate constant, (c) final degradation percentile for MB degradation (d) FTIR spectra of the samples with indication of absorbing groups for each sample.

respectively. P2 and M3 have the lowest charge transfer resistance with finite charge diffusion lines in low frequencies indicating a well-defined double-layer formation. Fig. 4-a&b shows the comparison of Nyquist plots and CV measurements of P2, and M3 along with the sole ZnO and CdS/Ag₂S samples, respectively. The spectacular feature of high resistance charge transfer of ZnO and CdS/Ag₂S samples and significantly low resistance of P2 and M3 by the order of 10 times, is the robust proof of effective charge diffusion in the hybrid ZnO-CdS-Ag₂S. Meanwhile, P2 shows superior charge transfer enhancement by reduction of ohmic resistance (real axis) compared to M3 by the order of 3 times. To quantitatively analysis the EIS results for M3 and P2, their equivalent circuits were suggested as they are plotted in Fig. S9-a&b, respectively, and their corresponding fitted curves are plotted in Figs. S9-c. It shows clearly the arc resistance is about 9 kΩ for M3 and 3.3 kΩ for P2 sample. Moreover, the Constant phase element (CPE) value for P2 is almost double times of M3, showing that the capacitive behavior of P2 due to the double layer formation is higher than M3, thus, the charge transfer is much faster for P2. The appearance of a loop of three elements of Warburg(W), resistance (Rp) and CPE inside the main circuit is an indication of semi-finite diffusion of carriers in low frequencies which is a characteristic of microporosity of the active layer [76]. Fig. 4-c&d show the BET and BJH analyses of gas adsorption/desorption isothermic experiments for the determination of effective surface area and mean pore size of the samples, respectively [20]. Fig. 4-e shows the type IV isotherm plots for M3 and P2 samples, which indicate a mesoporous type structure [20]. Table 1 summarized numerically the effective surface area and mean pore sizes for the samples. Apparently, the CdS-Ag₂S sample has the highest surface area of 191 m²/g, because they are pure QDs with very fine particles of 3–7 nm [63], while P2 and M3 possess about 132 and 76 m²/g, respectively with a small pore diameter of 5–7 nm. The high surface area of P2 is one of the highest values reported

about the ZnO heterogeneous composites for H₂ production [21–23].

Fig. S10-a&b shows the LSV measurements and Fig. S10-c&d demonstrates Tafel plots of the samples prepared with Microwave irradiation and photochemical treatment, respectively to emphasize the performance of each sample in each synthesis method. Fig. 5-a shows the linear polarization curve of champion samples and CdS/Ag₂S and ZnO samples modified on GC electrodes. It shows the significance of charge separation and HER for ZnO-CdS-Ag₂S nanocomposites. The ternary samples P2 and M3 show a current density of the order of 100 mA cm⁻² at voltages of about −0.5 V vs. RHE. Fig. 5-b depicts the Tafel plots and Table 2 shows the HER parameters of samples extracted from LSV measurements. The low values of onset potentials −0.238 V and −0.267 V vs. RHE and low values of Tafel slopes of 45 and 49 mV dec⁻¹ for P2 and M3, respectively, have not been reported for these ternary nanocomposites to the best of our knowledge. The obtained values are comparable with the values reported for 2D dichalcogenide compounds such as MoS₂ [67] and MoSe₂ [69]. Fig. 5-c demonstrates the HER cyclic behavior of the samples. Sample M3 and P2 show excellent recovery after 1000 consecutive CV measurements. Moreover, the slurry solution of sample P2 was stored for 6 months at ambient temperature, and after this time, a freshly modified GC electrode was prepared from it again and LSV measurement was performed, that the results (Fig. 5-c) show the stability of P2 sample with high HER activity after a long time of ink storage after 6 months. These results are to the best of our knowledge the first report on clear HER activity of ZnO-CdS-Ag₂S by means of LSV measurement with high stability of cyclic measurements. To clearly show the robust proof of competitive HER activity of the synthesized ternary compounds of ZnO-CdS-Ag₂S, a transient photocurrent measurement was performed at zero bias and in 0.5 M H₂SO₄ solution in Fig. 5-d. Sample P2 has roughly 2 times higher photocurrent exposed to UV light than M3 sample in analogy with the LSV results and EIS analysis

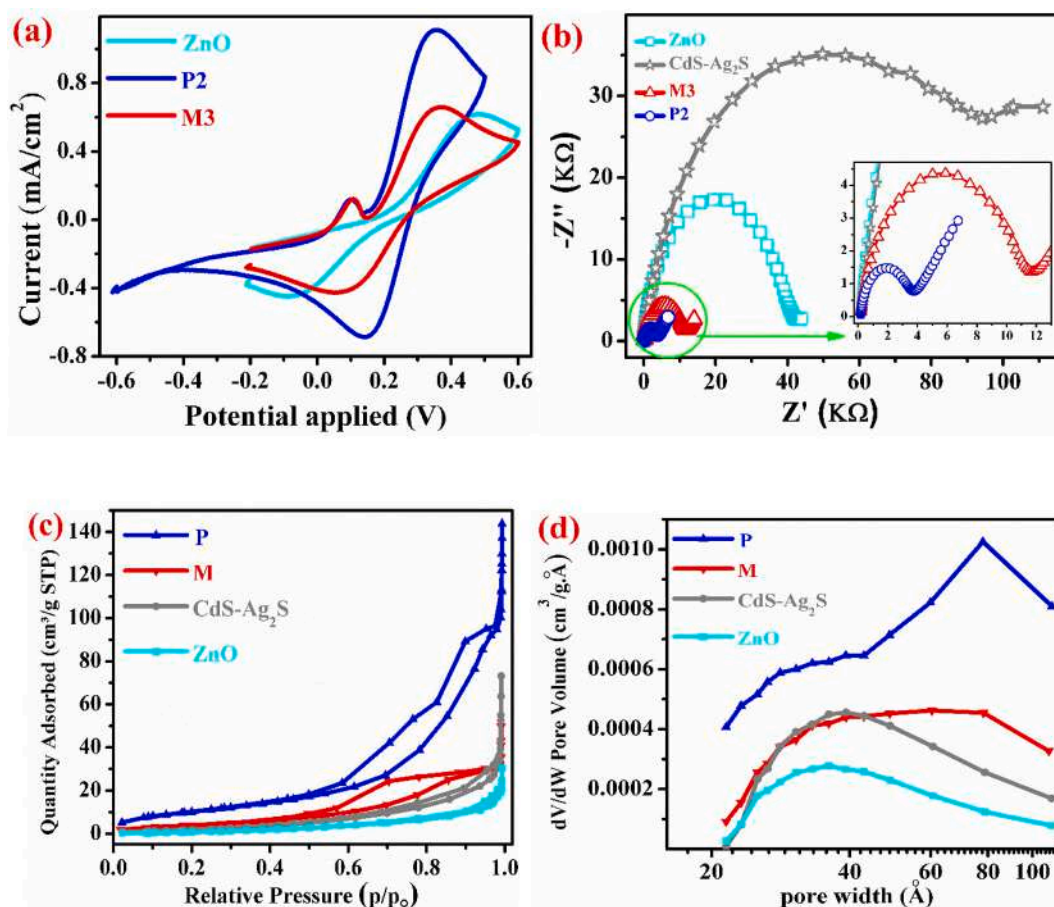


Fig. 4. (a) CV of samples in 0.5 M H_2SO_4 at the scan rate of 100 mV/s (b) Nyquist plots of samples obtained in the $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution at a bias of 0.35 V, (c) gas adsorption/desorption measurement for BET analysis, (d) BJH plots of the samples.

Table 1

Effective surface area (a_s) and mean pore size (r_p) values obtained from BET and BJH analyses, respectively.

sample	a_s (BET) ($\text{m}^2 \text{g}^{-1}$)	r_p (BJH) [nm]
P2	132.45	6.9
M3	76.58	5.4
CdS-Ag ₂ S	191.87	5.7
ZnO	26.88	4.9

and its effective surface area. Moreover, both samples show a photo-current step function with light off-on evolution that is comparable with our previous report on the very thin MoSe_2 nanosheets with large surface area and high HER performance [69]. What makes the synthesis method applied in this study more efficient compared to other studies is the extensively ZnO NRs embedding inside the CdS/Ag₂S QDs network using the application of TGA as a double role agent. It assisted to etch the ZnO NRs and at the same time effectively attaching the CdS and Ag₂S QDs to the surface of ZnO nanoparticles (after etching they become spherical) as inferred by FTIR analyses in Fig. 3-d. Thus, continuous growth of QDs was possible to yield a uniform growth as observed in FESEM images. Moreover, the Photochemical approach was found to be more effective compared to microwave irradiation towards the functionality of prepared ternary compounds. The reason lies in the slower kinetic nucleation of QDs by photochemical approach compared to microwave irradiation [75,77]. Microwave activated growth has a very rapid nucleation mechanism due to the delivery of energy via both conversion of electromagnetic radiation to mechanical vibration, rotation and translation of species and heat exchange due to the high

absorption of microwaves by water as the media of reactions. So, it is expected to have a higher level of defects in the formation mechanism as the charge transfer resistance was confirmed to be higher as well. Another important aspect is the concentration of ZnO NRs from XPS results, since in the microwave method, the etching of ZnO is higher therefore less ZnO concentration is obtained and thus less HER active centers are available as Table S3 indicates this fact that Zn concentration is 15.9 % for M3 while for P2 is about 23.8 %. In addition to that, generally both synthesis methods have indicated excellent HER activity with significant low Tafel slopes and high current density output for the ternary compounds. To investigate optically the concept of charge dissociation due to energy band alignment [23,45,50], in addition to EIS analyses, Photoluminescence spectra of samples in aqueous media were measured and are shown in Fig. 5-e. It clearly indicates that individual synthesized structures of ZnO and CdS/Ag₂S have emission peaks. ZnO NRs show a broad emission around 600 nm, which originates from Oxygen vacancies inside the band gap of ZnO [70]. CdS-Ag₂S QDs emit two separate peaks, the first one is a rather sharp emission at around 480 nm which corresponds to CdS QDs [60] and a broad emission with a peak about 680 nm which is due to the growth of Ag₂S on CdS as reported at before [63]. Surprisingly, the ternary ZnO/CdS/Ag₂S samples do not show any luminescence pattern which indicates non-radiative recombination of electron-hole that could be due to charge dissociation as reported for the metal dichalcogenide compounds [67] and heterogeneous ZnO structures [21,22]. To tailor more the origin of high electrochemical activities of ternary samples, electrochemical surface area (ECSA) of the samples was investigated by measuring their Cyclic voltammetry in non-Faradic region in the solution of 0.5 M H_2SO_4 with different scan rates (Fig. S11) and the double layer capacitance as a

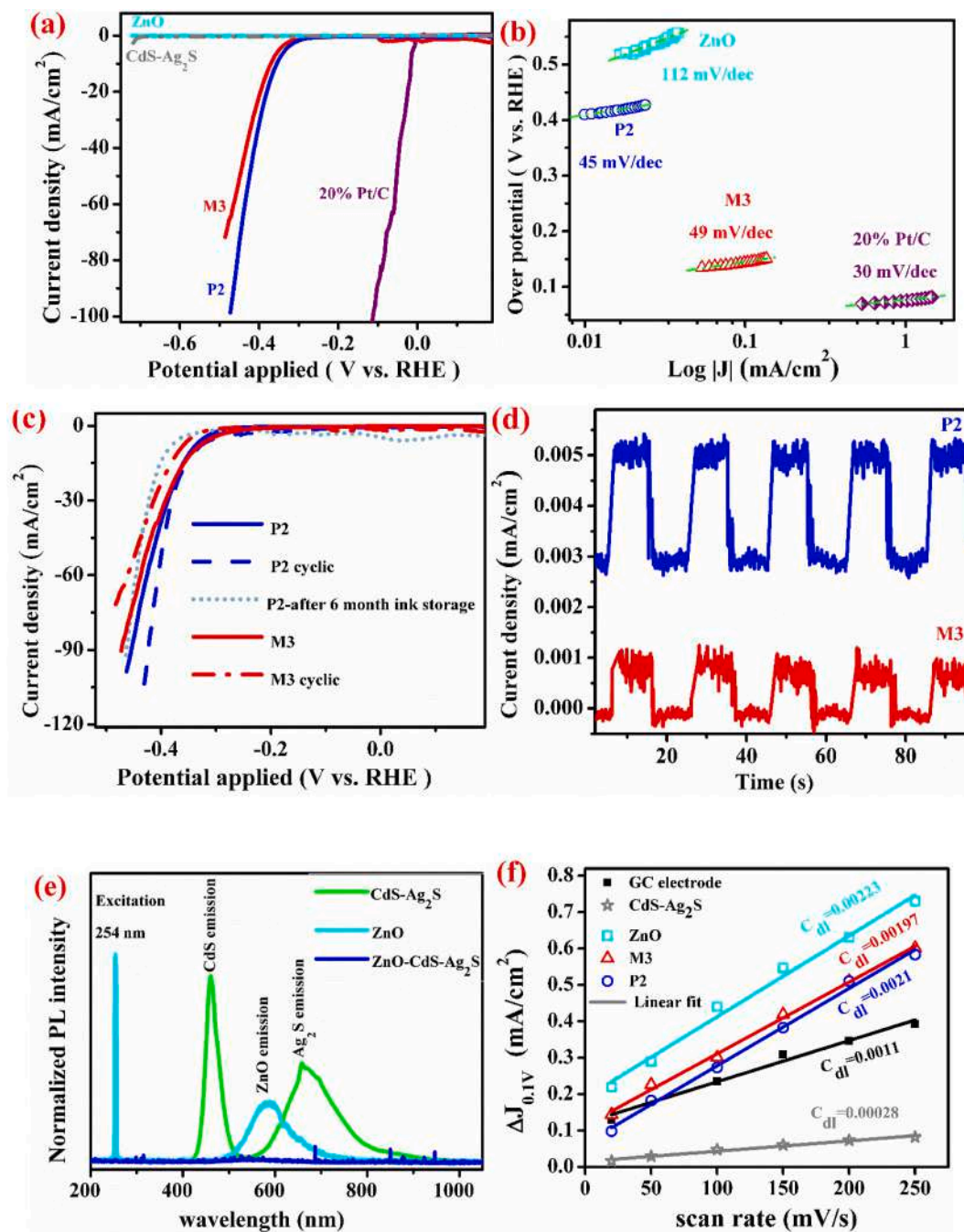


Fig. 5. (a) LSV of samples with scan rate 10 mV/s, (b) Tafel plots of the samples, (c) cyclic LSV of M3, and P2, and LSV plot of P2 electrode repeated after 6 months of ink storage, (d) The transient photocurrent response (TPR) measurements of samples P2 and M3 (10s off- 10s on), (e) PL spectra of the ZnO NRs, CdS-Ag₂S, and ternary ZnO-CdS-Ag₂S (P2), (f) Capacitive current density Vs. scan rate in non-faradic region with their corresponding linear fitting for the calculation of ECSA.

Table 2

HER parameters of the samples.

sample	Onset Potential (RHE) (mV)	Over Potential (RHE) (η ₁₀) (mV)	Tafel slope (mV/dec)	Tafel region [mV]	J ₀ (mA/cm ²)
Pt	0	39	30	0–50	1.10
M1	356	471	58	129–145	0.43
M2	384	–	56	137–163	0.44
M3	267	371	49	131–157	0.51
P1	334	457	54	215–254	0.46
P2	238	353	45	405–435	0.55
ZnO	711	–	112	518–558	0.22

direct indication of ECSA was calculated by plotting ΔJ versus different scan rates at a given voltage of 0.1 vs. Ag/AgCl [78], and extracting the slope of linear extrapolation as shown in Fig. 5-f. It clearly indicates the highest ECSA belongs to ZnO NR, P2 and M3, respectively. P2 and M3 show high ECSA that is almost double the bare GC electrode, and the reason behind their lower values compared to the ZnO sample could be due to the low ECSA value of CdS-Ag₂S QDs. Thus, to relate the enhancement of HER activity in this ternary nanocomposite, to the efficient charge dissociation and enhanced ECSA, Fig. 6 schematically illustrates the mechanism of HER in ZnO-CdS-Ag₂S nanostructures based on the S-scheme mechanism [17,22,33]. Since conduction bands (CBs) of both Ag₂S and CdS are slightly higher than that of ZnO, thus two interfaces are formed with electron depletion on the sides of ZnO and

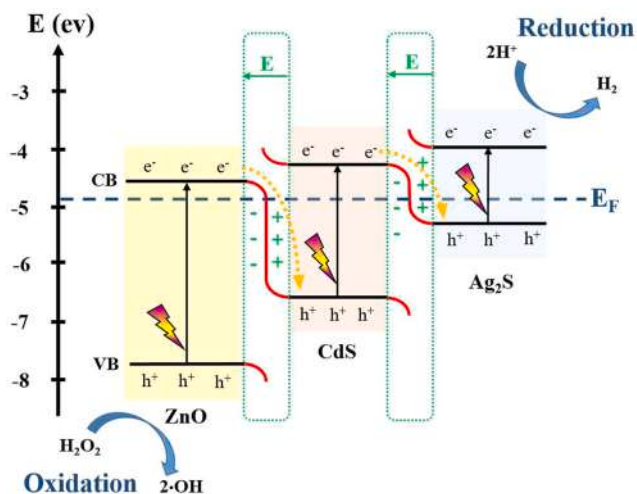


Fig. 6. S-Scheme energy diagram of ternary ZnO-CdS-Ag₂S hybrid structure and suggested mechanism of charge injection enhancement in photoexcitation process.

CdS in contact with CdS and Ag₂S, respectively. This results in the formation of internal electric fields from Ag₂S to CdS and from CdS toward ZnO, resulting in charge extraction from the CB of CdS to Valence band (VB) of Ag₂S, and from CB of ZnO to VB of CdS. Thus, there are remaining h⁺ in the VB of ZnO and e⁻ in CB of Ag₂S [17,22,23,33]. Exposed to light, the charge injection even tunes the charge transfer and increases the number of h⁺ and e⁻ in CB of Ag₂S, and VB of ZnO, respectively as demonstrated in Fig. 6. Therefore, an induced photocatalyst activity as well as HER activity can be obtained for this ternary compound. This unique charge injection together with the appropriate particle size tuning, mesoporous, large effective surface area, enhanced electrochemical active area, and charge transfer/separation properties has yielded high throughput of both photochemical and electrochemical hydrogen generation.

4. Conclusion

Free template ternary ZnO-CdS-Ag₂S nanostructure was prepared in an aqueous media using rapid, facile methods of Microwave irradiation and photochemistry treatment. The prepared nanocomposites showed excellent HER activities with both methods such that HER parameters are in competitive ranges with MoS₂ and MoSe₂ nanosheets. Samples synthesized with the Photochemical approach showed superior functionality in both Photo-degradation properties and HER activity as a dual-functioning structure. Photo-electrochemical measurements showed a clear stepwise current signal as an indication of H₂ production to the best of our knowledge for the first time for this ternary compound. The photochemical synthesis method was found to be less defect creative method and more efficient in internal charge transfer and therefore led to the enhanced catalyst activities of the final product. A S-Scheme model was suggested to indicate the importance of interface electric fields for the charge extraction resulting in CB of Ag₂S and VB of ZnO mainly responsible for reduction and oxidation reactions, respectively. This method can be pioneering as a basis for the synthesis of other ternary oxides semiconductor-QDs compounds. Thioglycolic acid (TGA) was found to have a crucial role in the growth mechanism of QDs as well as the shaping of ZnO nanostructures.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2023.10.077>.

References

- [1] Tashie-Lewis BC, Nnabuife SG. Hydrogen production, distribution, storage and power conversion in a hydrogen economy - a technology review. *Chem Eng J Adv* 2021;8:100172. <https://doi.org/10.1016/j.cej.2021.100172>.
- [2] Song H, Luo S, Huang H, Deng B, Ye J. Solar-driven hydrogen production: recent advances, challenges, and future perspectives. *ACS Energy Lett* 2022;7:1043–65.
- [3] Zhao W, Chen Z, Yang X, Qian X, Liu C, Zhou D, et al. Recent advances in photocatalytic hydrogen evolution with high-performance catalysts without precious metals. *Renew Sustain Energy Rev* 2020;132:110040.
- [4] Shi Y, Yang A-F, Cao C-S, Zhao B. Applications of MOFs: recent advances in photocatalytic hydrogen production from water. *Coord Chem Rev* 2019;390:50–75.
- [5] Rana S, Kumar A, Sharma G, Dhiman P, García-Penas A, Stadler FJ. Recent advances in perovskite-based Z-scheme and S-scheme heterojunctions for photocatalytic CO₂ reduction. *Chemosphere* 2023;139765.
- [6] Rosman NN, Mohamad Yunus R, Jeffery Minggu L, Arifin K, Salehmin MNI, Mohamed MA, et al. Photocatalytic properties of two-dimensional graphene and layered transition-metal dichalcogenides based photocatalyst for photoelectrochemical hydrogen generation: an overview. *Int J Hydrogen Energy* 2018;43:18925–45. <https://doi.org/10.1016/j.ijhydene.2018.08.126>.
- [7] Andoshe DM, Jeon JM, Kim SY, Jang HW. Two-dimensional transition metal dichalcogenide nanomaterials for solar water splitting. *Electron Mater Lett* 2015;11:323–35. <https://doi.org/10.1007/S13391-015-4402-9>.
- [8] Li D, Lao J, Jiang C, Shen Y, Luo C, Qi R, et al. Heterostructured MoS₂@Bi₂Se₃ nanoflowers: a highly efficient electrocatalyst for hydrogen evolution. *J Catal* 2020;381:590–8. <https://doi.org/10.1016/j.jcat.2019.11.039>.
- [9] Lei Y, Zhang Y, Li Z, Xu S, Huang J, Hoong Ng K, et al. Molybdenum sulfide cocatalyst activation upon photodeposition of cobalt for improved photocatalytic hydrogen production activity of ZnCdS. *Chem Eng J* 2021;425:131478. <https://doi.org/10.1016/j.cej.2021.131478>.
- [10] Yahia IS, Shkir M, AlFaify S, Ganesh V, Zahran HY, Kilany M. Facile microwave-assisted synthesis of Te-doped hydroxyapatite nanorods and nanosheets and their characterizations for bone cement applications. *Mater Sci Eng C* 2017;72:472–80. <https://doi.org/10.1016/j.msec.2016.11.074>.
- [11] Fan J, Dou Y, Jiang R, Du K, Deng B, Wang D. Electro-synthesis of tungsten carbide containing catalysts in molten salt for efficiently electrolytic hydrogen generation assisted by urea oxidation. *Int J Hydrogen Energy* 2021;46:14932–43. <https://doi.org/10.1016/j.ijhydene.2020.07.193>.
- [12] Carminati SA, Rodríguez-Gutiérrez I, De Moraes A, Da Silva BL, Melo MA, Souza FL, et al. Challenges and prospects about the graphene role in the design of photoelectrodes for sunlight-driven water splitting. *RSC Adv* 2021;11:14374–98. <https://doi.org/10.1039/d0ra10176a>.
- [13] Maeda K. Photocatalytic water splitting using semiconductor particles: history and recent developments. *J Photochem Photobiol C Photochem Rev* 2011;12:237–68. <https://doi.org/10.1016/J.JPHOTOCHEMREV.2011.07.001>.
- [14] Shi JW, Ma D, Zou Y, Fan Z, Shi J, Cheng L, et al. Rational construction of multiple interfaces in ternary heterostructure for efficient spatial separation and transfer of photogenerated carriers in the application of photocatalytic hydrogen evolution. *J Power Sources* 2018;379:249–60. <https://doi.org/10.1016/j.jpowsour.2018.01.031>.
- [15] Sun J, Li X, Guo W, Zhao M, Fan X, Dong Y, et al. Synthesis methods of two-dimensional MoS₂: a brief review. *Crystals* 2017;7:1–11. <https://doi.org/10.3390/cryst7070198>.
- [16] Velásquez DAP, Sousa FLN, Soares TAS, Caires AJ, Freitas DV, Navarro M, et al. Boosting the performance of TiO₂ nanotubes with ecofriendly AgIn₅Se₈ quantum dots for photoelectrochemical hydrogen generation. *J Power Sources* 2021;506. <https://doi.org/10.1016/j.jpowsour.2021.230165>.
- [17] Fu J, Xu Q, Low J, Jiang C, Yu J. Ultrathin 2D/2D WO₃/g-C₃N₄ step-scheme H₂-production photocatalyst. *Appl Catal B Environ* 2019;243:556–65.
- [18] Liu X, Zhao Y, Yang X, Liu Q, Yu X, Li Y, et al. Porous Ni₅P₄ as a promising cocatalyst for boosting the photocatalytic hydrogen evolution reaction performance. *Appl Catal B Environ* 2020;275:119144. <https://doi.org/10.1016/j.apcatb.2020.119144>.
- [19] Fu F, Shen H, Xue W, Zhen Y, Soomro RA, Yang X, et al. Alkali-assisted synthesis of direct Z-scheme based Bi₂O₃/Bi₂MoO₆ photocatalyst for highly efficient photocatalytic degradation of phenol and hydrogen evolution reaction. *J Catal* 2019;375:399–409. <https://doi.org/10.1016/j.jcat.2019.06.033>.
- [20] Li Z, Ma T, Zhang X, Wang Z. In₂Se₃/CdS nanocomposites as high efficiency photocatalysts for hydrogen production under visible light irradiation. *Int J*

- Hydrogen Energy 2021;46:15539–49. <https://doi.org/10.1016/j.ijhydene.2021.02.098>.
- [21] Ahmad I, Shukrullah S, Naz MY, Ahmed E, Ahmad M, Rehman SU, et al. The role of synthesis method in hydrogen evolution activity of Ce doped ZnO/CNTs photocatalysts: a comparative study. *Int J Hydrogen Energy* 2021;46:30320–33. <https://doi.org/10.1016/j.ijhydene.2021.06.148>.
- [22] Zhao Y, Guo Y, Li J, Li P. Efficient hydrogen evolution with ZnO/SrTiO₃ S-scheme heterojunction photocatalyst sensitized by Eosin Y. *Int J Hydrogen Energy* 2021;46:18922–35. <https://doi.org/10.1016/j.ijhydene.2021.03.051>.
- [23] Bahadoran A, Masudy-Panah S, De Lile JR, Li J, Gu JJ, Sadeghi B, et al. Novel OD/1D ZnBi₂O₄/ZnO S-scheme photocatalyst for hydrogen production and BPA removal. *Int J Hydrogen Energy* 2021;46:24094–106. <https://doi.org/10.1016/j.ijhydene.2021.04.208>.
- [24] Lu Y, Chen R, Wu F, Gan W, Zhao Z, Chen L, et al. A novel SiP/TiO₂ S-scheme heterojunction photocatalyst for efficient degradation of norfloxacin. *Sep Purif Technol* 2023;324:124572.
- [25] Fang X, Wang J, Yu Y, Kang S, Cui L. Self-assembled CdS@BN core-shell photocatalysts for efficient visible-light-driven photocatalytic hydrogen evolution. *Int J Hydrogen Energy* 2020;45:14841–8. <https://doi.org/10.1016/j.ijhydene.2020.03.199>.
- [26] Yang W, Sun K, Wan J, Ma Y-A, Wang Y, Liu L, et al. Dual-site oxygen activation for enhanced photocatalytic aerobic oxidation by S-scheme Ni₂P/Bi₂O₃Br-OVs heterojunction. *Chem Eng J* 2023;452:139425.
- [27] Li S, Wang K, Wang G, Xie H, Jin Z. An atomic-level charge transfer channels constructed with special Co-S bond and PS bond in ZnCdS/CoSP S-scheme heterojunction for hydrogen evolution. *Colloids Surfaces A Physicochem Eng Asp* 2023;656:130335.
- [28] Mostafa MMM, Shawky A, Zaman SF, Narasimharao K, Salam MA, Alshehri AA, et al. Enhanced and recyclable CO₂ photoreduction into methanol over S-scheme PdO/GdFeO₃ heterojunction photocatalyst under visible light. *J Mol Liq* 2023;377:121528.
- [29] Wang S, Zhang D, Zhang D, Pu X, Liu J, Li H, et al. A novel hydrangea-like ZnIn₂S₄/FePO₄ S-scheme heterojunction via internal electric field for boosted photocatalytic H₂ evolution. *J Alloys Compd* 2023;967:171862.
- [30] Hong X, Luo X, Xu X, Ji P, Yue S, Li R, et al. CoO QDs/Bi₂MoO₆ monolayer: a novel S-scheme heterojunction for highly efficient photocatalytic C₂H₄ degradation. *Sep Purif Technol* 2023:124948.
- [31] Kumar A, Khosla A, Sharma SK, Dhiman P, Sharma G, Gnanasekaran L, et al. A review on S-scheme and dual S-scheme heterojunctions for photocatalytic hydrogen evolution, water detoxification and CO₂ reduction. *Fuel* 2023;333:126267.
- [32] Dharani S, Vadivel S, Gnanasekaran L, Rajendran S. S-scheme heterojunction photocatalysts for hydrogen production: current progress and future prospects. *Fuel* 2023;349:128688.
- [33] Wang L, Zhu B, Zhang J, Ghasemi JB, Mousavi M, Yu J. S-scheme heterojunction photocatalysts for CO₂ reduction. *Matter* 2022;5:4187–211.
- [34] Lu J, Gu S, Li H, Wang Y, Guo M, Zhou G. Review on multi-dimensional assembled S-scheme heterojunction photocatalysts. *J Mater Sci Technol* 2023;160:214–39.
- [35] Zheng C, Jin F, Wang X, Jiang G, Jin Z. Constructing S-scheme heterojunctions through electrostatic self-assembly of Co₃O₄ quantum dots and CuBr for photocatalytic hydrogen evolution. *Int J Hydrogen Energy* 2023. In Press, Corrected Proof, doi:10.1016/j.ijhydene.2023.08.012.
- [36] Tahir M, Tasleem S, Tahir B. Recent development in band engineering of binary semiconductor materials for solar driven photocatalytic hydrogen production. *Int J Hydrogen Energy* 2020;45:15985–6038.
- [37] Liu J, Wei X, Sun W, Guan X, Zheng X, Li J. Fabrication of S-scheme CdS-g-C₃N₄-graphene aerogel heterojunction for enhanced visible light driven photocatalysis. *Environ Res* 2021;197:111136. <https://doi.org/10.1016/j.envres.2021.111136>.
- [38] Li F, Li X, Tong S, Wu J, Zhou T, Liu Y, et al. S-scheme heterojunction Cu₂V₂O₇/α-Fe₂O₃ nanosheets with effective photocatalytic activity toward organic pollutant degradation. *Nano Energy* 2023:108849.
- [39] Zhao Y, Fan X, Zheng H, Liu E, Fan J, Wang X. Bi₂WO₆/AgInS₂ S-scheme heterojunction: efficient photodegradation of organic pollutant and toxicity evaluation. *J Mater Sci Technol* 2023;170:200–11.
- [40] Wang K, Luo Z, Xiao B, Zhou T, Zhao J, Shen C, et al. S-Scheme Cu₃P/TiO₂ heterojunction for outstanding photocatalytic water splitting. *J Colloid Interface Sci* 2023;652:1908–16.
- [41] Zhang M, Zhao F, Feng K, Hu X, Fan J, Sun T, et al. Construction of Co₉Se₈/TiO₂ S-scheme heterojunction photocatalyst for efficient hydrogen production. *J Alloys Compd* 2023;963:171302.
- [42] Liu Z, Xu J, Li Z, Xu S, Liu X. Compound SnS₂ sensitizer in the S-scheme of Ag₂Mo₂O₇/CoMoO₄ heterojunction to improve the hydrogen evolution of semiconductor powder. *Int J Hydrogen Energy* 2023;48:20303–13.
- [43] Xu Q, Zhang L, Cheng B, Fan J, Yu J. S-scheme heterojunction photocatalyst. *Chem* 2020;6:1543–59.
- [44] Song M, Li M, Li H, Wang P, Wu Y, Li L. Novel through-holes g-C₃N₄/BiOBr S-scheme heterojunction: charge relocation mechanism and DFT insights. *Surface Interfac* 2023;41:103227.
- [45] Wang P, Liu Y, Jiang N, Jing R, Li S, Zhang Q, et al. Double S-scheme AgBr heterojunction co-modified with g-C₃N₄ and black phosphorus nanosheets greatly improves the photocatalytic activity and stability. *J Mol Liq* 2021;329:115540. <https://doi.org/10.1016/j.molliq.2021.115540>.
- [46] Pan J, Liang J, Xu Z, Yao X, Qiu J, Chen H, et al. Rationally designed ternary CdSe/WS₂/g-C₃N₄ hybrid photocatalysts with significantly enhanced hydrogen evolution activity and mechanism insight. *Int J Hydrogen Energy* 2021;46:30344–54. <https://doi.org/10.1016/j.ijhydene.2021.06.165>.
- [47] Liu J, Lin C, Yao H, Zhang S, Fang D, Jiang L, et al. Construction of high-proportion ternary dual Z-scheme Co₃O₄/NiCo₂O₄/NiO photocatalytic system via incomplete solid phase chemical reactions of Co(OH)₂ and Ni(OH)₂ for organic pollutant degradation with simultaneous hydrogen production. *J Power Sources* 2021;506:230159. <https://doi.org/10.1016/j.jpowsour.2021.230159>.
- [48] Chen J, Liu T, Zhang H, Wang B, Zheng W, Wang X, et al. One-pot preparation of double S-scheme Bi₂S₃/MoO₃/C₃N₄ heterojunctions with enhanced photocatalytic activity originated from the effective charge pairs partition and migration. *Appl Surf Sci* 2020;527:146788. <https://doi.org/10.1016/j.apsusc.2020.146788>.
- [49] Varghese AP, Rabiee N, rdshaw Neppolian B, Lakhera SK. Synergistic hydrogen generation through a 2D-2D NiCuInS₂: In₂S₃/g-C₃N₄ dual S-scheme heterojunction nanosheets. *Carbon N Y* 2023:118441.
- [50] Xu Shengming, Xu Jing, Wu Jiandong, Zhou Zhengyang, Bixian Wang TL. Designing of a novel Mn_{0.2}Cd_{0.8}@ZnO heterostructure with Type-II charge transfer path for efficient photocatalytic hydrogen evolution reaction. *Int J Hydrogen Energy* 2023;48:7670–82. <https://doi.org/10.1016/j.ijhydene.2022.11.263>.
- [51] Zhang G, Zhang H, Wang R, Liu H, He Q, Zhang X, et al. Preparation of Ga₂O₃/ZnO/WO₃ double S-scheme heterojunction composite nanofibers by electrospinning method for enhancing photocatalytic activity. *J Mater Sci Mater Electron* 2021;32:7307–18. <https://doi.org/10.1007/s10854-021-05441-4>.
- [52] Xie H, Wang K, Li S, Jin Z. Construction of Co₉S₈/MoS₂/Ni₂P double S-scheme heterojunction for enhanced photocatalytic hydrogen evolution. *Surface Interfac* 2023:103353.
- [53] Karimipour M, Sadeghian M, Molaei M. Fabrication of white light LED photocatalyst ZnO-rGO heteronanoshet hybrid materials. *J Mater Sci Mater Electron* 2018;29:13782–93. <https://doi.org/10.1007/s10854-018-9509-y>.
- [54] Karimipour M, Mohammad-Sadeghipour A, Molaei M, Khanzadeh M. Rapid synthesis of white-light emissive ZnO nanorods using microwave assisted method. *Mod Phys Lett B* 2015;29. <https://doi.org/10.1142/S0217984915502383>.
- [55] Karimipour M, Molaei M, Allahyar S. Tunable luminescence of pure ZnO nanowires prepared by microwave irradiation in ethanol. *J Mater Sci Mater Electron* 2016;27:4771–6. <https://doi.org/10.1007/s10854-016-4357-0>.
- [56] Zhang Y, Xu M, Zhou W, Song X, Liu X, Zhang J, et al. Fabricated ZnO@ZnIn₂S₄ S-scheme heterojunction photocatalyst for enhanced electron-transfer and CO₂ reduction. *J Colloid Interface Sci* 2023;650:1762–72.
- [57] Ren Y, Li Y, Pan G, Wang N, Xing Y, Zhang Z. Recent progress in CdS-based S-scheme photocatalysts. *J Mater Sci Technol* 2023;171:162–84.
- [58] Ma D, Shi JW, Zou Y, Fan Z, Ji X, Niu C. Highly efficient photocatalyst based on a CdS quantum dots/ZnO nanosheets OD/2D heterojunction for hydrogen evolution from water splitting. *ACS Appl Mater Interfaces* 2017;9:25377–86. <https://doi.org/10.1021/acsami.7b08407>.
- [59] Fujii M, Nagasuna K, Fujishima M, Akita T, Tada H. Photodeposition of CdS quantum dots on TiO₂: preparation, characterization, and reaction mechanism. *J Phys Chem C* 2009;113:16711–6. <https://doi.org/10.1021/JP9056626>.
- [60] Abbasi S, Molaei M, Karimipour M. CdSe and CdSe/CdS core-shell QDs: new approach for synthesis, investigating optical properties and application in pollutant degradation. *Luminescence* 2017;32:1137–44. <https://doi.org/10.1002/bio.3300>.
- [61] Molaei M, Bardsiri FS, Bahador AR, Karimipour M. One-pot microwave assisted approach for synthesis of CdSe/CdS core-shell quantum dots (QDs) and investigating optical properties. *Mod Phys Lett B* 2016;30. <https://doi.org/10.1142/S0217984916500743>.
- [62] Molaei M, Hasheminejad H, Karimipour M. Synthesizing and investigating photoluminescence properties of CdTe and CdTe/CdS core-shell quantum dots (QDs): a new and simple microwave activated approach for growth of CdS shell around CdTe core. *Electron Mater Lett* 2015;11:7–12. <https://doi.org/10.1007/S13391-014-4039-0>.
- [63] Karimipour M, Izadian L, Molaei M. Reviving near infra-red emission of Ag₂S nanoparticles using interfacial defects in the Ag₂S/CdS core-shell structure. *Luminescence* 2018;33:202–8. <https://doi.org/10.1002/bio.3402>.
- [64] Di T, Cheng B, Ho W, Yu J, Tang H. Hierarchically CdS-Ag₂S nanocomposites for efficient photocatalytic H₂ production. *Appl Surf Sci* 2019;470:196–204. <https://doi.org/10.1016/j.apsusc.2018.11.010>.
- [65] Xie X, Wang R, Ma Y, Chen J, Shi Z, Cui Q, et al. Sulfate-functionalized core-shell ZnO/CdS/Ag₂S nanorod arrays with dual-charge-transfer channels for enhanced photoelectrochemical performance. *ACS Appl Energy Mater* 2022;2:11. <https://doi.org/10.1021/acsaem.2c00608>.
- [66] Chen C, Li Z, Lin H, Wang G, Liao J, Li M, et al. Enhanced visible light photocatalytic performance of ZnO nanowires integrated with CdS and Ag₂S. *Dalton Trans* 2016;45:3750–8. <https://doi.org/10.1039/C5DT04533A>.
- [67] Khazraei S, Karimipour M, Molaei M, Moghadam MR. Synergistic effect of ascorbic acid on the synthesis of mesoporous rGO-MoS₂(100)nanocomposites and promotion of hydrogen evolution reaction. *Int J Hydrogen Energy* 2019;44:13284–95. <https://doi.org/10.1016/j.ijhydene.2019.03.209>.
- [68] Salehi S, Molaei M, Karimipour M. Mo-rich rGO-2H-MoSe₂ nanocomposites with novel crystal growth plane of (106) for high hydrogen evolution reaction activity. *Mater Sci Semicond Process* 2022;142:106475. <https://doi.org/10.1016/j.mssp.2022.106475>.
- [69] Setayeshgar S, Karimipour M, Molaei M, Moghadam MR, Khazraei S. Synthesis of scalable 1T/2H-MoSe₂ nanosheets with a new source of Se in basic media and study of their HER activity. *Int J Hydrogen Energy* 2020;45:6090–101. <https://doi.org/10.1016/j.ijhydene.2019.12.102>.
- [70] Karimipour M, Khesabnia A, Molaei M. Red luminescence of Zn/ZnO core-shell nanorods in a mixture of LTZA/Zinc acetate matrix: study of the effects of Nitrogen bubbling, Cobalt doping and thioglycolic acid. *J Lumin* 2016;178:234–40. <https://doi.org/10.1016/j.JLUMIN.2016.06.003>.

- [71] Fu Y, Ding Y, Zheng L, Zhu YF, Han S. Morphology- and size-controlled fabrication of CdS from flower-like to spherical structures and their application for high-performance photoactivity. *Eur J Inorg Chem* 2019;2019:2086–92. <https://doi.org/10.1002/ejic.201801464>.
- [72] Malik R, Singh C, Garg R, Kumar V, Singhal S. Morphology controlled CdS nanostructures: a proficient visible-light-driven photocatalyst. *Anal Chem Lett* 2016;6:492–507. <https://doi.org/10.1080/22297928.2016.1241718>.
- [73] Kabir R, Saifullah MAK, Ahmed AZ, Masum SM, Molla MAI. Synthesis of n-doped ZnO nanocomposites for sunlight photocatalytic degradation of textile dye pollutants. *J Compos Sci* 2020;4. <https://doi.org/10.3390/jcs4020049>.
- [74] Sadovnikov SI, Gusev AI, Rempel AA. Artificial silver sulfide Ag₂S: crystal structure and particle size in deposited powders. *Superlattice Microst* 2015;83:35–47. <https://doi.org/10.1016/j.spmi.2015.03.024>.
- [75] Mirhosseini HN, Karimipour M, Molaei M, Bagheri M. One pot and room temperature photochemical synthesis of high quantum yield NIR emissive Ag₂S@Ag(In, Zn)S₂ core-shells at the presence of air in water. *J Photochem Photobiol Chem* 2019;380:111854. <https://doi.org/10.1016/j.jphotochem.2019.111854>.
- [76] Bag M, Renna LA, Adhikari RY, Karak S, Liu F, Lahti PM, et al. Kinetics of ion transport in perovskite active layers and its implications for active layer stability. *J Am Chem Soc* 2015;137:13130–7.
- [77] Sanchooli A, Karimipour M, Molaei M. Room temperature synthesis of Au NR@Ag₂S and Au NR@Ag₂S/CdS core-shells using a facile photochemical approach. *Phys E Low-Dimensional Syst Nanostructures* 2019;109:133–9. <https://doi.org/10.1016/j.physe.2019.01.014>.
- [78] Bae H, Seong C, Burungale V, Seol M, Yoon CO, Kang SH, et al. Nanostructured Au electrode with 100 h stability for solar-driven electrochemical reduction of carbon dioxide to carbon monoxide. *ACS Omega* 2022;7:9422–9. <https://doi.org/10.1021/acsomega.1c06720>.