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Novel electrospun nanofiber mats as effective catalysts for water photosplitting

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Abstract

Two novel photocatalysts based on ceramic materials for hydrogen production from water splitting under the solar radiation are introduced. CdS-doped and CdS–PdS-doped poly(vinyl acetate) electrospun nanofiber mats reveal good activity toward water photosplitting. The efficient ceramic nanoparticles were in situ synthesized in the polymer solution which was subjected to the electrospinning process. CdS–PdS-doped poly(vinyl acetate) nanofibers produce more hydrogen compared to the naked CdS NPs. Immobilization of the CdS and CdS–PdS nanoparticles inside the polymer nanofibers is an effective strategy to overcome the photocorrosion and toxicity problems of the CdS-based materials.

Keywords: Water photosplitting; Hydrogen production; CdS; Nanofibers; Electrospinning

1. Introduction

Photocatalysis is one of the key technologies to solve both energy and environmental problems using solar energy, in which an efficient photocatalyst is necessary. Energy is the material basis of human survival, developing new energy sources to replace traditional ones becomes increasingly important with the energy depletion. Hydrogen, as a kind of renewable energy, has attracted more and more attention due to its pollution-free and efficiency and other advantages [1–4]. CdS as one of the most well known semiconductor photocatalysts has been used for photocatalysis due to its proper band gap of approximately 2.4 eV [5] and good absorption properties of visible light. Electrospun nanofibers posses approximately double the surface area of continuous thin films. The electrospun nanofiber mat collects many feature advantages making it unique candidate for the nanotechnological approaches; high surface area, porosity and ease of handling and separation from the reaction media. PVAc was chosen as template because of its cheap availability, conductivity, hydrophobicity and acting as matrix to control the morphology of semiconductors by the self-assembly route.

Simplicity of the electrospinning process, the diversity of the electrospinnable materials, and the unique features of the obtained electrospun nanofibers provide especial interest for both of the technique and resultant products. The past decades have witnessed tremendous progress in the development of the electrospinning technique to widen the applications of the obtained products.

Solar-light-driven photocatalysts attracted interest in recent years because solar-light is an important clean energy and can be easily utilized. Cadmium sulfide (CdS) is a well-known powerful photocatalyst under the solar light, but it has two critical problems; toxicity and photocorrosion. To exploit the advantages of the nanofibrous morphology as well as a remedy to the problems, we introduce CdS–PdS nanoparticles as a core inside the poly(vinyl acetate) nanofibers. Electrospinning was

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invoked to produce this core–shell structure. Moreover, CdS NPs were incorporated inside polymeric nanofibers. The CdS and CdS–PdS photocatalysts were hybridized with PVAc by electrospinning for the first time. Our study revealed that the doped nanofiber mats were efficient and stable towards water splitting processes. The hydrophobicity of the introduced mats allows them to float on water and which improves the photocatalytic activity.

2. Experimental procedure

2.1. Materials

Cadmium acetate (CdAc, reagent grade, 98%, Sigma Aldrich), palladium acetate (PdAc, reagent grade, 98%, Sigma–Aldrich), N,N-dimethylformamide (DMF, 99.5 assay, Showa Chemical Ltd., Japan), poly(vinyl acetate) (PVAc, MW 5500,000 g/mol, Sigma–Aldrich), ammonium sulfide (40–48 wt% solution in water, Sigma–Aldrich), methylene blue (MB) and methyl red (MR) (Showa Chemical Ltd., Japan) were used in this study without further treatment.

2.2. Preparation of CdS-doped CdS–PdS-doped PVAc hybrid electrospun nanofiber mat

Cadmium sulfide (CdS)/poly(vinyl acetate) (PVAc) colloidal solution was prepared by using this strategy. First, 0.5 g cadmium acetate dihydrate (CdAc) was dissolved in 1 ml N,N-dimethylformamide (DMF). The prepared solution was mixed with 2.5 ml of 18 wt% poly(vinyl acetate) (PVAc) dissolved in DMF. The resulted solution was kept under stirring for 2 h to ensure good mixing. Then 0.25 ml of ammonium sulfide was added carefully in a drop wise manner to the solution with vigorous stirring to make the fine dispersion of CdS nanoparticles. Therefore, CdS content in the final polymer solution can be determined to be almost 10 wt%. With the same procedure, CdS–PdS/PVAc colloid was prepared, however 0.125 g of palladium acetate (PdAc) was dissolved in 0.5 ml DMF and added to the CdAc/PVAc mixture before addition of the ammonium sulfide solution which was increased to be 0.75 ml. Accordingly, the formed PdS in this polymeric solution was about 1.5 wt%. Electrospinning of both formulations was carried out at 15 kV and 16 cm distance between the collector and the tip of the syringe. According to the utilized procedure, in the final polymeric electrospun nanofibers, Cd to Pd weight ratio is almost 3.4 to 1. Almost the same ratio can be determined for CdS to PdS.

2.3. Characterization

The surface morphology of the nanofibers was studied by field emission scanning electron microscopy (FE-SEM, S-7400, Hitachi, Japan). Images of nanofibers containing CdS nanoparticles (NPs) and PdS–CdS NPs were obtained via transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) with a 200 kV accelerating voltage. The samples were prepared by directly collecting the nanofibers on the TEM grid during electrospinning. In addition, FE-SEM EDX spectrum of the hybrid electrospun nanofiber mat also recorded. Information about the phase and crystallinity was obtained with a Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with Cu Kα ($\lambda = 1.540$ Å) radiation over Bragg angles ranging from10° to 80°. Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets using an ABB Bomen MB100 Spectrometer (Bomen, Canada). UV absorbance was measured by UV–visible spectrophotometer (HP 8453 UV–vis spectroscopy system, Germany).

2.4. Photocatalytic activity investigation

The photocatalytic activity of CdS NPs-doped and CdS–PdS NPs-doped PVAc hybrid electrospun nanofiber mat were evaluated by observing the degradation of methylene blue (MB) and methyl red (MR) dyes solutions in a simple photochemical reactor. Prior to irradiation, the suspensions were magnetically stirred for 10 min under dark condition to establish an adsorption/desorption equilibrium between dyes and photocatalyst surface. In the present investigation, the reactions were carried out in inverted glass bottles under the sunlight. The experiment was conducted in a natural atmospheric environment on a sunny day (between 11 AM and 2 PM) in October (the average amount of solar radiation 16.21 MJ/m^2). For the photodegradation experiments, 50 ml of the dye solution (10 ppm concentration) was treated with 100 mg of CdS NPs and CdS–PdS NPs-doped PVAc hybrid electrospun nanofiber mat in the glass bottles. In addition, a control experiment with 100 mg of pristine PVAc mats and catalyst-free were also carried out to monitor PVAc photocatalytic activity and self-degradation, respectively. The samples were taken at regular intervals of time, and the concentration of the dye was measured by recording the absorbance at 663 and 430 nm for MB and MR dye solutions, respectively using a UV–visible spectrophotometer. After full treatment, the clear solution was replaced by another 50 ml from the stock dyes solutions for the two dyes; this process has been repeated two successive times to check the reusability of the hybrid mats.

2.5. Photocatalytic hydrogen production

The hydrolysis of water was determined by measuring the rate of hydrogen generation in a typical water-filled gas burette system. A burette filled with water was connected to the reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction. A weighed amount of hybrid mats (150 mg) was transferred into the reaction flask having an aqueous solution (200 ml) consisting of Na_2SO_3 (0.5 M) and Na_2S (0.5 M) as electron donors. The experiment was conducted in a natural atmospheric environment on a sunny day (between 11 AM and 2 PM) in October (the average amount of solar radiation 16.21 MJ/m^2). The volume of hydrogen gas evolved was measured by recording the displacement of water level every 30 min. The reaction was continued for 3 h to study the hydrogen gas generation property of our hybrid mat. The amount of the obtained hydrogen in the collected gas over the water surface was estimated using the simple ideal gas laws after estimating the pressure and measuring the actual temperature.

3. Results and discussion

Cadmium and palladium sulfides are insoluble in most of the common solvents. Therefore, addition of sulfide ion (S^{-2}) to any solution having cadmium or palladium ions leads to form a fine precipitates. From the chemistry point of view, these reactions have high yield as the product are precipitates (CdS and PdS). Accordingly, upon addition of the first drop of ammonium sulfide the solutions directly became turbid. Fig. 1A depicts FESEM image of the pristine PVAc nanofibers. Synthesizing of CdS and CdS–PdS nanoparticles inside the polymer solution did not affect the nanofibrous morphology as shown in Fig. 1B and C, respectively. The complete absence of nanoparticles on the surface of the hybrid nanofibers was confirmed in these FE-SEM images. The FESEM image of CdS-doped PVAc nanofiber (Fig. 1B) shows some morphological defects compared to the other two samples. It might be due to the agglomeration of the CdS nanoparticles inside the nanofibers. This morphological defect was confirmed by the HRTEM image shown in Fig. 1D. The perfectly aligned structure of CdS–PdS nanoparticles, and the polymer fiber boundary were clearly visible in the HRTEM image shown in Fig. 1E, the particle diameter were appears to be around 5–10 nm in range. This alignment of nanoparticles inside the polymer can be explained as follows: the position of metallic ions based on electrospun nanofibers should be adjusted by controlling the interaction between the polymer and metallic ions [6]. In our experiment an electrified polymeric PVAc solution with CdS–PdS nanoparticles were extruded through a spinneret. During electrospinning, the Coulomb repulsion between charged Cd^{2+} and Pd^{2+} nanoparticles might be the main factor making the nanoparticles uniformly dispersed and it might have increased the interaction with the PVAc polymer. As the interaction of this metallic nanoparticle increases with PVAc, it tends to place inside to the polymer and stretched by the high voltage supply during the electrospinning process and continuously aligned to attain such morphology. However, in case of CdS-doped PVAc, the produced nanoparticles were very small and tend to agglomerate inside the polymeric nanofiber (Fig. 1D). Fig. 2 displays the EDX result of CdS and CdS–PdS-doped PVAc nanofibers. As shown, Cd and S elements could be detected in the case of CdS-doped PVAc nanofibers (Fig. 2A). Moreover, Pd is observed in the PdS-containing nanofibers (Fig. 2B).

3.1. Phase study

The crystalline phase of the as-fabricated samples was analyzed by X-ray diffraction (XRD). The XRD patterns of the CdS–PdS-doped PVAc hybrid electrospun nanofiber mat compared with CdS-doped PVAc nanofiber mat and the pristine PVAc nanofibers are shown in Fig. 3. The peaks at $2\theta \sim 26.2^\circ$, 43.50° and 52.6° representing (1 1 1), (2 2 0) and (3 1 1) crystal planes, respectively indicate formation of CdS (JCPDS 10-454) [7]. No peaks assigned to PdS were observed in CdS–PdS-doped PVAc hybrid electrospun nanofiber mat

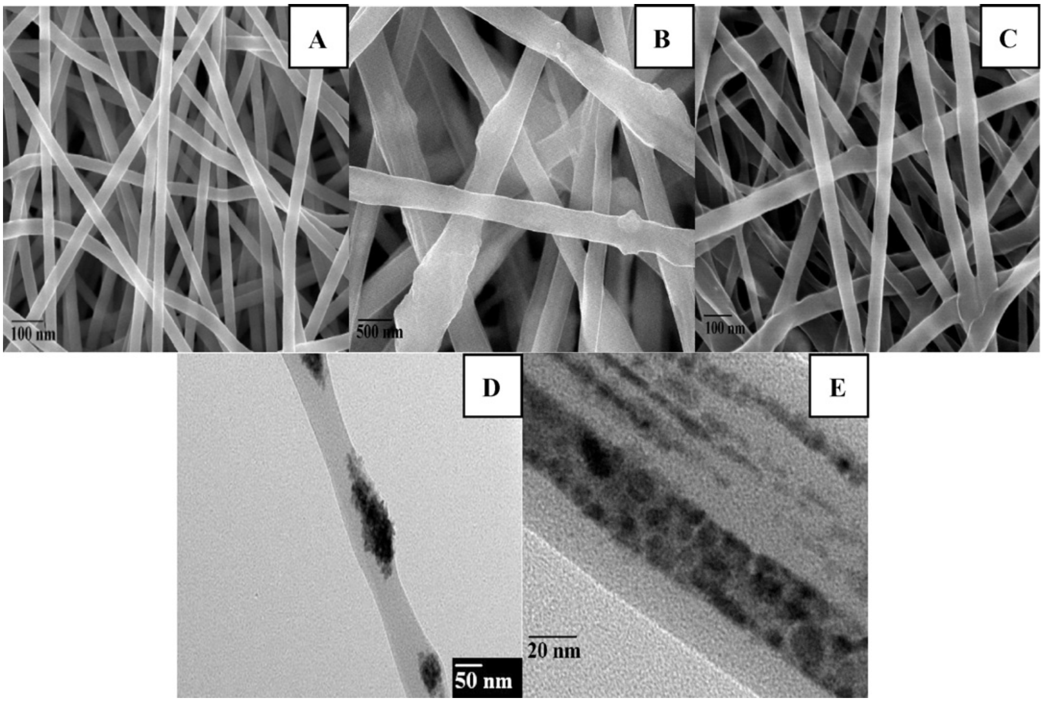

Fig. 1. (A) SEM image of the pristine PVAc electrospun nanofiber mat. (B) FESEM images of CdS-doped PVAc hybrid electrospun nanofiber mat. (C) CdS–PdS-doped PVAc hybrid electrospun nanofiber mat. (D) TEM images of CdS–PdS-doped PVAc hybrid electrospun nanofiber. (E) HR TEM image of the CdS–PdS-doped PVAc shows the hybrid core and fiber boundary.

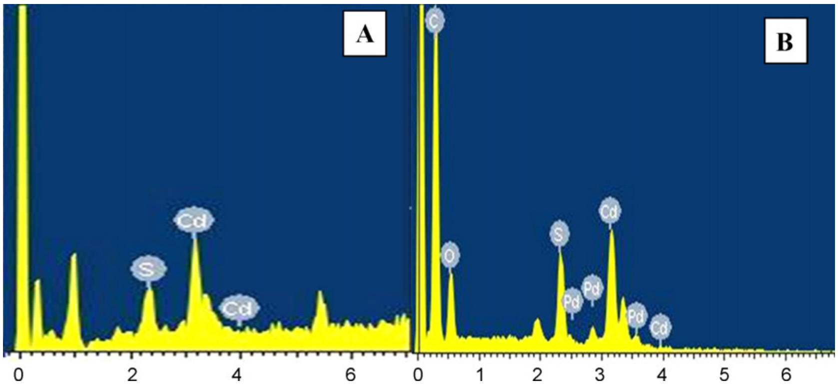

Fig. 2. EDX analysis of (A) CdS-doped and (B) CdS–PdS-doped PVAc hybrid electrospun nanofiber mat.

because the tiny amount of PdS to be identified by XRD; however presence of palladium was already confirmed by FESEM EDX (Fig. 2).

FT-IR spectra of pristine, CdS-doped and CdS–PdS-doped PVAc nanofibers were illustrated in Fig. 4. The peak at 1739.4 cm^{-1} ($\upsilon_{C=O}$), and characteristic ones at 1239.9, 1020.9 cm^{-1} ($\upsilon_{C\text{–}O}$), and 1375.7 cm^{-1} (δ_{CH_3}) corresponding to PVAc are clearly seen. The FT-IR spectrum is similar to the standard IR spectrum of PVAc (Sprouse collection of IR, card no. 187-189) [8]. The CdS–PdS-doped PVAc hybrid electrospun nanofiber mat also showed the same pattern of the pristine PVAc with some reduced intensity. Therefore, it can be claimed that the chemical structure of the polymer was not influenced by the utilized synthesizing procedure of CdS and CdS–PdS NPs.

3.2. Photocatalytic activity of CdS/PVAc hybrid mat

Solar photocatalytic degradation technology can be considered as feasible for the developing nations where the treatments of wastewaters containing hazardous contaminants were needed to be done more economically. The photocatalytic performance of introduced hybrid electrospun nanofiber mats was evaluated by degrading the methylene blue (MB) and methyl red (MR) under solar light irradiation. Temporal changes in the concentration of MB and MR were monitored by examining the variations in the maximal absorption in UV–vis spectra as shown in the following obtained results.

Fig. 5 shows the results of degradation of MB and MR in the presence of different samples. In order to check the self-degradation of dyes under sunlight, we carried out the experiment without the hybrid mats. The absorption property of PVAc mat towards both dyes were also evaluated and found to be negligible. From the results, it is clear that the complete degradation of MB occurred within 60 min and for MR in 90 min in case of utilizing of CdS–PdS-doped PVAc electrospun mat as photocatalyst under the solar radiation. The well-aligned structure of CdS–PdS NPs inside the PVAc nanofibers mainly contributes to the enhanced photocatalytic activity, as the morphology is a key factor for photocatalysis. It was also found that the self-degradation of MB and MR were negligible under our experimental conditions. In actual situations CdS particles tend to aggregate, forming larger particles, which results in a reduced surface area and a higher recombination rate of photo-induced electron–hole pairs. This phenomenon was also observed in our study as shown in Fig. 1, this might be reason for getting relatively lower photocatalytic

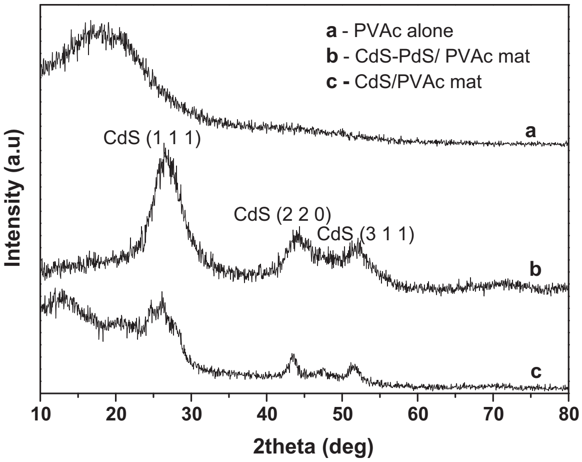

Fig. 3. XRD patterns of the pristine PVAc nanofiber mat, CdS–PdS-doped PVAc hybrid electrospun nanofiber mat and CdS-doped PVAc mat.

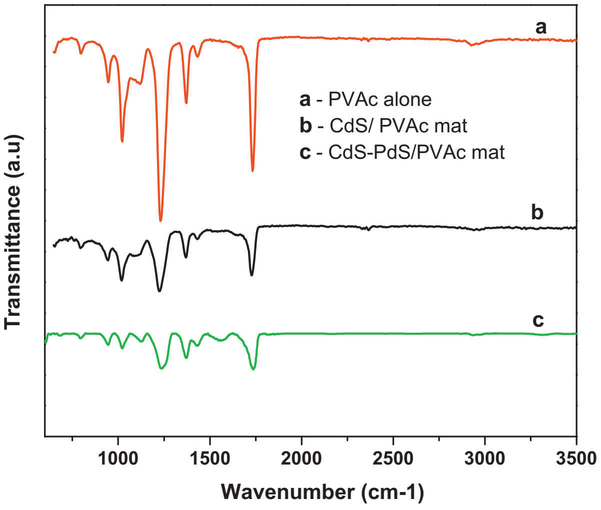

Fig. 4. FT-IR spectrum of pure PVAc electrospun mat, CdS-doped PVAc hybrid electrospun nanofiber mat and CdS–PdS-doped PVAc hybrid electrospun nanofiber mat.

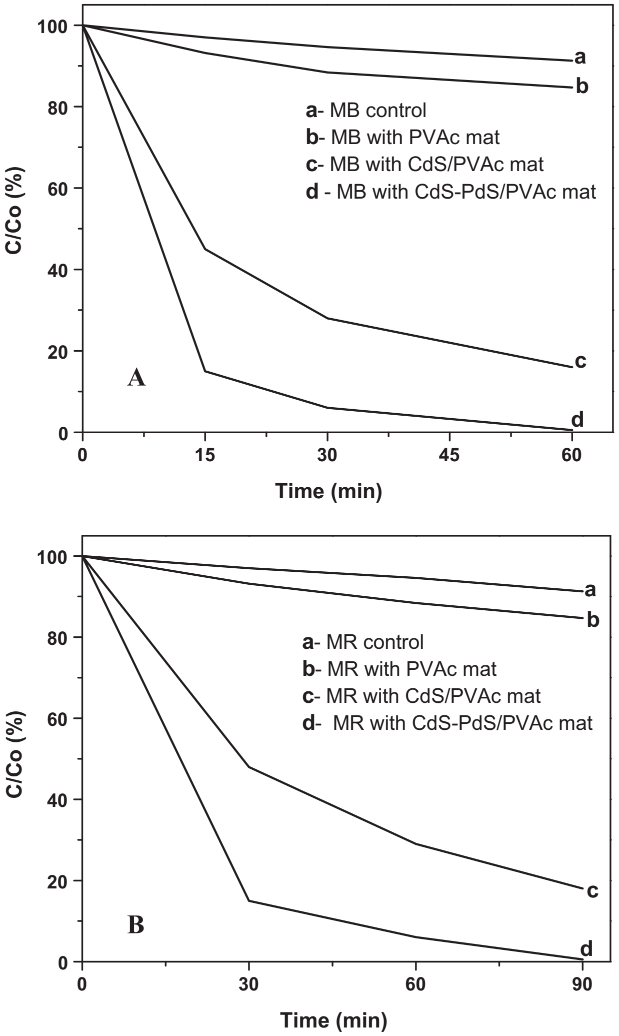

Fig. 5. De-colorization results of (A) methylene blue (MB) and (B) methyl red (MR) dyes using different photocatalysts and experimental conditions.

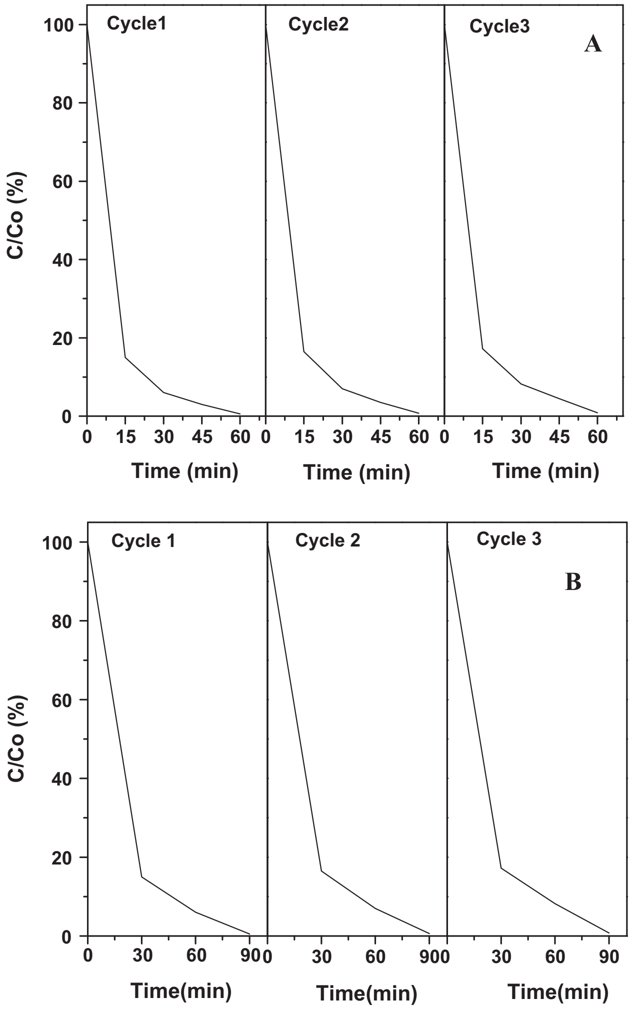

Fig. 6. Cyclic photocatalytic activity of CdS–PdS NPs-doped PVAc hybrid nanofiber on (A) MB and (B) MR.

efficiency compared with the another formulation. It is clear that the efficiency of PVAc mat contain CdS is greatly increased by the deposition of Pd due to the morphology modification and/or decrease the electrons–holes. This outcome may occur because of the palladium deposited on the CdS–PdS/PVAc which act as electron traps and enhance the electron–hole separation and the subsequent transfer of the trapped electrons to the adsorbed O_2, which acts as an electron acceptor [9].

3.3. Cyclic use of the CdS–PdS-doped PVAc nanofiber photocatalyst

In order to verify the reusability of the hybrid mat, we carry out 3 successive cyclic tests with the same nanofiber mats. In more detail, the same hybrid mat (100 mg) was used to treat three 50 ml of the dye solution (10 ppm) successively. Fig. 6 shows the cyclic degradation results. As shown in the figure, reuse of the proposed mat does not affect the photocatalytic activity which is considered as an interesting characteristic for the introduced electrospun mats. It was founded that the introduced mats were stable for many continuous cycles with both MB and MR dyes and gave very promising results. In addition, the combined effect of the hydrophobicity of these hybrid nanofiber mats, the unique morphology and the effectiveness of the incorporated ceramics nanoparticles made these interesting results.

3.4. Photocatalytic hydrogen production

Both mats reveal good activity toward water splitting process under solar radiation as shown in Fig. 7; however CdS–PdS/PVAc electrospun nanofibers have better efficiency. The obtained hydrogen production rate in case of CdS–PdS/PVAc is higher than the reported values corresponding to the naked CdS NPs due to the photocorrosion of the later [10,11], moreover the obtained results corresponding to CdS-doped PVAc nanofibers are considerable. The enhanced photocatalytic activity of CdS–PdS components could be predicted according to their energy band structures [12]. The conduction band edge of PdS is estimated to be −0.5 V vs. SCE (−0.26 V vs. NHE) by Mott–Schottky analysis [13], and the valence band potential of PdS can be determined by deduction the conduction band from the

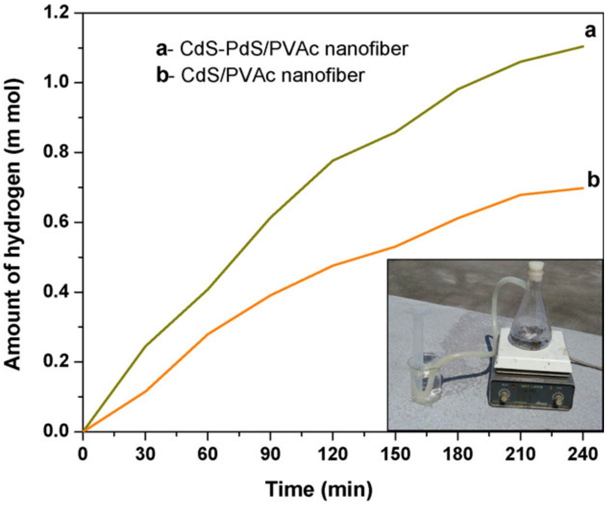

Fig. 7. Reaction time courses of H_2 evolution under solar irradiation. The inset represents a photo for the utilizing experimental setup.

band gap (1.6 eV) to be approximately +1.34 V vs. NHE, which is less positive than that of CdS (+1.5 V) [14]. This implies that the holes transfer from CdS to PdS is a favorable process, and that the PdS could act as an oxidation cocatalyst here. Therefore, the existence of PdS acting as an oxidation cocatalyst is supposed to be beneficial for the efficient separation and transfer of the photoexcited electrons and holes, thus contributing to the high efficiency. The PdS acting as the oxidation cocatalyst can protect CdS from photocorrosion, and make the CdS–PdS very stable under the photocatalytic reaction conditions. As reported before [15], PVAc has good electrical properties due to the abundant methyl group in the polymer chains. Accordingly, the good electric conductivity of the PVAc polymer plays a key role. PVAc form a layer of conductive network on the surface of CdS/PdS, which can promote the generation of the photogenerated electrons (e^-) and holes (h^+), accelerates the migration of photogenerated holes from VB of CdS to PdS, and prevents the recombination of them.

4. Conclusion

Addition of ammonium sulfide to PVAc solution containing Cd and Pd acetates leads to the in situ formation of CdS–PdS nanoparticles. Electrospinning of the formed colloid resulted in producing the metallic counterpart as a core-shelled with the PVAc polymer. CdS-doped PVAc nanofibers can be prepared by the same fashion. The introduced nanofibers revealed good performance towards dye photodegradation and water photo splitting process for hydrogen production; however CdS–PdS-doped PVAc nanofibers have better efficiency.

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