Controlled Engineering of WS$_2$ Nanosheets-CdS Nanoparticle Heterojunction with Enhanced Photoelectrochemical Activity

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Abstract

We report the well-controlled preparation of WS$_2$ nanosheets-CdS nanoparticle heterojunction potentially applicable for photoelectrochemical (PEC) water splitting under visible light. The WS$_2$-few layers nanosheets with an average thickness of ~5 nm and lateral dimensions of ~200 nm were synthesized via a convenient liquid phase exfoliation of bulk WS$_2$ in water/ethanol solution, which can be readily deposited onto ITO substrate via electrophoretic deposition. CdS nanoparticle thin films were synthesized via facile successive ion layer absorption and reaction (SILAR) method. By combining these two simple and well-controlled methods, CdS/WS$_2$/ITO and WS$_2$/CdS/ITO thin films were fabricated. The loadings of WS$_2$ nanosheets and CdS nanoparticles were carefully controlled by the deposition condition and the heterojunction was
optimized for enhanced photoelectrochemical response under simulated sunlight irradiation. The obtained heterojunction structures were characterized by various techniques, including scanning electron microscopy (SEM), PEC response and electrochemical impedance spectroscopy (EIS). Our results showed that the CdS/WS$_2$/ITO heterojunction can exhibit a very stable photo-current density 3 times higher than the conventional CdS/ITO thin films under the same conditions. In contrast, photo-current density of the WS$_2$/CdS/ITO thin films was lower than that of the bare CdS/ITO, indicating that an appropriate energy level cascade is essential for achieving enhanced PEC response. A charge transfer mechanism was proposed to explain the observed PEC enhancement. This work indicates that the liquid phase exfoliated WS$_2$ nanosheet is a promising new material for photoelectrochemical applications and our applied method is very simple but effective to deposit CdS and WS$_2$ nanostructures to give stable performance under long time light irradiation.

**Keywords:** WS$_2$-CdS heterojunction, well-controlled growth, photoelectrochemical performance, visible light, charge transfer mechanism

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1. Introduction

Recently, there has been considerable interest in the study of the two-dimensional (2D) layered materials such as graphene and transition-metal dichalcogenides (TMDs). TMDs as graphene analogues are a family of compounds with the formula of MX$_2$, where M is a transition metal element and X is a chalcogen (S, Se or Te). The covalently bonded 2D X-M-X layers are separated by weak Van der Waals interactions, which can be exfoliated into
single-layer or few-layers via various methods. Several 2D TMD materials have exhibited attractive properties including high mobility, large surface area, structure-dependent band structure and high catalytic activity.

It is known that the electronic properties of 2D TMD materials are strongly dependent on their morphology and preparation method. For instance, WS$_2$ is an indirect band gap material in its bulk form (1.35 eV) and becomes a direct band semiconductor with a gap of 2.05 eV in the mono-layer form, which exhibits extraordinary electrical and optical properties. Besides, 2D-WS$_2$ layers prepared by lithium intercalation and exfoliation show metallic properties, while that prepared by solvent exfoliation method exhibit semiconductor properties.

It is well established that 2D layered composite materials possess larger specific surface areas that lead to a large number of active sites on their surface, which can significantly enhance the catalytic activity. Based on the recent reports, among the TMDs family, exfoliated MoS$_2$ and WS$_2$ are less toxic compared to graphene oxide and therefore, they can be employed as a safer alternative in future applications. WS$_2$ has a higher intrinsic electrical conductivity than MoS$_2$, and therefore is a more suitable candidate for fabrication of hybrid composite. Layered hybrid composites of the WS$_2$, including WS$_2$/CN, WS$_2$/rGO and ZnS–WS$_2$/CdS with enhanced hydrogen production activity were reported.

Few layers of WS$_2$ with the large surface area, high active sites and broadband light absorption is predicted to enhance the CdS photo-activity. Chen et al. reported the co-loading of ZnS and WS$_2$ on CdS particles to produce ZnS-WS$_2$/CdS powders and demonstrated that the loading increased the photocatalytic activity of CdS particles significantly. But the used preparation method was time and energy consuming.

To the best of our knowledge, there is no report about preparation of WS$_2$-CdS thin film electrode and investigation of its PEC performance. Herein, we have introduced a very simple
combined method to prepare the CdS-WS$_2$ heterojunction thin film electrodes with stable PEC performance for the first time. We have fabricated the WS$_2$/CdS hybrid films, composing 2D WS$_2$ nanosheets and CdS nanoparticles using a facile and safe deposition method at room-temperature. Herein, CdS/WS$_2$/ITO and WS$_2$/CdS/ITO thin film electrodes with various amounts of CdS and WS$_2$ nanosheet loading were prepared by simple and well-controlled successive ion layer adsorption and reaction (SILAR) and electrophoretic deposition (EPD) methods. Different properties of the hybrid thin films, including their photoelectrochemical performance, were carefully studied, using various analytical techniques. The charge transfer mechanism in the CdS-WS$_2$ interface of the both CdS/WS$_2$/ITO and WS$_2$/CdS/ITO thin films is proposed to account for the observed PEC behavior. Our simple applied method was very effective to deposit CdS nanoparticles and WS$_2$ nanosheets with excellent cohesion to the substrate which results in robust photoresponsibility under continuous long time light irradiation.

2. Experimental

Preparation of exfoliated WS$_2$ few layers

Based on our previous study, exfoliated WS$_2$ few layer nanosheets were obtained via mixed-solvent strategy. Typically, 500 mg bulk WS$_2$ powder was dispersed in 100 mL flask containing 50 mL mixed water/ethanol solution (with the volume fraction of water:ethanol=65:35). The flask was capped tightly and put in the sonication bath and then sonicated for 15 h. After 48 h rest in the room condition, the 2/3$_{rd}$ of the supernatant was selected and centrifuged at 3800 rpm for 45 min and finally, the upper 2/3$_{rd}$ of the centrifuged solution was decanted into glass vials and kept for further use.

Preparation of WS$_2$ few layers thin films
Electrophoretic deposition (EPD) was utilized to prepare WS$_2$ exfoliated few-layers thin films. Before deposition, the ITO sheets were cleaned as following: they were washed by dish soap carefully and then sonicated for 30 min in DI water. The procedure was repeated again. After that the ITO sheets were sonicated in Acetone for 30 min and sonication in Acetone was also repeated again. Finally the ITO sheets were sonicated in Isopropyl alcohol 2 times and each time for 30 min.

Two pre-cleaned ITO sheets were chosen as an anode and cathode, respectively, and placed at the distance of 15mm from each other in a parallel alignment. The WS$_2$ suspension in water:ethanol was the electrolyte. Based on zeta potential measurement studies, WS$_2$ flakes carry electrical charges in water:ethanol solution. So, there is no need to add a conductive electrolyte. By applying 8V between these two electrodes for different time intervals (30 s, 1 and 2 min), the WS$_2$ thin films were deposited on the ITO cathode. Since, the EPD lower than 30s resulted in no significant WS$_2$ deposition, 30s was selected as a minimum required deposition time.

CdS nanoparticles deposition

Based on our previous works, the successive ion layer adsorption and reaction (SILAR) method was employed for CdS nanoparticles loading. The ITO or WS$_2$/ITO electrodes were separately immersed into 50 mM Cd(NO$_3$)$_2$, and then 50 mM Na$_2$S aqueous solutions for 20 s. The layers were rinsed with deionized (DI) water after each immersion step. This sequential process (known as SILAR cycle) was repeated 20 times. To prepare WS$_2$/CdS/ITO thin films, CdS were being loaded via SILAR technique and then WS$_2$ was deposited on CdS/ITO thin film by EPD method. In order to fabricate CdS/WS$_2$/ITO films, as the first step, WS$_2$ was deposited
on ITO via EPD, and then CdS nanoparticles were deposited on the prepared WS$_2$/ITO thin film using SILAR method.

**Material characterization**

UV-Visible absorption spectra of the samples were obtained via PGENERALE T6 spectrophotometer. To investigate the topographical properties and morphology of the prepared thin films, tapping-mode atomic force microscopy, AFM (Agilent SPM 5500, USA) and field-emission scanning electron microscopy (FE-SEM) (Hitachi S4800) were employed. The AFM data were analyzed with SPIP 6.2.8 software. High resolution transmission electron microscopy, HRTEM (Tecnai-G2-F30, USA) equipped with X-ray energy dispersive spectrometer, EDS (Oxford Link-ISIS) was used to study the morphology chemical composition of the nanostructures. The Invia Renishaw Raman microscope was also employed to identify the composition of the samples. The exciting laser wavelength was 514.5 nm and the Raman spectra were calibrated using Si Raman peak at 520 cm$^{-1}$ as reference.

**3. Results and Discussion**

Various properties and performance of the prepared samples were investigated using the above analytical techniques. In this section, we report the results of optical study, AFM analysis, Raman spectroscopy, TEM observations, Photoelectrochemical activity as well as a proposed mechanism for the photo-enhancement of water splitting under visible light as follows:

**Optical Analysis**

The layered structure of 2H-WS$_2$ is shown in Fig. 1 inset. The thickness of a single-layer WS$_2$ is 6.162 Å. Each layer consists of an atomic plane of hexagonally-arranged W atoms sandwiched between two similar hexagonally-arranged atomic S planes. The bond within the
layers is covalent while these layers are bonded together by weak van der Waals forces in AbA|BaB stacking order in 3D crystal. This 2H crystal structure of WS$_2$ has a specific UV-visible absorption spectrum. So, it can be a good criterion to understand if the prepared WS$_2$ solution has a 2H crystal structure or not.

The optical spectrum of the WS$_2$ few layer solutions (after scattering subtraction) is shown in Fig. 1. Excitonic A and B absorption peaks appeared at about 628 and 525 nm, respectively. These two peaks are arising from direct gap transitions at the K point of the 2H-WS$_2$ unit cell. The weak absorption peak C appeared at ~ 455 nm is related to the optical transitions between the density of states in the valence band (VB) and conduction band (CB).

**Fig. 1**

The relationship of $(\alpha \theta h \nu)^n = A(h \nu - E_g)$ is used to calculate the energy band gap ($E_g$) of the direct band gap semiconductors ($n=2$) and indirect band gap semiconductors ($n=1/2$). These plots for various WS$_2$/CdS/ITO and CdS/WS$_2$/ITO thin films are shown in Figure 2a and Figure 2b, respectively. The insets are the corresponding absorption spectra. Evaluated energy band gaps of the samples are presented in Table 1. For all of the samples, the increase in the EPD time (which resulted in an increase in WS$_2$ loading) cause a shift in the $E_g$ from 2.5 eV (in bare CdS) to 1.7 eV for bare WS$_2$ (Figure S1, Supporting Information).

**Table 1**

The $E_g$ values were decreased from 2.5 to 1.7 eV for the WS$_2$/CdS/ITO samples, but for the CdS/WS$_2$/ITO thin film samples, the $E_g$ values were reduced to 2.1 eV, which indicates that in the latter system, the CdS crystal plays an important role for light harvesting.

**Figure 2**
AFM Observations

The AFM analysis was employed to reveal both thickness and lateral dimension of the exfoliated nanosheets. WS$_2$ solution was spin-coated on a mica substrate at 2000 rpm for 20 s. The results are shown in Figure 3. As it can be seen, there are a distribution of flakes with thickness between 1-5 nm and lateral dimensions varied between 50 - 350 nm. The average thickness and lateral dimension of the WS$_2$ flakes were measured to be about 5 nm and 200 nm, respectively. The thickness of a monolayer MoS$_2$ and WS$_2$ prepared via chemical methods was reported to be about 0.8–1.2 nm. Hence, the obtained flakes are estimated to be 5 layers in average. The observed thickness below 1 nm in Figure 3e is as a result of AFM technique. Tapping mode was used to get AFM images. The real thickness and size should be determined after subtraction of these effects of AFM instrument. It is worth to note that these flakes (with above mentioned thickness and sizes) make clusters with different thickness and sizes after deposition on ITO substrate with various deposition time which can affect the PEC performance of the layers. The effect of various deposition time on PEC performance is carefully discussed in following sections.

Figure 3

Raman characterization

The bulk 2H-WS$_2$ belongs to the space-group (P6$_3$/mmc, #194), with unit cell consisting of two W atoms lie in (2d) Wyckoff position ±(1/3,2/3,3/4) and four S atoms in (4f) Wyckoff position ±(1/3,2/3,1/4±z) with z=0.1225≈1/8. The 2H notation stands for Hexagonal form with 2 molecular units in the primitive unit cell to distinguish from the other Rhombohedral polytype, 3R, with 3 molecular units in the unit cell, (Figures S2a and S2b). Details of crystal structure,
Raman active modes of WS\textsubscript{2} layers and their corresponding atomic displacements are illustrated in Figure S2c.

To ensure that both CdS and WS\textsubscript{2} are successfully deposited together onto ITO substrate, the final thin films were subjected to Raman spectroscopy. The exciting laser wavelength was 514.5 nm (Ar laser) in the back scattering geometry. To assess the possibility of oxidation during Electrophoretic Deposition (EPD), the Raman spectra of the samples prepared with longest EPD time (2 min) were examined and the results are shown in Figure 4. Two obvious Raman peaks located at 355.0 and 419.6 cm\textsuperscript{-1} are attributed to E\textsubscript{12g} and A\textsubscript{1g} first-order optical modes of WS\textsubscript{2}, respectively. The separation between the two modes is 64.6 cm\textsuperscript{-1}, lies between 64.8 cm\textsuperscript{-1} for bulk WS\textsubscript{2} and 62 cm\textsuperscript{-1} for monolayer formation, which indicates the presence of few-layer WS\textsubscript{2}.

The thickness of WS\textsubscript{2} flakes would affect the positions of the peaks in Raman spectra as well as their intensities. In particular, the peak position of out-of-plane mode, A\textsubscript{1g}, has a strong dependency to the number of layers in WS\textsubscript{2} flakes and can be quantified to estimate the average number of layers using an exponential model \[ \omega_{A_{1g}}(N) = \omega_{bulk} + (\omega_{L} - \omega_{bulk}) \exp\left[-\chi (N-1)\right] \]
and a fractional model \[ \omega_{A_{1g}}(N) = \omega_{bulk} + (\omega_{L} - \omega_{bulk}) / \left[1 + \chi (N-1)\right] \] where \( N \) is the number of layers, \( \chi \) the fitting parameter and \( \omega_{A_{1g}}, \omega_{bulk} = 420.1 \) and \( \omega_{L} = 417.2 \) are measured, bulk and mono-layer A\textsubscript{1g} peak position of WS\textsubscript{2} in cm\textsuperscript{-1}, respectively. By fitting these two models and based on the reported data for various WS\textsubscript{2} thickness in literatures, we have obtained \( \chi = 0.495 \) for exponential model and \( \chi = 0.796 \) for fractional model using Raman spectroscopy at exciting laser wavelength of 514.5 nm. However, the mean absolute deviation (MAD) as a criterion for the fitting goodness is better for the exponential model than the fractional model. Thus, by using
the exponential model, the average number of layers for $\omega_{A_{1g}} (N) = 419.6 \ cm^{-1}$ in Figure 4 is estimated to be $N \approx 5$ layers, which confirms the AFM observations.

The two characteristic CdS longitudinal optical (LO) phonon mode peaks can be seen at about 300 cm$^{-1}$ (1LO) and 600 cm$^{-1}$ (2LO). The line shape asymmetry and the shift of the peak toward lower frequencies compared to the bulk CdS (305 cm$^{-1}$ and 605 cm$^{-1}$) can be attributed to optical phonon confinement and formation of CdS nanoparticles. Figure 4 clearly verifies the presence of both CdS nanoparticles and WS$_2$ few layers in both WS$_2$/CdS/ITO and CdS/WS$_2$/ITO thin films without any trace of oxides.

**Figure 4**

**TEM Analysis**

To further study and verify successful junction formation between the CdS particles and WS$_2$ sheets, TEM analysis was also employed. The CdS-WS$_2$ materials were crashed from the CdS/WS$_2$/ITO (8V-30s) sample with a keen blade and then dispersed in water and exposed to vigorous sonication for 1h.

TEM results are shown in **Figure 5**.

As it can be seen, the CdS particles are blended into WS$_2$ sheets. Higher magnification of the selected area (**Figure 5b and c**) shows clearly the presence of both WS$_2$ sheet and CdS planes (220). The hexagonal structure of WS$_2$ sheet can be seen obviously in **Figure 5c**, indicating that no crystal structural change occurred during our preparation method, which is in good agreement with the obtained optical absorption spectrum and Raman analysis. The EDS spectrum and atomic percentage of the elements are shown in **Figure 5d**.
Photoelectrochemical Measurements

Chronoamperometry

J-t curves of the CdS/WS$_2$/ITO and WS$_2$/CdS/ITO samples are shown in Figure 6 and Figure 7 and the results are compared to the bare CdS/ITO thin films, respectively. Photo-current density measured for the CdS/ITO thin films was about 125 μA/cm$^2$. All of the CdS/WS$_2$/ITO thin films have higher photo-activity than the bare CdS thin film, while, the bare CdS thin film exhibits a higher photo-activity than the WS$_2$/CdS/ITO samples. Photo-current density of 350, 290 and 274 μA/cm$^2$ is measured for the CdS/WS$_2$/ITO thin films prepared with 30s, 1 and 2 min deposition time by EPD method, respectively.

The order of photoactivity of the prepared samples is as following:

$$\text{CdS/WS}_2/\text{ITO} > \text{CdS/ITO} > \text{WS}_2/\text{CdS/ITO}$$

So, if the ITO substrate is covered with few layers of WS$_2$ before deposition of CdS nanoparticles, the photo responsivity of the system can be improved to about 3 times.

The charge transfer condition is different in CdS/WS$_2$/ITO and WS$_2$/CdS/ITO thin film systems. The photoresponsivity of bare WS$_2$/ITO thin films prepared with various EPD time is also measured and the results are shown in Figure S3, indicating low photoactivity of WS$_2$/ITO thin films compared with WS$_2$-CdS/ITO thin films.

Figure 6, Figure 7
The effective surface area of samples plays a decisive role in both light absorption and catalytic reactions as reported by others. Thus, the surface areas of the prepared thin films were compared through their surface roughness (S_{r}) measured via AFM technique. The different regions of the surface were examined in a statistical manner.

The results are summarized in Table 1.

In CdS/WS_{2}/ITO thin films the WS_{2} flakes are deposited on conductive ITO substrate. In this situation, the induced E is strong and WS_{2} flakes are deposited more quickly. Therefore the highest surface roughness is obtained by short deposition time (30 s) and after that the roughness decrease and reaches to a saturated value (table 1). In the other hand, for WS_{2}/CdS/ITO thin films, the WS_{2} flakes are deposited on CdS/ITO substrate. Deposition of semiconducting layer of CdS on ITO decrease the net electrical filed. The roughness of WS_{2}/CdS/ITO thin films increase by increasing deposition time. It is expected that their S_{r} reach to a maximum value and then to a saturated one in deposition times longer than 2 min. because the PEC performance of these samples decrease with increase in EPD time, it is not reasonable to prepare the samples with deposition time longer than 2 min. The S_{r} value for the CdS/WS_{2}/ITO thin films is also higher than that of the bare CdS layer. The highest S_{r} is obtained for the sample grown under 30s deposition of the WS_{2} few layers (Table 1). This result agrees well with the highest photo-current density measured for this sample. Therefore, in these systems, the higher S_{r} is in favor of photo-current enhancement. The 2D-AFM images representing the surface topography of various synthesized samples are shown in Figure S4.

The photo-current density as a function of light intensity spectra and also their logarithmic spectra, to obtain the scaling exponent, for the CdS/WS_{2}/ITO and the WS_{2}/CdS/
ITO thin films are shown in Figure S5 and Figure S6, respectively, which are in good agreement with corresponding J-t curves (Figure 6 and Figure 7).

The photo-current density of the bare CdS/ITO is less than CdS/WS$_2$/ITO and higher than WS$_2$/CdS/ ITO thin films in all of various light intensities (CdS/WS$_2$/ITO>CdS>WS$_2$/CdS/ITO). The β exponents for these systems are evaluated and listed in Table 1. The obtained β for CdS/WS$_2$/ITO is greater than bare CdS, indicating favorable situation for charge transfer in these samples compared to CdS thin films. The greatest β value is related to CdS/WS$_2$/ITO prepared with 30 s EPD which has also the highest photo-responsibility. Further deviation from linear behavior by increasing EPD time indicates that both the layers charge transfer resistance and their saturated effect are increasing and this can be signs of bimolecular recombination.

It was found that all of the WS$_2$/CdS/ ITO thin films have smaller β values, meaning that the conversion of light to current is less efficient in these samples and loading of WS$_2$ nanosheets on the CdS/ITO thin film is not in favor of charge separation and transportation. Figure 7 and Table 1 show that higher WS$_2$ loading in these samples resulted in lower photo-current density and also smaller β value. WS$_2$ deposition in the WS$_2$/CdS/ ITO thin films increased the surface area and as a result the light absorption was enhanced (Figure 2 and Table 1), which however cannot generate higher current density in an efficient manner. The obtained value of β= 0.68 for the WS$_2$/CdS/ ITO (8V- 2 min) sample is the minimum and the nearest value to $\beta_{\text{free}}$, indicating that bimolecular recombination is the most dominant effect in this configuration.

**Electrochemical Impedance Spectroscopy**

Nyquist plots of the bare CdS/ITO, CdS/WS$_2$/ITO(8V -30s) and WS$_2$/CdS/ITO(8V –30s) thin films are shown and compared in Figure 8. Semicircle of the CdS/WS$_2$/ITO(8V-30s) thin film is smaller than that of the bare CdS/ITO thin film indicating lower charge transfer resistance in the
CdS/WS$_2$/ITO thin film. The data can be fitted with a Randles circuit (Figure 8 inset) which is reported for similar systems elsewhere. The charge transfer resistances ($R_{ct}$) for the samples are listed in Table 1. $R_{ct}$ for bare CdS/ITO thin film is 2365 Ω which is larger than 2088 Ω for CdS/WS$_2$/ITO (8V –30s) thin film and smaller than 6755 Ω for WS$_2$/CdS/ITO (8V–30s) layer.

**Figure 8**

Nyquist plots of the CdS/WS$_2$/ITO layers are shown in Figure S7. Increase in EPD time resulted in an increase in charge transfer resistance (Table 1) leading to reduction of the photo-current density of the samples. On the other hand, Nyquist plots of other WS$_2$/CdS/ITO systems show a higher $R_{ct}$ as compared to the bare CdS thin film (Figure S8).

**Stability of the photoelectrodes**

One of most important properties of a photoelectrode in solar driven water splitting and solar cell application is its stability under continuous sunlight irradiation for a long time. The stability of the CdS/WS$_2$/ITO (8V-30s) which has given the best photo-current density was investigated under continuous irradiation of our Xe lamp for 90 min and compared with bare CdS/ITO electrode. The results are shown in Figure 9. Low stability of CdS thin films because of photo-corrosion effect is a well known fact which is clear in Figure 9. But the CdS/WS$_2$/ITO (8V-30s) sample gives a stable photo-current with nearly no decrease after 90 min continuous light irradiation. The results indicate that charge carrier separation and transport is more dominant than CdS photo-corrosion in CdS-WS$_2$ heterojunction. Adding appropriate amount of few-layer WS$_2$ to highly photo-active CdS thin film, increase its photo-activity and also its stability which both of these factors are very important issues in solar energy material fabrication. The results indicate that our applied method was very simple but effective to prepare CdS-WS$_2$ heterojunction thin
film with excellent cohesion to the substrate which results in robust photoresponsibility under continuous long time light irradiation.

**Figure 9**

**Mechanism of photo-enhanced PEC property**

Investigation and comparison of the WS$_2$/CdS/ITO and CdS/WS$_2$/ITO thin film systems with different photoelectrochemical behavior provide obvious evidence to understand the charge transfer mechanism in CdS-WS$_2$ heterojunction. By contrast, this good electron pathway should be blocked in the WS$_2$/CdS/ITO thin film, resulting in lower photo-current density. The schematic representation of charge transport processes in these two thin film systems are illustrated in **Figure 10**. These issues are verified by SEM observation (**Figure S8**). Uniform coating of both CdS and WS$_2$ layer on ITO substrate can be clearly observed in Figure S8b and Figure S8c, respectively. Upon visible sunlight irradiation, both CdS and WS$_2$ can be excited to generate $e^-\cdot h^+$ pairs. This suitable condition is observed only for the CdS/WS$_2$/ITO thin films. As shown in **Figure 10a**, for the CdS/WS$_2$/ITO system, the appropriate position of conduction band (CB) alignment, the photo-generated electrons can be transferred stepwise from CB of CdS to CB of WS$_2$ and then to ITO substrate. Meanwhile, photo-generated holes can also transfer stepwise from the CdS valence band (VB) to WS$_2$ nanosheets VB and accumulate for the subsequent oxidation process. This efficient electron-hole separation and transport is the key factor to protect the CdS layer against photo-corrosion, resulting in generation of a sustainable photo-current (**Figure 9**). If the excess CdS loading is covering most areas of the WS$_2$ nanosheets it may prevent the transfer of holes to the solution and as a result, their recombination process may occur, leading to reduction of photo-current density of the sample. Based on Table 1, the optimum condition for the CdS/WS$_2$/ITO thin film is 30 s EPD time.
The impedance spectroscopy results indicate that the CdS/WS$_2$/ITO (8V-30s) system has the lowest charge transfer resistance as compared with other samples prepared with higher EPD time. Because of the anisotropic conductivity of WS$_2$, a higher resistance is detected when the amount of the WS$_2$ layers increase, also supported by our EIS results (See Figure 8). So it is logical that higher EPD deposition time increases the WS$_2$ layer thickness resulting in deterioration of the photocurrent density. Accordingly, increase in EPD time results in increase in deposited WS$_2$ flakes, less surface roughness and higher charge transfer resistance (Table 1).

For the WS$_2$/CdS/ITO thin film system, we have also found the appropriate conditions for hole transport process. The pathway for hole migration is the same as in the CdS/WS$_2$/ITO thin films. As a result, these electrons accumulate in CB of WS$_2$ and recombine with the generated holes in the VB of WS$_2$. This proposed mechanism is also verified by impedance results (Figure S7). Based on our data analysis and the results in Table 1, the WS$_2$/CdS/ITO thin films prepared by longer EPD deposition have a higher surface area and as a result, they have more surface sites for reactions. But, due to blockage of electron pathways toward back contact, increasing surface sites resulted in increasing recombination centers leading to a drastic reduction of photo-activity of the sample.

**Figure 10**

**Conclusions**

WS$_2$ few layer nanosheets were prepared through solvent exfoliation in a mixed water/ethanol solution without using any additives. The obtained WS$_2$ flakes were combined with CdS nanoparticles to produce WS$_2$/CdS/ITO and CdS/WS$_2$/ITO thin films electrodes via simple electrophoretic and SILAR methods. Taking advantages of this combined method, loading of both CdS nanoparticles and WS$_2$ few layers can be well controlled and various architectures
were easily designed and produced. In this approach, CdS-WS\textsubscript{2} heterojunction was fabricated and its photoelectrochemical (PEC) activity was investigated systematically under sunlight irradiation. The PEC results indicate that in the CdS/WS\textsubscript{2}/ITO thin film system, there is an appropriate pathway for photo-generated charge carriers and synergistic effect of CdS and WS\textsubscript{2} material resulted in a much higher photo-current density as compared to individual components and also protect them against photo-corrosion and therefore a stable photo-current can be achieved. However, in the WS\textsubscript{2}/CdS/ITO thin film system, the photo-generated electrons in the CB of WS\textsubscript{2} flakes cannot transfer to back contact through the CdS nanoparticle mediator. Thus, these trapped electrons may recombine with the accumulated holes in VB of WS\textsubscript{2} nanosheets. As a result, the photo-current density of the WS\textsubscript{2}/CdS/ITO thin films is reduced as compared with the bare CdS thin film. The obtained results for the WS\textsubscript{2}/CdS/ITO and the CdS/WS\textsubscript{2}/ITO thin films support our charge transfer mechanism in the CdS-WS\textsubscript{2} heterojunction. The results herein can provide useful information for future device applications of these materials.

Appendix A. Supporting information

Electronic Supplementary Information (ESI) is available in a separate file.
Fig. 3

Fig. 4

![Graph showing Raman shift vs intensity for different samples: CdS/WS₂/ITO (8V-2min) and WS₂/CdS/ITO (8V-2min). Peaks labeled 1LO, 2LO, E₁₂g, and A₁g.](image)
Fig. 5
Fig. 6

Fig. 7
Fig. 10