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1 Amorphous TiO₂ Coated Hierarchical WO₃ Nanosheet/CdS Nanorod Arrays for
2 Improved Photoelectrochemical Performance
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33 **Abstract**
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36 This work demonstrates hierarchical WO₃ nanosheet/CdS nanorod (WO₃-NS/CdS-NR)
37 arrays as a type-II heterojunction photoanode for improved photoelectrochemical
38 (PEC) water splitting. Due to the synergistic effect of different constituents in the
39 novel hierarchical structure, WO₃-NS/CdS-NR arrays as a photoanode yield a
40 photocurrent density of 5.4 mA cm⁻² at 0.8 V versus reversible hydrogen electrode for
41 sulfite oxidation. This is 12 times that of WO₃-NS arrays (0.45 mA cm⁻²) and 3 times
42 that of CdS-NR arrays (1.85 mA cm⁻²). In this hybrid WO₃-NS/CdS-NR arrays
43 photoanode, the favorable heterojunction between WO₃ and CdS enhances the charge
44 separation efficiency and widens the light absorption spectrum. Furthermore, the
45 optimization of the loading amount and size of CdS-NRs allows for a larger specific
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1 surface area as well as more effective light scattering, which further improves the
2 PEC performance of WO₃-NS/CdS-NR arrays. Finally, the coating of an ultrathin
3 layer of amorphous TiO₂ also enhances the photostability of WO₃-NS/CdS-NR arrays.

4 Keywords: Photoanode, CdS nanorod, WO₃ nanosheet, Hierarchical structure

6 1. Introduction

7 Photoelectrochemical (PEC) water splitting allows the direct conversion of solar
8 energy into renewable hydrogen fuel. Since hydrogen is considered an
9 environmentally-friendly and storable energy carrier, PEC water splitting has become
10 one of the most promising methods for tackling global warming and energy shortage
11 [1-3]. In a PEC device, the photoanode is responsible for oxygen evolution while the
12 photocathode is responsible for hydrogen generation [4]. Efforts have mostly been
13 devoted to the fabrication of efficient photoanodes for the complex oxygen evolution
14 process [5]. To date, various semiconductors, such as Fe₂O₃ [6], BiVO₄ [7], TiO₂ [8],
15 WO₃ [9], and CdS [10], have been investigated as photoanode materials. However,
16 none of these materials can simultaneously fulfill all the requirements for an ideal
17 photoanode in terms of efficient visible light absorption, suitable band edge position,
18 high photo-stability, large electrical conductivity and hole diffusion length [11, 12].
19 Several techniques, such as the development of novel nanostructure [13],
20 heterojunction engineering [14], have thus been proposed to enhance PEC
21 performance.

22 Among these materials, CdS with a direct band gap of 2.4 eV has attracted much
23 attention in PEC water splitting applications for its efficient visible light absorption

1 and favorable band edge position [15, 16]. Various CdS nanostructures, such as CdS
2 quantum dots (QDs) [17, 18], CdS nanosheets (NSs) [19], and CdS nanorods (NRs)
3 [20], have been used to fabricate different photoanodes. Owing to the direct electron
4 transport pathways, large specific surface area, and short hole transfer path length,
5 CdS-NRs have recently been reported for their better PEC performance than other
6 CdS nanostructures [21, 22]. However, the self-oxidation of CdS by photogenerated
7 holes and low light scattering ability of pristine CdS-NR arrays still posed a
8 significant challenge in the production of highly efficient CdS-NRs based
9 photoanodes [23, 24]. To tackle these problems, CdS-NRs-based heterojunctions,
10 such as CdS-NRs/Cu₂O p-n heterojunctions [21] and CdS-NRs/SnS_x nanosheets
11 heterojunction [25], were reported to have enhanced charge separation efficiency. In
12 addition, some well-designed CdS-NRs-based nanostructures, such as CdS-NRs@
13 SnO₂ nanobowl arrays [23], were proposed to increase the light scattering ability.
14 Recently, passivation layer with the ability to reduce surface defect states and mitigate
15 the photocorrosion of semiconductors have attracted much attention.[26] Studies on
16 the combination of the passivation layer with novel CdS-NRs-based nanostructures
17 could provide the necessary insight into concurrently achieving efficient light
18 absorption, enhanced charge separation efficiency and prolonged photostability. WO₃
19 is one of the most promising semiconductors for fabrication of type II heterojunctions
20 when combined with other semiconductors, such as BiVO₄ [27], Fe₂O₃ [28], and
21 Bi₂S₃ [29], due to its superior electron transport properties and high photostability. In
22 WO₃-based type II heterojunctions, WO₃ not only enables accelerated charge
23 separation and thus suppresses the internal charge recombination, but also plays the
24 role of an electron conductor for quick transfer of photogenerated electrons to the

1 conductive substrate [30-32]. The WO_3/CdS heterostructures in the form of WO_3 -
2 nanowires/ CdS -film [33], platelike $\text{WO}_3/\text{TiO}_2/\text{CdS}$ -QDs [34], platelike
3 $\text{WO}_3/\text{CdWO}_4/\text{CdS}$ -QDs [35], and WO_3/CdS -QDs [36], have also been investigated
4 for potential applications as photoanodes. However, the combination of WO_3 and
5 CdS -NRs as a heterojunction photoanode, which has the potential to further enhance
6 PEC performance due to the superior characteristics of CdS -NRs, has yet to be
7 investigated.

8 Recently, the nanosheet/nanorod (NS/NR) hierarchical structure has been utilized in
9 the fabrication of various heterojunction photoanodes. This hierarchical structure has
10 high light utilization efficiency and large effective surface area, which are both
11 beneficial for the improvement of the PEC efficiency [37, 38]. Thus, in this work, we
12 developed WO_3 -NS/ CdS -NR arrays as a novel type II heterojunction photoanode for
13 efficient PEC water splitting, which showed a higher photocurrent than pristine CdS -
14 NR arrays and WO_3 -NS arrays. The enhanced photocurrent can be ascribed to the
15 enhanced charge separation efficiency due to the strong electrons collection by WO_3
16 and the formation of a heterojunction between CdS and WO_3 . The high specific
17 surface area and effective light scattering due to the well-designed NR/NS
18 nanostructure also contributed to the improved PEC performance. The photostability
19 of the WO_3 -NS/ CdS -NR arrays was further improved by an ultrathin layer of
20 amorphous TiO_2 .

21 **2. Experimental section**

22 *2.1. Materials*

23 Fluorine-doped tin oxide (FTO) substrates were purchased from USA Pilkington
24 (Model: Tec-7, $8 \Omega \text{ sq}^{-1}$). Tungstic acid (H_2WO_4), poly(vinyl alcohol) (PVA), oxalic

1 acid, acetonitrile, cadmium nitrate, glutathione, thiourea, urea, and hydrochloric acid
2 were obtained from Sigma-Aldrich. Hydrogen peroxide (H_2O_2) was acquired from
3 VWR International.

4 *2.2. Fabrication of WO_3 -NS arrays*

5 WO_3 -NS arrays on FTO glass substrate were prepared according to previous reports,
6 which involves the preparation of WO_3 seed layer and hydrothermal growth of WO_3 -
7 NS arrays [39]. Three solutions were prepared and then labeled as solution A, B, and
8 C. Solution A was prepared with H_2WO_4 (1.25 g), PVA (0.5 g) and H_2O_2 (20 mL) and
9 stirred at 80 °C for 1 h. Solution B was prepared with H_2WO_4 (1.25 g), H_2O_2 (17 mL)
10 and deionized (DI) water (25 mL). After stirring at 90 °C for 1 h, more DI water was
11 then added to dilute the solution to make up a volume of 100 mL. Solution C was
12 prepared with oxalic acid (20 mg), urea (20 mg), solution B (3 ml), HCl (0.5 mL, 6 M)
13 and acetonitrile (12.5 mL).

14 WO_3 seed layer was coated onto a clean FTO glass substrate by spin-coating. 100 μL
15 of solution A was dropped on the FTO glass and spun at 500 rpm for 2 min. This
16 process was repeated once more before annealing at 500 °C for 2 h in the air.

17 WO_3 -NS arrays were fabricated on the WO_3 seed layer by a hydrothermal reaction.
18 Solution C was first added into a Teflon-lined stainless autoclave (45 mL, Parr). Then,
19 a piece of FTO glass coated with WO_3 seed layer was put into solution C with the
20 seed layer facing down. Finally, the autoclave was placed in the oven at 180 °C for 2
21 h, followed by a post-heat treatment at 500 °C in air for 2 h.

22 *2.3. Fabrication of WO_3 -NS/CdS-NR arrays*

23 CdS-NRs were grown on the surface of WO_3 -NS arrays by a hydrothermal reaction.

1 The precursor solution, which is composed of cadmium nitrate (69 mg), thiourea (17
2 mg), glutathione (41 mg) and DI water (15 ml), was first added into a Teflon-lined
3 stainless autoclave (23 mL, Parr). Then, a piece of FTO glass coated with WO₃-NS
4 arrays was immersed in the precursor with the conductive surface facing down.
5 Finally, the sealed autoclave was placed in an electric oven at 200 °C for 1 to 4 h,
6 followed by annealing at 450 °C for 1h under Ar atmosphere.

7 A reference was prepared using the same method, but the CdS-NRs were grown on
8 pure FTO substrate instead.

9 *2.4. Fabrication of WO₃-NS/CdS-NR arrays/amorphous TiO₂*

10 A customized atomic layer deposition (ALD) system was utilized for the deposition of
11 a thin film of TiO₂ on the surface of WO₃-NS/CdS-NR arrays at 80 °C [40]. DI water
12 and titanium tetrachloride (TiCl₄) were utilized as the oxygen and titanium precursors,
13 respectively. In each ALD cycle, TiCl₄ pulse, H₂O pulse and purging time were set as
14 0.25 s, 0.06 s, 4 s, respectively. 10, 20, 30 and 40 ALD cycles were performed to
15 deposit different thicknesses of TiO₂ films on the surface of the WO₃-NS/CdS-NR
16 arrays.

17 *2.5. Characterization*

18 Field-emission scanning electron microscope (FESEM, JEOL, JSM 7600F),
19 Transmission electron microscope (TEM, JEOL, 2010) and high-resolution
20 Transmission electron microscope (HRTEM, JEOL, 2010) were used to investigate
21 the morphology and microstructure of the as-prepared samples. X-ray photoelectron
22 spectroscopy (XPS) with a multichannel energy analyzer (SPECS Phoibos 100 MCD-
23 5) and a monochromatic Ma K α source at 1253 eV was used to analyze the

composition and surface chemical state. C 1s (284.5 eV) was used for calibration. X-ray diffraction (XRD) pattern was obtained by using the X-ray diffractometer (Bruker D8). The radiation source is Cu-K α . UV-Vis absorption spectra were measured on a spectrophotometer (Varian, Cary 5000).

2.6. PEC measurements

PEC performance of the as-prepared samples was measured by a testing system consisting of a workstation (Autolab 270), a solar simulator equipped with an air mass 1.5 filter (300W Xe lamp, Newport) and a three-electrode electrochemical cell. The power of the output light was calibrated to 1 sun illumination (air mass 1.5, 100 mW cm⁻²) by a standard Si solar cell. In the three-electrode electrochemical cell, a mixture of 0.25 M Na₂SO₃ and 0.35 M Na₂S was used as the electrolyte. The working electrode is the as-prepared sample. The reference electrode and the counter electrode are Ag/AgCl electrode and platinum mesh, respectively. Electrochemical impedance spectroscopy (EIS) data were measured by the same testing system by applying a bias of 0.8 V versus reversible hydrogen electrode (RHE) over a frequency range from 10⁻¹ to 10⁵ Hz with a 10 mV amplitude.

3. Results and discussion

3.1. Fabrication of the WO₃-NS/CdS-NR arrays

The fabrication process of the WO₃-NS/CdS-NR arrays is illustrated in Figure 1. WO₃-NS arrays were grown on a WO₃ seed layer coated FTO substrate through a hydrothermal reaction. Prior to the growth of the CdS-NRs, a calcination process was performed not only for the crystallization of WO₃ but also for better cohesion between WO₃-NS arrays and FTO substrate, which is crucial to the secondary growth of CdS-

NRs. Subsequently, the direct hydrothermal growth of CdS-NR arrays on WO₃-NS arrays formed a hierarchical structure. The growth mechanism can be explained by the following chemical reactions [41, 42]:

The WO₃ nuclei are obtained by the thermal decomposition of peroxopolytungstic acid (PTA), which act as the growth sites and nucleation for the hydrothermal growth of WO₃-NS arrays under the capping agent of oxalic acid and urea. In the second hydrothermal reaction, CdS nuclei form on the WO₃-NS arrays through the decomposition of the Cd(NO₃)₂·x(NH₂)₂CS complex, which is obtained through the reaction between Cd²⁺ and thiourea. With glutathione-assisted orientation, CdS-NR arrays could be grown on WO₃-NS arrays.

In this hierarchical structure, multiple CdS-NRs are randomly dispersed on both surfaces of a single WO₃-NS. This morphology is beneficial for light absorption due to the multiple light scattering within the structure. In addition, the random dispersion of CdS-NRs on WO₃-NS also prevents the overlapping of CdS-NRs at the bottom, thus giving rise to a greater contact area with the electrolyte for the more efficient redox reaction.

3.2. Morphology analysis

Figure 2a shows a typical SEM image of WO₃-NS arrays. The WO₃-NS arrays are observed to be perpendicular to the FTO substrate, leaving enough space between adjacent nanosheets for the secondary growth of other nanostructures. After a 2 h hydrothermal reaction, CdS-NR arrays were grown on the surface of WO₃-NS arrays. As shown in Figures 2b and 2c, the WO₃-NS arrays are fully covered with small CdS nanocrystals and partially covered with CdS NRs. These CdS-NRs have an average length of 400 nm and a diameter of 50 nm. After the growth of CdS-NRs, the surface area of the single WO₃ NS increases by 1.6 times. The calculation is shown in the supplementary materials (Part III). Figure 2c shows that these CdS-NRs were grown on both sides of single WO₃ NS in random orientations, instead of simply stacking on the surface. In the hydrothermal growth process, CdS seeds were first formed on the surface, followed by the epitaxial growth of CdS-NRs.[23] The direct contact of CdS with WO₃ is beneficial for the transfer of electrons between them. Energy dispersive X-ray Spectroscopy (EDS) was performed to characterize the elemental composition of the as-prepared WO₃-NS/CdS-NR arrays, as shown in Figure S1. The EDS results show the presence of elements Sn, O, W, Cd and S in the samples. The transition from WO₃-NS arrays to WO₃-NS/CdS-NR arrays can also be observed through the color change (Figure S2). The bare WO₃-NS arrays are white and translucent. Upon the growth of CdS-NRs, the color of WO₃-NS/CdS-NR arrays became light yellow. Figure 2d shows the cross-section SEM image of WO₃-NS/CdS-NR arrays. It can be observed that the sheet-like structure of WO₃ is well maintained with CdS-NRs dispersed on both the upper and bottom surfaces. To investigate the growth process of CdS-NRs on WO₃-NS arrays, the hydrothermal reaction was carried out over different durations. After 1 h of hydrothermal growth, CdS-NRs with smaller lengths were obtained, as shown in Figure 2e. By extending the reaction time to 3 h, both the

loading amount and the length of the CdS-NRs increased sharply. In some areas, the density of CdS-NRs is so high that flower-like structures can be observed (Figure 2f and Figure S3), which fully cover the sheet-like structure of WO₃-NS arrays. The further increment of the reaction time to 4 h led to the peeling of a large area of nanostructures off the FTO substrate after rinsing with DI water. The corresponding optical image is shown in Figure S4a. SEM was utilized to observe the remaining parts of the sample and more flower-like CdS-NRs were obtained on the surface (Figure S4b). Due to the excessive loading of CdS-NRs, the adhesion between WO₃-NS arrays and FTO substrate is insufficient to support a large amount of CdS-NRs, which may cause the nanostructures to peel off from the FTO substrates. This phenomenon demonstrates that CdS-NRs cannot be continuously loaded by prolonging the hydrothermal growth durations.

3.3. XRD and XPS analysis

Figure 3a shows the XRD patterns of WO₃-NS/CdS-NR arrays, WO₃-NS arrays, CdS-NR arrays, and FTO substrate. For the WO₃-NS arrays and CdS-NR arrays, except for some peaks of the FTO substrate, all other peaks can be well indexed to the monoclinic phase of WO₃ and the wurtzite phase of CdS [39, 43]. In the case of WO₃-NS/CdS-NR arrays, the peaks corresponding to WO₃, CdS, and FTO can be distinguished, as marked in Figure 3a. XPS spectra were applied to further analyze the composition and surface chemical state of WO₃-NS/CdS-NR arrays. As shown in Figure S5, the XPS survey spectrum demonstrates that the WO₃-NS/CdS-NR arrays contain Cd, S, W and O elements. Figures 3b-3e further show the high-resolution XPS spectrum of WO₃-NS/CdS-NR arrays. The peaks at W 4d_{7/2} (34.8 eV), W 3d_{3/2} (37.2 eV) and O 1s (531.2 eV) are assigned to W⁶⁺ and O²⁻ in WO₃, respectively, while the

peaks at Cd 3d_{5/2} (404.7 eV), Cd 3d_{3/2} (411.4 eV) and S 2p_{3/2} (161.2 eV), S 2p_{1/2} (162.5 eV) can be assigned to Cd²⁺ and S²⁻ in CdS respectively [21, 36]. These observations from both XRD and XPS indicate that the heterostructures with high purity had been successfully synthesized.

3.4. UV-Vis absorption spectra analysis

Figure 3f shows UV-Vis absorption spectra of WO₃-NS arrays, CdS-NR arrays and WO₃-NS/CdS-NR arrays. The pristine WO₃-NS arrays have an absorption edge at around 440 nm, showing poor visible light absorption. Upon the growth of CdS-NR arrays, the visible light absorption is greatly enhanced with the absorption edge shifting to 540 nm. As shown in the Figure S6, the band gap (E_g) of WO₃-NS arrays, CdS-NR arrays and WO₃-NS/CdS-NR arrays are 2.72 eV, 2.34 eV and 2.31 eV respectively, as calculated with the following equation [33]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (5)$$

In this equation, A is a constant, α presents the absorption coefficient and $h\nu$ is the light energy. WO₃ has an indirect E_g, while CdS has a direct E_g, so the value of n is 1/2 and 2, respectively. This enhanced visible light absorption is essential to the improvement of PEC efficiency of WO₃-NS/CdS-NR arrays as it allows the generation of more electron-hole pairs.

3.5. PEC performance

The measuring of linear sweep curves under front-side illumination is used to evaluate the photocurrent of the as-prepared samples with Na₂S/Na₂SO₃ mix solution as an efficient hole scavenger. Due to the fast oxidation kinetics of sulfite, this hole scavenger can prevent the oxidation of CdS and bring about a near 100% of surface

1 charge transfer efficiency. Thus, the sulfite oxidation allows the investigation of
2 charge separation efficiency in the heterostructures. As shown in Figure 4a, the
3 pristine WO₃-NS arrays and CdS-NR arrays show photocurrents of 0.45 mA cm⁻² and
4 1.85 mA cm⁻² at 0.8 V versus RHE respectively, which are comparable to previously
5 reported values [23, 39]. After the 2 h hydrothermal growth of CdS-NRs on the
6 surface of WO₃-NS arrays, the resultant WO₃-NS/CdS-NR arrays showed a
7 significant increase in the photocurrent to 5.4 mA cm⁻² at the same applied voltage,
8 which is approximately 12 times that of WO₃-NS arrays and 3 times that of the CdS-
9 NR arrays. The dark current density of these photoanodes is negligible between 0 V
10 and 1.4 V versus RHE, attesting that these currents were produced by light
11 illumination. It can also be observed that the onset potential of these three
12 photoanodes is different. WO₃-NS arrays electrode has the highest onset potential of
13 0.45 V versus RHE. After the growth of CdS-NRs, the onset potential of WO₃-
14 NS/CdS-NR arrays electrode decreases to -0.05 V versus RHE due to the formation of
15 a heterojunction between WO₃ and CdS, which is close to that of the pristine CdS-NR
16 arrays (-0.1 V versus RHE). The negative shift of onset potential can be ascribed to
17 the enhanced charge separation efficiency [44]. The Incident-photon-to-current-
18 conversion efficiency (IPCE) tests showed that WO₃-NS/CdS-NR arrays have higher
19 IPCE maximum (55%) in the wavelength between 300-550 nm compared to that of
20 CdS-NR arrays (20%) and WO₃-NS arrays (10%), as shown in the supplementary
21 material (Part IV).

22 Figure 4b further shows the linear sweep curves of the WO₃-NS/CdS-NR arrays, CdS-
23 NRs arrays, and WO₃-NS arrays electrodes with light ON/OFF cycles. The current
24 density of these photoanodes increases with larger applied voltage and WO₃-NS/CdS-

NR arrays show the higher photocurrent density compared to WO₃-NS arrays and CdS-NR arrays, which complies with Figure 4a. Compared with bare WO₃-NS arrays, the improved PEC performance of WO₃-NS/CdS-NR arrays, to some extent, can be ascribed to the extended visible light absorption range resulting from the introduction of CdS-NRs, which was reflected in the UV-Vis absorption characterization. The hierarchical structure of WO₃-NS/CdS-NR arrays also contributes to the improvement of their PEC performance. Compared to pristine CdS-NR arrays, NS/NR hierarchical structure ensures large light scattering within the whole structure and provides a higher surface area of contact with the electrolyte. In addition, the formation of a heterojunction between CdS and WO₃ accelerates the charge separation process, thus leading to the improvement of PEC performance of the hierarchical arrays. The calculation and comparison of charge separation efficiency of CdS-NR arrays and WO₃-NS/CdS-NR arrays are shown in the supplementary material (Part V). WO₃-NS/CdS-NR arrays show a higher charge separation efficiency (78.2%) than CdS-NR arrays (20.8%) at 0.8 V versus RHE. Due to this hierarchical structure, the as-prepared WO₃-NS/CdS-NR arrays showed a higher photocurrent compared to other reported WO₃/CdS heterostructures, as shown in Table S1.

To further investigate the effect of the loading amount as well as the size of CdS-NRs on the PEC performance of the hierarchical arrays, the hydrothermal growth durations of CdS-NRs were varied. Only samples prepared with hydrothermal reactions between 1-3 h were investigated since previous SEM and optical characterizations had shown that longer hydrothermal growth durations of CdS-NRs would destroy the WO₃-NS arrays. The photocurrent of the as-prepared samples is shown in Figure 4c. WO₃-NS/CdS-NR arrays-2h show higher photocurrent density (5.4 mA cm⁻²) than

1 WO₃-NS/CdS-NR arrays-1h (3.6 mA cm⁻²) and WO₃-NS/CdS-NR arrays-3h (5.0 mA
 2 cm⁻²) at 0.8 V versus RHE. The change of photocurrent can be ascribed to the
 3 variation of loading amount and length of the CdS-NRs, as reflected by SEM
 4 characterization. Compared to 1 h hydrothermal growth, the prolonged hydrothermal
 5 growth duration to 2 h resulted in the loading of longer CdS-NRs at a higher quantity.
 6 The increment in loading amount and length improve light absorption and provide a
 7 larger specific surface area, which in turn increases the photocurrent. However,
 8 further increase of hydrothermal growth duration to 3 h caused the photocurrent
 9 density to be lowered despite more CdS-NRs grown on the WO₃-NR arrays. This
 10 decrease is attributed to the formation of the flower-like structures on the top surface
 11 of WO₃-NR arrays which had covered the NR/NS hierarchical structures. Unlike the
 12 close contact between CdS-NRs and WO₃-NR in the NR/NS hierarchical structures,
 13 the photogenerated electrons in flower-like CdS-NR arrays were not able to transfer
 14 as quickly to the WO₃-NRs, which resulted in larger charge recombination rate and
 15 thus a lower the photocurrent.

16 *3.6. EIS analysis and charge transfer mechanism*

17 To investigate the charge separation and recombination dynamics of the as-prepared
 18 electrodes, EIS measurements were performed under light illumination. The middle
 19 frequency (1-10⁵ Hz) semicircular diameter in the Nyquist plots can reflect charge
 20 transfer at the electrolyte/photoanode interface [45]. As shown in Figure 4d, WO₃-
 21 NS/CdS-NR arrays electrode presents a smaller semicircular diameter in the Nyquist
 22 plots than pristine WO₃-NS arrays and CdS-NR arrays, indicating the facilitated
 23 interface charge transfer between WO₃-NS and CdS-NR. Furthermore, the equivalent
 24 circuit used to fit the EIS data was also provided in Figure 4d. R_s represents the series

1 resistance, such as the resistance of FTO substrate, while R_{ct} characterizes charge
2 transfer resistance at the electrode/electrolyte interface. The fitting results showed that
3 R_s value of WO_3 -NS/CdS-NR arrays (37.6 Ω) was similar to that of WO_3 -NS arrays
4 (32.8 Ω) and CdS-NR arrays (31.4 Ω), while the R_{ct} value of WO_3 -NS/CdS-NR
5 (593.9 Ω) arrays was much smaller than that of WO_3 -NS (9311 Ω) and CdS-NR
6 (1092 Ω). The smallest R_{ct} confirmed the WO_3 -NS/CdS-NR arrays could facilitate
7 charge separation and transportation.

8 The formation of a heterojunction and the PEC water splitting process in the WO_3 -
9 NS/CdS-NR arrays are schematically illustrated in Figure 5. Due to the well-matched
10 band edge position, a type-II heterojunction forms upon the contact of CdS with WO_3 .
11 Electrons generated in the conduction band (CB) of CdS transfer to the lower CB of
12 WO_3 , while holes transfer from lower valence band (VB) of WO_3 to higher VB of
13 CdS for the sulfite oxidation. In this way, the recombination rate of photogenerated
14 carriers is depressed. In addition to the formation of type-II heterojunction, the high
15 conductivity of WO_3 ensures effective charge collection and thus lowers the bulk
16 charge recombination rate. The detailed charge separation process in the PEC device
17 is shown in Figure 5 b. In pristine CdS-NR arrays, the photogenerated electrons can
18 only transfer to FTO substrate through the less conductive CdS-NRs before
19 transferring to the FTO substrate. Hence there are more chances for charge
20 recombination. When CdS-NRs are grown on the highly conductive WO_3 -NS,
21 electrons generated in the CdS can be transferred to FTO substrate with the assistant
22 of conductive WO_3 skeleton, and finally, reach to the Pt electrode for the generation
23 of hydrogen. These factors result in improved PEC performance of WO_3 -NS/CdS-NR
24 arrays compared to that of WO_3 -NS arrays and CdS-NR arrays.

3.7. PEC stability

It was reported that amorphous TiO_2 films by ALD could mitigate photocorrosion of CdS-based photoanodes as well as act as a passivation layer to suppress surface charge recombination [46]. Thus, an ultrathin layer of amorphous TiO_2 films was deposited on WO_3 -NS/CdS-NR arrays to increase the photo-stability. EDS result is shown in Figure S7, proving the presence of elements Sn, O, W, Cd, S and Ti. Representative TEM images of WO_3 -NS/CdS-NR arrays/ TiO_2 are shown in Figure 6 (a) and 6 (b). As shown in Figure 6 (a), the morphologies of CdS-NR and WO_3 -NS can be clearly distinguished. The inset of Figure 6 (a) is the HRTEM image of WO_3 NS. The d-spacing of 0.365 nm can be ascribed to (200) plan of WO_3 . Figure 6 (b) shows a single CdS NR coated with a thin TiO_2 layer. The boundary between lattice fringes of CdS and amorphous TiO_2 was marked with a red dash line. The thickness of the TiO_2 film is around 2 nm. The inset image shows clear lattice fringes with a d-spacing of 0.34 nm, which corresponds to (002) plan of CdS. As shown in Figure 6 (c), the photocurrent of WO_3 -NS/CdS-NR arrays/ TiO_2 -10 cycles is comparable to that of the uncoated WO_3 -NS/CdS-NR arrays. With the deposition of more TiO_2 , WO_3 -NS/CdS-NR arrays/ TiO_2 -20 cycles showed a slightly higher photocurrent than that of pure WO_3 -NS/CdS-NR arrays at lower applied potentials. However, the further deposition of TiO_2 causes the decrease of the photocurrent of WO_3 -NS/CdS-NR arrays/ TiO_2 -30 cycles and WO_3 -NS/CdS-NR arrays/ TiO_2 -40 cycles. In the ALD process, the thickness of TiO_2 films increases linearly with the number of ALD cycles [47]. The amorphous TiO_2 acts as a protective layer as well as a passivation layer. When 10 and 20 ALD cycles were performed, the amorphous TiO_2 layer produced is so thin that some pinholes exist, providing channels for holes transfer from CdS to the

1 electrolyte. In addition, amorphous TiO_2 can passivate the surface state on the CdS-
2 NR arrays, thus reducing charge recombination probability. At this point, the
3 photocurrent increases with the increase of ALD cycles. However, the further increase
4 of ALD cycles brings about a thicker TiO_2 layer on the surface of CdS. The thick
5 TiO_2 layer takes on the role of a tunneling barrier rather than a passivation layer,
6 which prevents the transfer of holes from the CdS to the electrolyte [48]. Thus, the
7 photocurrent decreases when 30 and 40 ALD cycles were performed. Figure 6(d)
8 shows the photostability test results of WO_3 -NS/CdS-NR arrays/ TiO_2 -20 cycles and
9 WO_3 -NS/CdS-NR arrays. After 1 hour of light illumination, the photocurrent density
10 of WO_3 -NS/CdS-NR arrays/ TiO_2 -20 cycles decreased from 4.7 mA cm^{-2} to 4.6 mA
11 cm^{-2} at 0.5 V versus RHE, while the photocurrent density of pure WO_3 -NS/CdS-NR
12 arrays dropped from 4.5 mA cm^{-2} to 4 mA cm^{-2} . After the photostability test, SEM
13 and XRD results show that there is no obvious change in the morphology and phase
14 of WO_3 -NS/CdS-NR arrays/ TiO_2 -20 cycles, as shown in Figure S8. The enhanced
15 photostability of WO_3 -NS/CdS-NR arrays/ TiO_2 -20 cycles could be ascribed to the
16 deposition of amorphous TiO_2 layer, which prevents direct contact between CdS and
17 the electrolyte. In addition, the TiO_2 layer can capture and store holes generated by
18 CdS and thus reduce the photocorrosion [49].

19 **4. Conclusion**

20 In summary, a type-II WO_3 /CdS heterojunction with a hierarchical structure has been
21 presented as a photoanode for PEC water splitting. Through the optimization of
22 hydrothermal growth of CdS-NRs, the as-prepared WO_3 -NS/CdS-NR arrays
23 demonstrated enhanced PEC performance compared to pristine WO_3 -NR arrays and
24 CdS-NR arrays. This improvement can be ascribed to the broader light absorption

1 spectrum, the depressed charge recombination rate due to the heterojunction between
2 CdS and WO₃, as well as the high charge collection ability of WO₃. The hierarchical
3 structure also enables better light scattering ability and provides a higher specific
4 surface area to the as-prepared photoanode. In addition, an ultrathin layer of
5 amorphous TiO₂ layer has been applied as a protection layer to enhance the
6 photostability of WO₃-NS/CdS-NR arrays. This work indicates that the construction
7 of a hierarchical nanostructure with the combination of a highly conductive skeleton,
8 favorable heterojunction and efficient light absorption is an effective route for
9 improving PEC performance of a photoanode.

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2 Figure 1 Schematic diagram for the fabrication of $\text{WO}_3\text{-NS/CdS-NR}$ arrays.

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2 Figure 2 Top-view SEM images: (a) WO_3 -NS arrays, (b)-(c) WO_3 -NS/CdS-NR arrays
 3 with 2 h hydrothermal growth of CdS-NRs. (d) Cross-section view SEM image of
 4 WO_3 -NS/CdS-NR arrays. Top-view SEM images: (e) WO_3 -NS/CdS-NR arrays with
 5 1h hydrothermal growth of CdS-NRs, (f) WO_3 -NS/CdS-NR arrays with 3 h
 6 hydrothermal growth of CdS-NRs.

7

1

2 Figure 3 (a) XRD characterization of the as-prepared samples. High resolution XPS
 3 spectrum of WO₃-NS/CdS-NR arrays: (b) W 4f, (c) O 1s, (d) Cd 3d, (e) S 2p. (f) UV-
 4 Vis absorption spectra of WO₃-NS arrays, CdS-NR arrays, and WO₃-NS/CdS-NR
 5 arrays.

Figure 4 (a) Linear sweep curves of $\text{WO}_3\text{-NS}$ arrays, CdS-NR arrays, and $\text{WO}_3\text{-NS/CdS-NR}$ arrays. (b) Linear sweep curves of $\text{WO}_3\text{-NS}$ arrays, CdS-NR arrays, and $\text{WO}_3\text{-NS/CdS-NR}$ arrays with the light on/off cycles. (c) Linear sweep curves of $\text{WO}_3\text{-NS/CdS-NR}$ arrays with different hydrothermal growth durations of CdS-NRs. (d) EIS Nyquist plots of $\text{WO}_3\text{-NS}$ arrays, CdS-NR arrays, and $\text{WO}_3\text{-NS/CdS-NR}$ arrays. Inset in (d) shows the equivalent circuit.

Figure 5 (a) Schematic of the formation of a type-II heterojunction between CdS and WO₃. (b) Schematic of the PEC water splitting process in WO₃-NS/CdS-NR arrays photoanode.

Figure 6 (a) TEM image of WO₃-NS/CdS-NR arrays/TiO₂-20 cycles. The inset is the HRTEM image of WO₃-NS. (b) TEM image of single CdS-NR coated with 20 ALD cycles of TiO₂. The inset is the HRTEM image of CdS-NR. (c) Linear sweep curves of WO₃-NS/CdS-NR arrays with different ALD cycles of TiO₂. (d) Photostability test of WO₃-NS/CdS-NR arrays and WO₃-NS/CdS-NR arrays/TiO₂-20 cycles.

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