Highly Efficient Photocatalytic Z-Scheme Hydrogen Production over Oxygen-Deficient WO$_{3-x}$ Nanorods supported Zn$_{0.3}$Cd$_{0.7}$S Heterostructure

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The demand for clean renewable energy is increasing due to depleting fossil fuels and environmental concerns. Photocatalytic hydrogen production through water splitting is one such promising route to meet global energy demands with carbon free technology. Alternative photocatalysts avoiding noble metals are highly demanded. Herein, we fabricated heterostructure consist of oxygen-deficient WO$_{3-x}$ nanorods with Zn$_{0.3}$Cd$_{0.7}$S nanoparticles for an efficient Z-Scheme photocatalytic system. Our as obtained heterostructure showed photocatalytic H$_2$ evolution rate of 352.1 $\mu$mol h$^{-1}$ with apparent quantum efficiency (AQY) of 7.3% at $\lambda = 420$ nm. The photocatalytic hydrogen production reaches up to 1746.8 $\mu$mol after 5 hours process in repeatable manner. The UV-Visible diffuse reflectance spectra show strong absorption in the visible region which greatly favors the photocatalytic performance. Moreover, the efficient charge separation suggested by electrochemical impedance spectroscopy and photocurrent response curves exhibit enhancement in H$_2$ evolution rate. The strong interface contact between WO$_{3-x}$ nanorods and Zn$_{0.3}$Cd$_{0.7}$S nanoparticles ascertained from HRTEM images also play an important role for the emigration of electron. Our findings provide possibilities for the design and development of new Z-scheme photocatalysts for highly efficient hydrogen production.

The increasing demand for energy and depleting crude oil resources forced researchers to find alternate options for rapidly growing world population. The burning of fossil fuels also deteriorating world’s climate by the emission of CO$_2$ and other greenhouse gases$^1$. Therefore, a sustainable and clean energy source is the biggest challenge for the 21st century. Photocatalytic hydrogen production emerges as environment friendly method since the pioneer work of Fujishima and Honda in 1972$^2$. Since then, a large number of photocatalysts have been synthesized for water splitting to generate hydrogen$^1$. However, most of catalysts either depend upon expensive noble metals as co-catalyst (Pt, Ru, and Rh) or only absorb in the ultraviolet region which accounts for only 4% of the incoming solar light. Metal oxides such as WO$_3$, NiO and RuO$_2$ emerges as new class of photocatalyst for efficient hydrogen production$^4$–$^9$. However, photocatalysts with maximum absorption in the visible region and suitable band-gap are highly desirable.

Cadmium sulphide (CdS) attracts considerable attention due to its narrow band gap (2.4 eV) for photocatalytic hydrogen evolution reaction. However the rate of H$_2$ production over CdS is very low because of its photo-corrosion property and fast-recombination of electron–hole pair which renders its practical applications impossible$^{10}$. The use of co-catalyst or incorporation of Zn ion into CdS to form Zn$_{1-x}$Cd$_x$S (0–1) greatly enhances the photocatalytic activity. Recently, the band-gap for Zn$_{1-x}$Cd$_x$S has been varied to achieve maximum visible absorption and greater charge separation efficiency for water splitting$^{11}$. However, there are only few reports which suggest room temperature synthesis with excellent photocatalytic property and recyclability. Moreover, a heterostructure comprising two different photocatalysts is considered a better option compared to conventional

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system. The Z-scheme multi-component photocatalyst system was first introduced by Bard et al. in 1979 based on the concept of artificial photosynthesis. In multi-component Z-scheme photocatalytic system, the photogenerated electrons from Photosystem I (PSI) in the conduction band transfer through the interface contact and recombine with the photogenerated holes in the valance band of Photosystem II (PSII). This system allows the visible light to use more efficiently and dramatically improves the photocatalytic H₂ production.

The photocatalytic reactions are surface bound reaction, in which photogenerated electron and holes take part in the reaction. It is well known that oxygen vacancies in a non-stoichiometric crystal also carries two electrons each which can act as double electron donor. There are few recent studies in which the role of surface oxygen vacancies (SOV) was investigated thoroughly for photo-catalytic water splitting. Oxygen vacancies significantly impact the electronic properties of the material and shifts absorption towards longer wavelength. Oxygen vacancies also influences magnetic, photocatalytic, optical, wettability, and electrical properties of the catalyst. In a recent study, it is discovered that the oxygen vacancies improves the overall conductivity and enhances the adsorption of reactants on its surface for organic conversions. Additionally, oxygen deficient metal oxide greatly enhances the visible-light driven hydrogen production by trapping the photo-induced charges and preventing the electron-hole recombination. Mao and co-workers also created surface disorder in TiO₂ by hydrogenation and increased solar absorption while promoting photocatalytic activity.

Herein, we propose to fabricate a Z-scheme heterostructure consisting of oxygen deficient WO₃ₓ and Zn₀.₃Cd₀.₇S. Introduced oxygen vacancies in WO₃ to form WO₃ₓ/Zn₀.₃Cd₀.₇S heterostructure significantly increases the photocatalytic hydrogen production compare to heterostructure analogue without oxygen vacancies WO₃/Zn₀.₃Cd₀.₇S. The rate of H₂ evolution for WO₃ₓ/Zn₀.₃Cd₀.₇S heterostructure is as high as 352.1 μmol h⁻¹ with apparent quantum efficiency (AQY) of 7.3% at λ = 420 nm in repeatable manner from aqueous solution containing Na₂SO₃ and Na₂S as sacrificial reagents.

Results and Discussion

The morphology, size and structure of as synthesized WO₃ₓ, Zn₀.₃Cd₀.₇S and WO₃ₓ/Zn₀.₃Cd₀.₇S heterostructure were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 1, Figs S1 and S2). As shown in Fig. S1, the Zn₀.₃Cd₀.₇S are irregular shaped nanoparticles with a size of about 10–20 nm while the WO₃ₓ exhibit the shape of nanorods with a size in microns (Fig. S2). The SEM and TEM analysis of WO₃ₓ/Zn₀.₃Cd₀.₇S heterostructure shows that Zn₀.₃Cd₀.₇S nanoparticles successfully anchored on the surface of WO₃ₓ nanorods (Fig. 1). The intimate contact between WO₃ₓ and Zn₀.₃Cd₀.₇S was observed by high resolution transmission electron microscopy (HRTEM) clearly demonstrating that WO₃ₓ/Zn₀.₃Cd₀.₇S heterostructure with strong interface contact were successfully fabricated. The lattice spacing of 0.33 nm and 0.39 nm...
corresponds to (002) and (001) planes of Zn$_{0.3}$Cd$_{0.7}$S and WO$_3$–x, respectively, which confirms the existence of heterostructure.

The XRD patterns of as synthesized samples are shown in Fig. 2. The XRD pattern of WO$_3$ shows diffraction peaks which can be readily indexed to hexagonal Tungsten Oxide (JCPDS #33-1387) having cell parameters $a = 7.298$ Å, $b = 7.298$ Å, $c = 3.899$ Å and space group $P6/mmm$. The oxygen-deficient WO$_3$–x nanorods does not shows any clear difference in XRD pattern due to large size. The characteristic XRD diffraction peaks of Cd$_{0.3}$Zn$_{0.7}$S was easily observed at 28.1°, 45.7°, and 53.9° well matched with the (111), (220) and (311) planes of Zinc blend phase respectively. However, the characteristic diffraction peak of WO$_3$ and WO$_{3}$–x in WO$_3$/Zn$_{0.3}$Cd$_{0.7}$S and WO$_{3}$–x/Zn$_{0.3}$Cd$_{0.7}$S were not observed may be due to low content, small size of Zn$_{0.3}$Cd$_{0.7}$S nanoparticles in the samples

Electron paramagnetic resonance (EPR) spectra of WO$_3$/Zn$_{0.3}$Cd$_{0.7}$S and WO$_{3}$–x/Zn$_{0.3}$Cd$_{0.7}$S were recorded to examine the paramagnetic character. (Fig. 3) The WO$_3$/Zn$_{0.3}$Cd$_{0.7}$S sample does not shows any signal in EPR while WO$_{3}$–x/Zn$_{0.3}$Cd$_{0.7}$S exhibits a sharp signal at $g = 2.00$ which can be readily assigned as electrons trapped on oxygen vacancies, thus generating an EPR signal at $g = 2.00$.

The Zn$_{0.3}$Cd$_{0.7}$S and WO$_{3}$–x/Zn$_{0.3}$Cd$_{0.7}$S were also characterized by X-ray photoelectron spectroscopy (XPS) analysis as show in Figs 4 and S3. XPS survey spectrum of Zn$_{0.3}$Cd$_{0.7}$S shown in Fig. S3 indicate the presence of Zn, Cd and S in the nanoparticles. Figure S3b shows the XPS spectrum of Zn2p with the characteristic peak at
1023.6 and 1046.8 eV for Zn2p3/2 and Zn2p1/2, respectively. The high resolution XPS spectrum of Cd3d exhibits peaks at binding energy 405.1 and 411.8 eV corresponding to Cd3d5/2 and Cd3d3/2, respectively. The S2p orbital shows a broad peak at binding energy 161.3 eV corresponding to S2−. The ratio of Zn:Cd obtained from XPS analysis is well in agreement with the experimental calculations.

A typical survey XPS spectrum of WO3–x/Zn0.3Cd0.7S is also shown in Fig. 4a which confirms the coexistence of Zn, Cd, S, W, and O elements. The XPS spectra of Zn2p and Cd3d are plotted in Fig. 4b and c, respectively. The binding energies of Zn2p3/2 and Zn2p1/2, observed at 1021.9 and 1045.1 eV and Cd3d exhibit peaks at 405.2 eV and 412.1 eV corresponding to Cd3d5/2 and Cd3d3/2, respectively which agree well with the values reported for the divalent zinc and cadmium in pure metal sulfides. The S2p also show a peak at 161.5 eV which corresponds to S2− in the sample. (Fig. 4d) There is a difference in binding energies of Zn, Cd, and S for pure Cd0.3Zn0.7S and WO3–x/Zn0.3Cd0.7S heterostructure, which suggests the difference in valence electron density and relaxation energy after heterostructure formation. The high resolution XPS spectrum of W4f orbital shows two strong peaks corresponding to W4f7/2 and W4f5/2. (Fig. 4e) These peaks can be further deconvoluted into two Gaussian components. The lower binding energy components centered at 34.8 eV and 36.9 eV represent W5+ while higher binding energy components at 35.3 eV and 37.4 eV matched with high oxidation state of tungsten (W6+). The presence of W5+ in XPS analysis is also consistent with the EPR data showing the existence of oxygen vacancies in the sample. Figure 4f shows O1s spectrum which can be deconvoluted into three Gaussian curves centered at 530.4 eV, 531.7 eV and 532.7 eV. The low binding energy component is ascribed to the O2− ions in WO3−x while the components at the higher binding energy region are related to the O− from sample holder and physisorbed water molecules.

Figure 5 shows UV-vis diffuse reflectance spectra of WO3, WO3–x, Zn0.3Cd0.7S and WO3/Zn0.3Cd0.7S and WO3–x/Zn0.3Cd0.7S heterostructure. It can be clearly seen that WO3 shows a white color and almost no absorption in the visible region while WO3–x exhibit violet color and wide absorption band extending from 440 nm to 800 nm. Additionally, Zn0.3Cd0.7S nanoparticles can absorb at wavelengths of about 475 nm to 800 nm.

In addition, Transient photocurrent response curves of WO3/Zn0.3Cd0.7S and WO3–x/Zn0.3Cd0.7S were also examined by photoelectrochemical test device under visible range for light with irradiation (λ ≥ 420 nm) using Ti foil. (see the Experimental section). As shown in Fig. 6a, the photocurrent value increases rapidly at a maximum value when the light turned on due to the separation of electron hole pairs at the heterostructure–electrolyte interface. The current value drops to zero when the light turned off, which is due to the recombination of electron–holes pairs. Notably, the WO3–x/Zn0.3Cd0.7S heterostructure shows much higher photocurrent than...
WO_3/Zn_0.3Cd_0.7S, suggesting that the oxygen-deficient WO_3-x facilitate the charge transfer process resulting in higher photocatalytic performance.

Electrochemical impedance spectroscopy (EIS) was also performed on a photoelectrochemical setup to investigate the charge separation efficiency of WO_3/Zn_0.3Cd_0.7S and WO_3-x/Zn_0.3Cd_0.7S heterostructure as is depicted in Fig. 6b. The large semicircle in the Nyquist plots represents the charge transfer process, while the smaller arc demonstrates fast separation of photogenerated electron–hole pairs and efficient interface charge flow. As shown in Fig. 6b, the WO_3/Zn_0.3Cd_0.7S have semicircle at the high frequency while WO_3-x/Zn_0.3Cd_0.7S showed low charge transfer resistance (Rct) and much smaller semicircle suggesting the oxygen vacancies increase electrical conductivity and enhance visible-light driven hydrogen production. The oxygen vacancies thus providing a key role of rapid electron transfer for our Z-scheme photocatalytic H_2 system. The results are also consistent with photocurrent response and diffuse UV-visible reflectance data.

The photocatalytic H_2-evolution reactions of WO_3, WO_3-x, WO_3/Zn_0.3Cd_0.7S and WO_3-x/Zn_0.3Cd_0.7S were performed in the presence of Na_2S and Na_2SO_3 as sacrificial reagents under xenon lamp irradiation (Figure 7a). WO_3 nanorods exhibit very low H_2-evolution rate (2 μmol h^-1). The band edge position of γ-monoclinic phase of WO_3 is not optimal for photocatalytic water splitting, however, the band edge of hexagonal-WO_3 match up with the redox potential of water, which is used in our case and exhibit very low H_2-evolution rate while the oxygen deficient WO_3-x shows a better performance for H_2 production (10 μmol h^-1) implying the presence of oxygen vacancies leads to increase in photocatalytic activity. Zn_0.3Cd_0.7S nanoparticles alone showed moderate photocatalytic H_2-evolution rate (19.2 μmol h^-1). Remarkably, the WO_3/Zn_0.3Cd_0.7S Z-scheme system showed an improvement in hydrogen production under visible light with H_2-evolution rate of 132 μmol h^-1. The defect rich WO_3-x/Zn_0.3Cd_0.7S heterostructure demonstrates highest rate of H_2 production 352.1 μmol h^-1 with apparent quantum efficiency (AQY) of 7.3% at 420 nm. The photocatalytic hydrogen production reaches up to 1746.8
WO3–x/Zn0.3Cd0.7S heterostructure for photocatalytic O2 production which shows 3.24 μmol in 5 h process which is considerably higher than some previous reports on photocatalytic H2 production such as TiO2/Pt/P2W17, TiO2/Au/CdS40, ZnO/Au/CdS41, WO3/PbBi2Nb1.9Ti0.1O9, BiVO4/Ru-SrTiO342, which showed rate 19.6, 3.2, 60.8, 14.8 and 22 μmol h–1, respectively. It is worth mentioning that no noble metals were used in our system44–46. Moreover, as it is seen from Fig. 7b, the process for production is repeatable and after 4 cycles was not observed decreasing in activities confirming stability, robustness and durability of this systems. The UV-vis diffuse reflectance spectra of oxygen deficient WO3–x nanorods show a prominent color change and strong absorption in the visible region which is favorable for the photocatalytic hydrogen production. The photocurrent response and EIS results also demonstrate more efficient photogenerated electron emigration in oxygen deficient-WO3–x/Zn0.3Cd0.7S heterostructure compared to oxygen-vacancy-free WO3/Zn0.3Cd0.7S sample. The fast electron transfer efficiently captures the photo induced holes in the valence band (VB) of Zn0.3Cd0.7S. The fast recombination of e/h by the photo-generated electrons from conduction band (CB) of WO3–x and holes from the VB of Zn0.3Cd0.7S results in excellent photocatalytic performance. For our oxygen-deficient WO3–x/Zn0.3Cd0.7S Z-scheme system, the photo-generated holes tend to be present in the VB WO3–x, while the electrons in the conduction band of WO3–x combine with the holes of Zn0.3Cd0.7S through the interface contact. As a result, the photo-generated charge carrier recombination can be significantly decreased. Therefore, more electrons in the CB of Zn0.3Cd0.7S are available to reduce H+ to H2, which results in highly efficient H2 production47. The visible light absorption can be attributed to the electron transition from the WO3–x valence band to the new oxygen vacancy energy bands near Fermi level, consequently, the electronic band gap decreases. Therefore, it is possible to use less energy per time to activate the photoelectrons and thus effectively improve the carrier separation efficiency48, 49. Oxygen vacancies also carry two electrons each which can act as double electron donors to capture photo-generated holes and enhances the H2 evolution performance. The strong interface contact in WO3–x/Zn0.3Cd0.7S ascertain from HRTEM images also strongly favors the efficient charge movement. We have also tested our as synthesized WO3–x/Zn0.3Cd0.7S heterostructure for photocatalytic O2 production which shows 3.24 μmol h–1 (Figure S4). However, the photocatalytic O2 production is not as high as H2 production.

The recyclability of any materials is an important marker to which it is applicable for practical applications. It has been observed that metal sulphides usually exhibit photo-corrosion property when used for prolonged photocatalytic hydrogen production. In order to analyze the stability of our as-synthesized catalyst, we have performed time course of photocatalytic hydrogen production under similar conditions. As was mentioned previously, our Z-scheme WO3–x/Zn0.3Cd0.7S heterostructure shows excellent stability for H2 evolution. The photo-generated electrons from WO3–x and oxygen vacancies also suppress the oxidation of Zn0.3Cd0.7S, thus inhibiting the photo-corrosion property resulting in enhanced photocatalytic performance. Previous reports showed that when there are small amount of oxygen vacancies in oxygen deficient material, the defect energy level is usually below the conduction band46. However in our case the, the concentration of oxygen vacancies in WO3–x is much higher (x = 0.4) thus the defect energy level delocalized over the conduction band. The Z-scheme electron transfer pathway needs to satisfy three conditions; i.e. PS I can only produce O2, PS II can only produce H2 and overall water splitting can occur in the presence of PS I and PS II. WO3 have been reported to produce O2 while Zn0.3Cd0.7S have shown potential to be used for photocatalytic H2 production51, 52. We have also tested photocatalytic O2 production using WO3–x/Zn0.3Cd0.7S heterostructure which shows 3.24 μmol h–1 and reaches up to 15.45 μmol after 5 hours. Moreover, the defect rich WO3–x/Zn0.3Cd0.7S heterostructure also demonstrates highest rate of H2 production 352.1 μmol h–1. This indicates that the photogenerated holes in the VB of WO3–x and photogenerated electrons in the CB of Zn0.3Cd0.7S are used to oxidize and reduce water into O2 and H2, respectively. Meanwhile, the photogenerated electrons in the CB of WO3–x recombine with the photogenerated holes in the VB of Zn0.3Cd0.7S through the solid-solid interface contact53. Meanwhile, the photo-generated electrons in the conduction band of Zn0.3Cd0.7S reduces H+ to H2 while the photo-generated holes in conduction band of WO3–x trapped by sacrificial reagents which undergo the oxidation of SO32– to SO42− (Figure 8). This possible Z-scheme mechanism is also consistent with the experimental data, EIS and transient photocurrent response.
results and various previous reports. Our multi-component Z-scheme system provides advancement in the design and development of low-cost highly efficient photocatalytic materials for water splitting.

Conclusions
In conclusion, we have synthesized a unique no noble metal Z-scheme photocatalyst by fabrication of oxygen-deficient WO$_{3-x}$ nanorods with Zn$_{0.3}$Cd$_{0.7}$S nanoparticles. The WO$_{3-x}$/Zn$_{0.3}$Cd$_{0.7}$S heterostructure shows visible light driven hydrogen production of 352.1 μmol h$^{-1}$ with apparent quantum efficiency (AQY) of 7.3% at 420 nm. The photocatalytic H$_2$ evolution reaches up to 1746.8 μmol after 5 hours in repeatable manner without decreasing activities over 4 cycles. The EIS and photocurrent response results suggest efficient charge separation which is key factor for the enhancement of the activity. The solid-solid interfacial contact between WO$_{3-x}$ and Zn$_{0.3}$Cd$_{0.7}$S favors photo-generated electron emigration from the conduction band of WO$_{3-x}$ to the valance band of Zn$_{0.3}$Cd$_{0.7}$S, thus capturing the photogenerated holes. The remaining photogenerated electrons in the conduction band of Zn$_{0.3}$Cd$_{0.7}$S efficiently reduce H$^+$ to H$_2$. Overall the hydrogen evolution rate over oxygen-deficient WO$_{3-x}$/Zn$_{0.3}$Cd$_{0.7}$S heterostructure is considerably high compared to WO$_3$/Zn$_{0.3}$Cd$_{0.7}$S and without the use of noble metals. Our approach opened up new avenue for to synthesis Z-scheme photocatalytic system for efficient hydrogen production from water splitting.

Experimental

Chemicals. Sodium tungstate (Na$_2$WO$_4$), Sodium sulfate (Na$_2$SO$_4$), Zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O), Cadmium acetate (Cd(CH$_3$COO)$_2$·2H$_2$O), Sodium sulfide nonahydrate (Na$_2$S·9H$_2$O), Sodium sulphite (Na$_2$SO$_3$) were purchased from Sinopharm Chemical Reagent. All other chemical reagents were of analytical grade and used as received without further purification.

Characterization. The morphology of the particles was observed by scanning electron microscope (SEM, JSM 6700F, JEOL). Transmission electron microscopic (TEM) images and high-resolution transmission electron microscopic (HRTEM) images were carried out on a JEM-2100F field emission electron microscope at an accelerating voltage of 200 kV. The X-ray powder diffraction (XRD) patterns of the products were performed on a Philips X’Pert Pro Super diffractometer with Cu-K$_α$ radiation ($\lambda=1.54178$ Å). The operation voltage was maintained at 40 kV and current at 200 mA, respectively. The X-ray photoelectron spectroscopy (XPS) was carried out on a PerkinElmer RBD upgraded PHI-5000C ESCA system. A Shimadzu spectrophotometer (Model 2501 PC) was used to record the UV–vis diffuse reflectance spectra of the samples in the region of 200 to 800 nm. The electron paramagnetic resonance (EPR) spectra were recorded on a JEOL JES-FA200 EPR spectrometer (140 K, 9064 MHz, 0.998 mW, X-band).

Synthesis. Heterostructure WO$_{3-x}$/Zn$_{0.3}$Cd$_{0.7}$S was synthesized in simple three steps. In the first hexagonal WO$_3$ nanorods were prepared by hydrothermal reaction. Subsequently calcination in Ar/H$_2$ environment was carried out to results WO$_{3-x}$. Finally Zn$_{0.3}$Cd$_{0.7}$S was introduced to nanorod surface by reaction of Zn$^{2+}$, Cd$^{2+}$ precursors and Na$_2$S in alkali conditions. Detailed synthesis is as follows:

Synthesis of WO$_{3-x}$ Nanorods. WO$_{3-x}$ nanorods were synthesized by adding 0.1 g of Sodium tungstate and 0.05 g of Sodium sulfate in 4 ml of water followed by drop wise addition of 0.5 M HCl to adjust the pH value of the solution to 2.0. Then, the solution was poured into Teflon-lined stainless steel autoclave and heated 190°C for 24 h. After cooling down the autoclave, the products was obtained by centrifugation and washed thoroughly with...
water, ethanol and dried at 60 °C. The centrifuge material was further treated for calcinations in a furnace for 2 h at 350 °C in Ar/H2 environment (10 mL min⁻¹) with heating rate of 5 °C min⁻¹. The final product obtained was further used for characterizations, heterostructure synthesis and applications. The synthesis of WO3 nanorods was same except the calcinations process.

**Synthesis of WO3-Zn0.3Cd0.7S Heterostructure.** In a typical synthesis, 50 mg WO3 nanorods were dispersed in 100 mL of distilled water, then a certain amount of Zn(CH3COO)2·2H2O and Cd(CH3COO)2·2H2O were added and pH of the solution was adjusted to 7.4 using 0.1 M sodium hydroxide. After 10–15 minutes, aqueous solution of sodium sulfide (Na2S·9H2O) was drop wise added into above solution. The resultant mixture was stirred at room temperature for 24 h. The obtained powders were washed with water and ethanol and dried in oven at 60 °C. The Synthesis of WO3/Zn0.3Cd0.7S heterostructure was same and bare Zn0.3Cd0.7S nanoparticles were also prepared following the same procedure except the use of WO3 nanorods. The optimum ratio of WO3, WO3–x, Zn0.3Cd0.7S in WO3/Zn0.3Cd0.7S, and WO3–x/Zn0.3Cd0.7S heterostructure was obtained to be 1:1.2 and 1:1.2, respectively.

**Photocatalytic reaction.** The photocatalytic H2 evolution from water splitting was performed in a vacuumed, gas–closed circulation system using 300 W Xe lamp equipped with a λ ≥ 420 nm cut–off filter. The average light intensity was 2.84 mW/cm². In a typical procedure, 100 mg of catalyst was dispersed in 100 mL water containing 0.1 M Na2S and 0.1 M Na2SO3. The on–line gas chromatography (Agilent, 6820, TCD detector, N2 carrier) was used to determine the amount of hydrogen evolved and compared with other samples. The photocatalytic O2 production performed vacuumed, gas–closed circulation system in 5 mM KIO3 solution using 300 W Xe lamp equipped with a λ ≥ 420 nm cut–off filter. The on–line gas chromatography (Agilent, 6820, TCD detector, N2 carrier) was used to determine the amount of oxygen evolved.

**Quantum efficiency measurement.** Apparent quantum yields (AQYs) were determined using a 420 nm band pass filter. The number of incident photons from the Xenon lamp were measured with a power meter (1831-R, Newport). Apparent quantum yields (AQYs) were calculated by the following equation:

\[
AQY(\%) = \frac{2 \times \text{The number of evolved H}_2 \text{ molecules}}{\text{The number of incident photons}} \times 100
\]

**Electrochemical and Photo-electrochemical measurements.** Electrochemical and photoelectrochemical measurements were conducted in 0.1 M Na2SO4 electrolyte solution with a three-electrode quartz cell. Ag/AgCl was used as reference electrode while platinum wire was used as counter electrode and catalysts film electrodes on Ti foil worked as working electrode. The catalysts films were prepared by dropping catalyst suspension (10 mg mL⁻¹ in ethanol) onto Ti foil by following doctor-blade coating method with a glass rod and scotch tape and resultant electrodes were annealed for 12 h at 90 °C. For the measurements, the electrodes were pressed against an electrochemical cell with a working area of 4.0 cm². Photo-electrochemical test systems were composed of a CHI 660B electrochemistry potentiostat (Shanghai Chenhui Limited, China).

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Author Contributions
M.I. and A.B.Y. conceived the idea of the synthesis method and performed the synthesis, measurement and characterizations. S.J.Z. evaluated data. P.K. evaluated data and revised the manuscript. M.I. wrote the first version of the manuscript and all authors discussed the results and contributed to the final version of the paper.

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