Facile Construction of Dual p–n Junctions in CdS/Cu$_2$O/ZnO Photoanode with Enhanced Charge Carrier Separation and Transfer Ability

Pan-Yong Kuang,† Xing-Jun Zheng,† Jia Lin,† Xian-Biao Huang,† Nan Li,† Xin Li,‡ and Zhao-Qing Liu†‡

†School of Chemistry and Chemical Engineering/Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, Guangzhou University, Guangzhou 510006, P. R. China
‡College of materials and energy, Key Laboratory of Energy Plants Resource and Utilization, Ministry of Agriculture, Key Laboratory of Biomass Energy of Guangdong Regular Higher Education Institutions, South China Agricultural University, Guangzhou 510642, P. R. China

ABSTRACT: With the gradually increasing demand for solving the environmental pollution problem and energy crisis, efficient photocatalysts with superior charge carrier separation and transfer ability have attracted extensive research attention. Herein, n-type CdS-decorated p-Cu$_2$O/n-ZnO nanorod arrays (CdS/Cu$_2$O/ZnO NRAs), integrating the merits of both highly ordered structure and synergistic effect derived from dual p–n junctions, were successfully fabricated and further applied to photoelectrocatalysis. In this ternary nanocomposite, fast generation, separation, and transfer of charge carriers were achieved in the Cu$_2$O/ZnO and Cu$_2$O/CdS dual p–n junction regions due to their built-in electric field and appropriate band structures. Moreover, both highly ordered ZnO NRAs and compact CdS shell play the role of an electron collector and a transport channel that efficiently consumes the photoinduced electrons in the conduction band of Cu$_2$O, which considerably reduces the recombination rate of charge carriers. As expected, the perfect cooperation of the three participators leads to the highest photoconversion efficiency of 6.1% at −0.275 V (versus saturated calomel electrode) and an incident photon-to-current conversion efficiency of 14.5% at 380 nm as well as the photoelectrocatalytic degradation ability of the optimized 30 min CdS/Cu$_2$O/ZnO NRAs photoanode as compared to that of the Cu$_2$O/ZnO and ZnO NRAs photoanodes. It is believed that the induced synergistic effect between dual p–n junctions and ZnO NRAs caused the superior performances of the CdS/Cu$_2$O/ZnO NRAs photoanode, and this ternary material with a unique structure may present a new way of thinking for potential applications in the photoelectrochemistry field.

INTRODUCTION

Highly efficient charge carrier separation and transfer are of critical importance for photocatalytic efficiency in a semiconductor material, yet it is hard to achieve in the case of a single semiconductor due to the serious recombination rate of charge carriers and photocorrosion. Therefore, one of the focuses in the recent photocatalytic technology is the construction of single semiconductor-based heterostructured materials to reduce the charge carrier recombination and promote the photocatalytic activity. Noble metal doping to form a metal/semiconductor hybrid with an Ohmic junction or other semiconductor coupling to form a heterostructure with a Schottky junction is quite beneficial for the separation of charge carriers due to the role of the noble metal as an electron sink in the former case or the development of an internal self-built electric field, which provides enough space charge layer, in the latter case.\(^1,^2\) Notably, the rational design and synthesis of a heterostructure composed of n-type and p-type semiconductors are a feasible strategy to solve this issue.\(^3\) The formed p–n junction with a depletion layer in the interfacial region subsequently induces an internal self-built electric field, then promotes the separation efficiency of charge carriers and boosts the photocatalytic activity.\(^4\) In addition, the p–n junction can accurately and effectively dominate the separation distance, transfer direction, and restrain the recombination rate of charge carriers.\(^5\) Fully taking advantages of the superiority in charge carrier separation and transfer, lots of p–n heterojunctions, such as p-MoS$_2$/n-rGO,\(^6\) p-LaFeO$_3$/n-Fe$_2$O$_3$,\(^7\) p-BiOI/n-ZnO,\(^8\) and so forth, have been successfully manufactured, and as expected exhibited enhanced photoelectrochemical water-splitting performance and photocatalytic activity as compared to those of the single semiconductor.
Among various n-type semiconductors, wide band gap zinc oxide (ZnO), especially with highly ordered one-dimensional arrays, attracts tremendous research attention due to its remarkable physicochemical properties, such as tunable alignment and morphology, high aspect ratio, deep-level defects, and a relatively large excitation binding energy of 60 meV. These above merits spontaneously lead to the wide application of ZnO in photocatalysis (PC), solar cells, and supercapacitors. Unfortunately, the practical application of ZnO is severely hindered by its wide band gap (∼3.2 eV), which restricts its use to the ultraviolet light region, and the high recombination rate of charge carriers relentlessly causes poor photocatalytic activity. Therefore, it is still a challenging task to exploit new approaches for improving the visible light absorption ability and photocatalytic activity. Recently, cuprous oxide (Cu2O) has attracted extensive interest toward applications in photoelectrochemical hydrogen production, photovoltaic cells, and solar cells because of its narrow band gap (∼2.2 eV), which matches well the solar visible spectrum. Moreover, as one of the few p-type direct band gap semiconductors, Cu2O has attracted interest as a promising candidate with great application potential in the construction of p–n junctions to serve as an efficient light absorber and photoinduced electron provider. To date, many Cu2O-based p–n heterostructures, such as Cu2O/TiO2, Cu2O/TaON, Cu2O/Fe2O3, and so forth, have been successfully prepared. In these nanomaterials, the space charge layer created by the nanoscale p–n junctions will not only promote the generation but also considerably suppress the recombination rate of charge carriers. It is worth noting that ZnO and Cu2O have a particular relative position of the band gap, where the conduction band minimum of Cu2O lies at a more negative position than that of ZnO; meanwhile, the valence band maximum of ZnO lies at a more positive position than that of Cu2O. The staggered band gap structure of ZnO and Cu2O followed the typical type-II mode, which could cause effective spatial separation and transfer of charge carriers, thus reducing the internal charge recombination and enhancing the photocatalytic activity. Therefore, constructing a Cu2O/ZnO heterostructure would make full use of the merits of the p–n junction and the type-II mode band gap structure to significantly improve the separation and transfer ability and hence result in enhanced photocatalytic performance.

Regrettably, Cu2O usually displays poor photocatalytic activity and could be deactivated by photocorrosion. Furthermore, Cu+ could be easily oxidized to form Cu2+ when Cu2O is exposed to light illumination, and non-negligible charge recombination still exists in Cu2O due to its short minority carrier transport length. So, it is imperative to improve the stability of Cu2O. To overcome this problem, we have introduced CdS, which is stable when exposed to light illumination, and successfully prepared a highly ordered CdS/Cu2O/ZnO NRAs photoanode. As CdS belongs to an n-type semiconductor with a suitable band gap structure, dual p–n junctions (p-Cu2O/n-ZnO and p-Cu2O/n-CdS) were formed in this ternary structure. In this ternary nanocomposite, fast generation, separation, and transfer of charge carriers were achieved in the Cu2O/ZnO and Cu2O/CdS dual p–n junction regions due to their built-in electric field and appropriate band structures. Moreover, both highly ordered ZnO NRAs and compact CdS shell play the role of the electron collector and transport channel that efficiently consumes the photoinduced electrons in the conduction band of Cu2O, which significantly reduces the recombination rate of charge carriers. As a consequence, the introduction of CdS has been proved to be an effective strategy to realize superior photoelectrochemical performance and photocatalytic activity for the CdS/Cu2O/ZnO NRAs photoanode, which can be ascribed to the induced synergistic effect between dual p–n junctions and ZnO NRAs as well as the compact CdS shell layer. Therefore, the fabricated ternary nanomaterial with a unique structure and superior performances may present a new way of thinking for potential applications in the photoelectrochemistry field.

### RESULTS AND DISCUSSION

The phases of the as-prepared samples are examined and the typical XRD patterns are shown in Figure 1. Several strong diffraction peaks corresponding to the hexagonal wurtzite phase of ZnO (JCPDS card no. 36-1451; lattice parameters: \( a = b = 3.25 \alpha, c = 5.21 \AA \)) can be found in all of the samples, indicating the stable existence of ZnO NRAs as a primary supporter to maintain the deposition of Cu2O and CdS, as well as the timely and rapid transfer of photoinduced electrons, thus prolonging the lifetime of charge carriers. For the Cu2O/ZnO pattern, four peaks located at 29.6, 42.4, 61.5, and 73.7° can be well indexed to the (110), (200), (220), and (311) lattice planes of cubic-phase Cu2O (JCPDS card no. 65-3288; lattice parameters: \( a = b = c = 4.26 \AA \)). Furthermore, five peaks located at 24.8, 26.5, 28.2, 43.7, and 51.8° in the CdS/Cu2O/ZnO pattern matches well with the (100), (002), (101), (110), and (112) lattice planes of hexagonal-phase CdS (JCPDS card no.41-1049; lattice parameters: \( a = b = 4.14 \alpha, c = 6.72 \AA \)). The diffraction peaks of Cu2O and CdS are relatively weak compared to those of ZnO due to the continuous growth of the (002) lattice plane along the [001] direction in the ZnO nanorod. Moreover, the sharp and intense diffraction peaks of ZnO, Cu2O, and CdS indicate their good crystalline nature. No traces of other peaks were observed, confirming the high purity of the three products.

Figure 2 shows the morphology and microstructure information of the representative 30 min CdS/Cu2O/ZnO NRAs. The surface morphology was studied using scanning electron microscopy (SEM). As shown in Figure 2a,b, CdS/
Cu₂O/ZnO NRAs were observed to be vertically aligned on the fluorine tin oxide (FTO) substrate with an average diameter of 350−370 nm, which increased by about 50−100 nm than that of the pure ZnO nanorod with a diameter of about 300 nm (see the Supporting Information, Figure S1a, b). Moreover, the surface of the CdS/Cu₂O/ZnO nanorod became rough instead of the hexagonal and smooth surface of the ZnO nanorod. It can be observed that the hexagonal and smooth surface also disappears of Cu₂O/ZnO NRAs, and the average diameter is about 330 nm (Figure S1c, d), which reasonably falls between those of the ZnO and CdS/Cu₂O/ZnO nanorods. Figure 2c shows the transmission electron microscopy (TEM) image of one representative CdS/Cu₂O/ZnO nanorod; the calculated diameter is consistent with that in the SEM images. Figure 2d exhibits the high-resolution TEM (HRTEM) image, the distinct lattice fringe reveals the highly crystalline nature of CdS/Cu₂O/ZnO. The lattice fringe spacing of 0.260 nm can be indexed to the (002) plane of wurtzite-phase ZnO. Moreover, the lattice fringe spacings of 0.213 and 0.207 nm match well with the interplanar distances of the (200) and (110) planes of cubic-phase Cu₂O and hexagonal-phase CdS, respectively. Notably, the interface between each component is quite compact and continuous, which could benefit the spatial vectorial transfer of charge carriers, and achieves superior photoelectrochemical performances. Figure 2e−i shows the element mapping images, including Zn, O, Cu, Cd, and S, which matches well with the EDS spectrum (Figure S2). Furthermore, these elements evenly distribute over the hybrid, further revealing the attainment of the ternary nanocomposite. Meanwhile, the homogeneous distribution of each element also demonstrates the dense and consecutive contact among these components.

To gain more insight into the surface electronic states and compositions of the photoanode, X-ray photoelectron spectroscopy (XPS) measurement was further conducted. Figure 3a presents the XPS survey spectrum of the CdS/Cu₂O/ZnO NRAs photoanode, and the peaks of Zn 2p, Cu 2p, O 1s, Cd 3d, S 2p, and C 1s can be clearly observed. The peak of C 1s came from adsorbed CO₂ on the sample surface or adventitious hydrocarbon from the XPS instrument itself. Figure 3b shows two symmetric peaks at binding energies of 1021.8 and 1044.9 eV assigned to Zn 2p₃/₂ and Zn 2p₁/₂, respectively, indicating the existence of ZnO in the CdS/Cu₂O/ZnO NRAs photoanode.24 The two peaks centered at 932.3 and 952.3 eV shown in Figure 3c are attributed to Cu 2p₃/₂ and Cu 2p₁/₂, respectively, which are characteristic of Cu⁺ in Cu₂O.25 Meanwhile, the characteristic and satellite peaks associated with Cu²⁺ species were not observed, suggesting negligible surface oxidation of Cu₂O/ZnO in the presence of CdS. Besides two strong peaks assigned to Cu⁺ at 932.3 and 952.1 eV, two smaller peaks, located at 934.5 and 954.2 eV, correspond to Cu²⁺ in CuO (Figure S3c).26 The appearance of two extra shake-up satellite peaks at higher binding energies of 943.7 and 962.7 eV also reveals the existence of Cu₂⁺ on the photoanode surface.27 The above results suggested that the introduced CdS may serve as a protective layer that prevents Cu₂O from being oxidized to some extent, which conduces to enhance the stability of Cu₂O. The high-resolution spectrum of Cd 3d in Figure 3d with featured peaks of 3d₅/₂ at 405.3 eV and 3d₃/₂ at 412.1 eV indicates +2 oxidation state (Cd²⁺) in the as-

Figure 2. (a, b) SEM images, (c) TEM image, and (d) HRTEM image of the 30 min CdS/Cu₂O/ZnO NRAs, and (e–i) EDX elemental mapping images of Zn, O, Cu, Cd, and S, respectively.
prepared CdS/Cu2O/ZnO NRAs photoanode.28 Two peaks located at 161.6 and 162.8 eV in Figure 3e are attributed to S 2p3/2 and S 2p1/2, respectively, which are associated with the hybrid chemical bond species of S2− in Cd—S.29 Meanwhile, the O 1s peak shown in Figure 3f can be deconvoluted into three peaks at 531.2, 531.9, and 532.5 eV, which correspond to the O2− in the Cu2O crystal (O1 peak),30 Zn—O bonds of ZnO (O2 peak),31 and the oxygen species on the surface (O3 peak),32 respectively. Therefore, the above analytical results demonstrate the successful preparation of a chemically coupled CdS/Cu2O/ZnO NRAs photoanode.

The photoelectrochemical properties of these ZnO NRAs-based photoanodes were then investigated in a three-electrode cell using a Pt foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in 0.5 M Na2SO4 + 0.1 M Na2S electrolyte (pH = 12.99). Figure 4a

Figure 3. XPS spectra of the CdS/Cu2O/ZnO NRAs photoanode: (a) Survey, (b) Zn 2p, (c) Cu 2p, (d) Cd 3d, (e) S 2p, and (f) O 1s.
shows the photocurrent−voltage (I−V) curves of the ZnO, Cu2O/ZnO, and CdS/Cu2O/ZnO NRAs photoanodes under visible light illumination (300 W Xe lamp, 100 mW cm−2) in a potential scan range of −0.8 to 1.2 V versus SCE. The bare ZnO NRAs photoanode shows an almost negligible current density in the full potential range, due to its poor ability of visible light absorption, which leads to the inability to generate photoinduced electron−hole pairs. After the deposition of Cu2O, an enhanced current density was obtained over the entire potential range, which arrived at a maximum value of 8.40 mA/cm2 at 1.2 V. Dramatically, after introducing CdS, the CdS/Cu2O/ZnO NRAs photoanode showed apparent enhancement in current density; the 30 min CdS/Cu2O/ZnO photoanode exhibited a maximum value of 14.93 mA/cm2 at the same applied voltage. These calculated current densities are also listed (Table S1), and the induced current density of other prepared photoanodes under light illumination are compared (Table S2). The improved photocurrent density may be attributed to the fact that the introduction of CdS would not only assemble the photoinduced electrons from Cu2O but also act as hole donors to facilitate the irreversible consumption of holes by sacrificial reagents, so that the recombination of photoinduced electron−hole pairs at the surface of interface areas of CdS/Cu2O/ZnO could be reduced.

When ZnO was decorated only by CdS, it can be seen that the CdS/ZnO NRAs photoanode shows a higher photocurrent density than that of the bare ZnO NRAs photoanode but lower value than those of the CdS/Cu2O/ZnO NRAs photoanodes (Figure S4), revealing the substantially enhanced electron−hole pair separation efficiency after combining CdS with Cu2O. On the other hand, due to the intimate contact of Cu2O and ZnO, photoinduced electrons enriched in the conduction band of Cu2O can be injected to ZnO via the Zn−O−Cu bonds. As a result, the ZnO nanorod can function as an electron collector and transfer the electrons to the counter electrode to generate H2. The synergistic effect between ZnO and CdS can significantly restrain the recombination rate of photoinduced electron−hole pairs in Cu2O, thus leading to a superior photoelectrochemical performance compared to that of Cu2O/ZnO. In addition, this effect could also be verified from the I−V curves under dark conditions shown in Figure 4b. As expected, CdS/Cu2O/ZnO NRAs photoanodes exhibited a much higher current density than Cu2O/ZnO and ZnO NRAs photoanodes at the same potential, demonstrating that CdS played a significant role in the separation and transfer of photoinduced electron-hole pairs. To quantitatively evaluate the efficiency of water-splitting performance of the photoanodes, the photo-
conversion efficiency (PCE) deduced from Figure 4a is calculated from the following equation:

\[ PCE = \frac{J(E_{\text{rev}} - E_{\text{RHE}})}{J_{\text{light}}} \]  

(1)

where \( J \) is the photocurrent density at the measured potential, \( E_{\text{rev}} \) is the standard reversible potential for the water-splitting reaction (1.23 V), \( E_{\text{RHE}} \) is the applied potential versus reversible hydrogen electrode (RHE), and \( J_{\text{light}} \) is the irradiance intensity (100 mW cm\(^{-2}\)). As shown in Figure 4c, the 30 min CdS/Cu\(_2\)O/ZnO NRAs photoanode achieves the highest efficiency of 2.61% at a very low bias of −0.275 V versus SCE; it is already 2.72 and 261 times higher than that of the Cu\(_2\)O/ZnO (0.96% at −0.215 V versus SCE) and ZnO (0.01% at −0.085 V versus SCE) NRAs photoanodes, respectively. These results quantitatively demonstrate that more efficient photoinduced electron–hole pairs separation and transfer rate were achieved in CdS/Cu\(_2\)O/ZnO dual p–n junctions.

Incident photon-to-current conversion efficiency (IPCE) is another vital measurement to quantitatively investigate the photoelectrochemical performance. Herein, the as-prepared photoanodes were examined using the IPCE curves at wavelengths ranging from 380 to 600 nm with an applied bias of 0.2 V versus SCE. Moreover, the IPCE is calculated using the equation as follows:

\[ \text{IPCE} = \frac{(1240I)/(\lambda I_{\text{light}})}{1} \]  

(2)

where \( I \) denotes the photocurrent density at 0.2 V versus SCE at a certain wavelength, \( \lambda \) is the incident light wavelength, and \( I_{\text{light}} \) is the irradiance intensity for a specific wavelength. As shown in Figure 4d, all CdS/Cu\(_2\)O/ZnO samples exhibited enhanced IPCE as compared to that of Cu\(_2\)O/ZnO and ZnO. With prolonging of the CdS deposition time, the IPCE of CdS/Cu\(_2\)O/ZnO exhibited an increasing trend, and the 30 min CdS/Cu\(_2\)O/ZnO showed the largest IPCE enhancement. However, with further increase in the CdS deposition time, the IPCE of CdS/Cu\(_2\)O/ZnO progressively reduced, which is consistent with the above photoelectrochemical performances. The 30 min CdS/Cu\(_2\)O/ZnO achieves the highest IPCE of 14.51% at 380 nm, which is about 2 and 20 times higher than those of Cu\(_2\)O/ZnO (IPCE\(_{380\ nm} = 7.08\%\)) and ZnO (IPCE\(_{380\ nm} = 0.73\%\)). The results show that introduction of an appropriate amount of CdS onto Cu\(_2\)O/ZnO to form dual p–n junctions can realize the highly efficient generation, separation, and transfer of charge carriers. In addition, the enhancement of IPCE is highly dependent on the CdS deposition time. As the deposition time increased to 40 min, the IPCE of CdS/Cu\(_2\)O/ZnO deteriorated as the CdS thickness increased. This phenomenon may be
ascribed to the following two factors: excess CdS aggregated on the surface could form a charge carrier recombination center to reduce the PCE. On the other hand, excessively thick CdS could weaken the incident light absorption of Cu$_2$O, which suppresses the generation rate of charge carriers. Therefore, a suitable CdS shell coating on Cu$_2$O/ZnO could achieve the most effective photoelectrochemical performance as well as PCE.

To further confirm the enhanced photoinduced electron–hole pair separation and transfer properties in the p–n heterojunction, Mott–Schottky (M–S) plots were collected by conducting impedance-potential spectroscopy at 10 kHz in 0.5 M Na$_2$SO$_4$ + 0.1 M Na$_2$S solution over a range of potentials from −0.7 to −0.3 V versus SCE. The M–S measurement is based on the Schottky barrier formed between the semiconductor materials and electrolytes and is commonly employed to determine the carrier density. The slope of such plots is usually used to judge the n-type semiconductor with a positive slope and p-type semiconductor with a negative slope, and also to estimate the carrier density. Figure 5a shows the M–S plots of the ZnO NRAs photoanode that are expressed as 1/$C^2$ versus potential, where $C$ is the space charge capacitance of the semiconductor electrode. It can be seen that the ZnO NRAs photoanode showed a positive slope, revealing the n-type behavior. It is well known that Cu$_2$O is a p-type semiconductor; dramatically, when ZnO was coupled with Cu$_2$O to form a heterostructure, an apparent inverted “V-shaped” p–n junction characteristic was observed in Figure 5b, indicating the successful construction of a p–n junction in the Cu$_2$O/ZnO NRAs photoanode. CdS is an n-type semiconductor, which can be verified from our previous research work. After depositing CdS, the inverted “V-shaped” characteristic still existed in the M–S plots of the CdS/Cu$_2$O/ZnO NRAs photoanode (Figure 5c), suggesting that the introduction of CdS would not damage the p–n junction, which is more better for the separation and transfer of charge carriers. In addition, the carrier density ($N$) of the samples can be calculated using the following equation:

$$N = \frac{2}{\varepsilon \varepsilon_0 e} \left[ \frac{d(1/C^2)}{dV} \right]^{-1}$$

where $\varepsilon$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity of vacuum $\left(8.854 \times 10^{-12} \text{ F m}^{-1}\right)$, $e_0$ is the electronic charge unit $\left(1.602 \times 10^{-19} \text{ C}\right)$, and $V$ is the potential applied at the electrode. The carrier densities of these samples are calculated and listed in Table S1; the 30 min CdS/Cu$_2$O/ZnO NRAs photoanode retained about 2 and 5 orders of magnitude higher carrier density than those of the Cu$_2$O/ZnO and ZnO NRAs photoanodes, respectively, indicating that the nanoscale p–n junctions of Cu$_2$O/ZnO and Cu$_2$O/CdS not only create enough space charge to enhance charge carrier
creation but also facilitate the separation efficiency, thus effectively reducing the recombination rate of charge carriers. The 30 min CdS/Cu2O/ZnO NRAs photoanode exhibited the highest current density and carrier density as compared to other samples, demonstrating that the optimal deposition time of CdS is 30 min (Figure S5). From the UV–vis diffuse reflectance spectra (DRS) of the as-prepared samples, it can be observed that there is an apparent enhancement of visible light absorption with the decoration of CdS (Figure S6), which may be attributed to the strong absorption of CdS in the visible light region. Notably, the absorbance of CdS/Cu2O/ZnO samples initially increases with increasing CdS deposition time but decreases for the 40 min CdS/Cu2O/ZnO NRAs photoanode; this may be caused by excess CdS covering on the surface of Cu2O, contrarily blocking the incidence of visible light, thus reducing the generation of charge carriers. Moreover, deposition of a relatively thicker CdS layer with a long channel for photoinduced electron transfer from Cu2O to CdS would increase the recombination rate of charge carriers in the transfer process.

Electrochemical impedance spectroscopy (EIS) is considered to be a fundamental theoretical technique to investigate the interfacial charge transfer property of an electrode. Generally, charge transfer resistance ($R_{ct}$) of the electrode surface can be reflected as the semicircle diameter of EIS curves, which controls the charge transfer kinetics of the redox probe at the electrode interface.38 Figure 5d shows the EIS plots of the as-prepared photoanodes recorded at 0.2 V versus SCE under visible light illumination. It can be seen that $R_{ct}$ of CdS/Cu2O/ZnO is much smaller as compared to those of ZnO and Cu2O/ZnO, demonstrating that $R_{ct}$ is considerably reduced by introducing CdS to form dual p–n junctions, which can substantially promote the separation efficiency and suppress the recombination rate of charge carriers. Furthermore, $R_{ct}$ of these photoanodes decreases in the following sequence order: ZnO > CdS/Cu2O/ZnO > 10 min CdS/Cu2O/ZnO > 20 min CdS/Cu2O/ZnO > 40 min CdS/Cu2O/ZnO > 30 min CdS/Cu2O/ZnO; these results are highly consistent with their photoelectrochemical behavior and M–S plots. Therefore, the formation of dual p–n junctions and the reduced $R_{ct}$ are considered to be the other significant factors for enhancing the photoelectrochemical performance and the organic pollutant degradation activity discussed in what follows.

The photoelectrocatalysis (PEC), photocatalysis (PC), and electrocatalysis (EC) performances of ZnO (Z), Cu2O/ZnO (ZC), and CdS/Cu2O/ZnO (ZCC) NRAs photoanodes were evaluated by degrading 0.1 mM Rhodamine B (Rhb) solution under visible light illumination with an anodic bias of 1.5 V versus SCE. As seen from Figure 6a–c, compared to those of the ZnO and Cu2O/ZnO NRAs photoanodes, the EC, PC, and PEC performances of the CdS/Cu2O/ZnO NRAs photoanode are improved. However, compared with PEC, the EC and PC processes of ZnO, Cu2O/ZnO, and CdS/Cu2O/ZnO NRAs photoanodes all exhibit relatively lower degradation efficiency, revealing that the combination of illumination and external applied potential can substantially enhance the catalytic activity and the external voltage can improve the separation and transfer efficiency of photoinduced electron–hole pairs. Thus, the degradation efficiencies of these photoanodes comply with the following order for each catalytic process: CdS/Cu2O/ZnO > Cu2O/ZnO > ZnO. Furthermore, the 30 min CdS/Cu2O/ZnO NRAs photoanode exhibits the highest degradation ability in all catalytic processes, which is consistent with the photoelectrochemical measurement results. The superior degradation ability of the 30 min CdS/Cu2O/ZnO NRAs photoanode can be attributed to the construction of dual p–n junctions that efficiently separate the charge carriers. Meanwhile, deposition of an appropriate amount of CdS results in the maximum absorptivity for incident visible light, leading to the maximum generation of charge carriers.

As mentioned above, the dual p–n heterostructured CdS/Cu2O/ZnO NRAs electrode is demonstrated to be one of the ideal photoanodes for photoelectrochemical water splitting and photoelectrocatalytic degradation. Owing to the nanorod-forest character, ZnO NRAs provide effective electron percolation pathways, high surface-to-volume ratio for more reactive sites, and more effective harvest of the light. Moreover, the coarse surface of the CdS shell reduces the reflection of the incident light, so as to increase the utilization of incident light.39 The uniform core–shell structure with a high-quality heterojunction leads to efficient light absorption and effective separation of charge carriers. Figure 7 shows the proposed mechanism for the superior catalytic property of the PEC process. Under visible light illumination, direct narrow band gap Cu2O and CdS with a high absorption coefficient act as excellent visible light absorbers to generate charge carriers. Owing to the p–n junction formed in Cu2O/ZnO, photoinduced electrons in the
Cu₂O/CdS also impels the photoinduced electrons to that of Cu₂O, which then react with the hole scavengers S²⁻. The photoinduced holes in the valence band of CdS are transferred to further transfer the electrons to the FTO substrate and external circuit. Simultaneously, the p–n junction formed in Cu₂O/CdS also impels the photoinduced electrons to flow to CdS, where CdS serves as a reduction site to consume the electrons. The stepwise band structure of Cu₂O/ZnO and Cu₂O/CdS p–n junctions limits the flux of electrons and effectively reduces the recombination rate, thereby leading to the efficient separation of charge carriers. Meanwhile, photoinduced holes in the valence band of CdS are transferred to that of Cu₂O, which then react with the hole scavengers S²⁻. On the other hand, CdS may act as a passivation layer, preventing Cu₂O from being oxidized to some extent, which is beneficial to keep the valence state stability of Cu₂O. The enhancement of photoelectrochemical performance and organic pollutant degradation ability of the CdS/Cu₂O/ZnO NRAs photoanode is higher than the sum of that of Cu₂O/ZnO and ZnO NRAs photoanodes, indicating that the synergistic effect among dual p–n junctions, ZnO NRAs, and the CdS shell is extremely favorable for charge carrier separation and transportation. Trapping experiments for the main reactive species, such as hole (h⁺), superoxide radicals (O₂⁻), and hydroxyl radical (OH⁻) are conducted to further investigate the possible catalytic mechanism and transfer trails of the photoinduced electron–hole pairs in CdS/Cu₂O/ZnO dual p–n junctions. Typically, 5 mL of triethanolamine (TEOA) and isopropyl alcohol (IPA) were added into the RhB solution to serve as scavengers of h⁺ and OH⁻, respectively. Meanwhile, N₂ purging (200 mL min⁻¹) was performed as an O₂⁻ scavenger. As shown in Figure 6d, few changes occurred for the RhB degradation rate in the presence of TEOA, revealing that h⁺ might not affect the degradation process under visible light illumination. Dramatically, there is an obvious decrease in RhB degradation efficiency upon the addition of IPA and N₂, suggesting that O₂⁻ and/or O₂− may serve as the main reactive species in the PC degradation process. It is worth noting that the degradation rate of RhB solution using IPA was lower than that of N₂ purging, which suggests that OH⁻ may play the most primary role in the PC degradation process. On the basis of the above trapping experiment results, the proposed charge carrier separation and transfer path in the PC process of the CdS/Cu₂O/ZnO dual p–n heterostructure were provided and are displayed in Figure 8. When CdS is decorated on Cu₂O/ZnO to form dual p–n junctions, two built-in electric fields with positive (filled with holes) and negative (filled with electrons) regions would develop to efficiently transfer the electrons to the conduction band of ZnO and CdS. Under visible light illumination, the separated electrons participate in the photoreduction reactions, and the formed main reactive species could effectively degrade the dye molecules eventually.

In addition, the proposed action trails for the main reactive species were put forward as follows:

\[ \text{Cu}_2\text{O} \xrightarrow{h^+ (\lambda \geq 420 \text{ nm})} \text{Cu}_2\text{O}(h^+ + e^-) \] (4)

\[ \text{Cu}_2\text{O}(e^-) \xrightarrow{\text{transfer}} \text{ZnO}(e^-) \] (5)

\[ \text{Cu}_2\text{O}(e^-) \xrightarrow{\text{transfer}} \text{CdS}(e^-) \] (6)

\[ \text{ZnO}(e^-) + \text{O}_2 \xrightarrow{\text{photoreduction}} \text{ZnO} + \cdot\text{O}_2 \] (7)

\[ \text{CdS}(e^-) + \text{O}_2 \xrightarrow{\text{photoreduction}} \text{CdS} + \cdot\text{O}_2 \] (8)

\[ \cdot\text{O}_2 + \text{H}_2\text{O} \rightarrow \cdot\text{OH} \] (9)

\[ \cdot\text{O}_2 + \text{RhB} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \cdots \] (10)

\[ \cdot\text{OH} + \text{RhB} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \cdots \] (11)

### CONCLUSIONS

In summary, an n-type CdS-decorated Cu₂O/ZnO p–n heterostructured nanorod array (n-CdS/p-Cu₂O/n-ZnO NRAs) photoanode with superior performance was successfully fabricated via electrochemical and chemical bath deposition (CBD) processes. The optimized 30 min CdS/Cu₂O/ZnO NRAs photoanode exhibited the highest current density of 14.93 mA cm⁻² compared to the Cu₂O/ZnO (8.40 mA cm⁻²) and ZnO (0.38 mA cm⁻²) NRAs photoanodes under visible light illumination. The PCE of the CdS/Cu₂O/ZnO NRAs photoanode was significantly enhanced in the visible light region by introducing CdS to form dual p–n junctions, which
greatly facilitated the separation and transfer of charge carriers. In such a ternary configuration, fast generation, separation, and transfer of charge carriers were achieved in the Cu2O/ZnO and Cu2O/CdS dual n-p junction region; n-type ZnO NRAs and the CdS shell played the role of the electron collector and transport channel, and the perfect cooperation of the three participants effectively reduced the recombination rate of charge carriers. The above factors are supposed to be the main reasons for the generation of the enhanced photoelectrochemical performance and photocatalytic activity of the CdS/Cu2O/ZnO NRAs photoanode. This work demonstrates that such an n-Cds/p-Cu2O/n-ZnO NRAs photoanode has great potential applications in the field of photoelectrochemical water splitting and photoelectrocatalytic degradation.

### EXPERIMENTAL SECTION

**Chemicals and Materials.** Zn(NO3)2·6H2O, Cd(NO3)2·4H2O, thiourea (CN2H4S), TEOA, IPA, nitrogen (N2), and Rhodamine B (RhB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the reagents were of analytical grade and used directly without further purification.

**Synthesis of the Cu2O/ZnO NRAs Photoanode.** The Cu2O/ZnO NRAs photoanode was synthesized through a simple two-step electrochemical deposition method on a clean FTO (with a sheet resistance of 14 Ω) substrate. First, the ZnO NRAs photoanode was prepared according to the previous report,15 an aqueous solution composed of 0.02 M Zn(NO3)2·6H2O, 0.01 M NH4Ac, and 0.01 M HMT was used as the electrolyte, and the deposition procedure was carried out in an oil bath for 30 min at a temperature of 90 °C under the potential of ~2.0 mA cm⁻², with a graphite rod serving as the counter electrode. Second, the electrodeposition of Cu2O on the ZnO NRAs was conducted in an alkaline aqueous solution containing 0.4 M CuSO4·5H2O and 3 M lactic acid whose pH value was adjusted to 12 by adding NaOH solid. The electrodeposition process was performed potentiostatically at ~0.5 V, and the deposition time was fixed at 10 min; moreover, the solution was kept at 80 °C during the entire process. To avoid etching of the ZnO nanorod or any possible surface corrosion, the negative potential was applied immediately after immersing the ZnO NRAs in the solution.

**Fabrication of the CdS/Cu2O/ZnO NRAs Photoanode.** Deposition of CdS on the Cu2O/ZnO NRAs photoanode was carried out via the facile CBD method, and the fabrication process is presented in Scheme 1. In the typical process, an aqueous solution composed of 0.01 M Cd(NO3)2·4H2O and 0.01 M CN2H4S was served as the electrolyte for CdS deposition. The FTO substrate grown with Cu2O/ZnO NRAs was immersed into the above solution for different times to eventually prepare the CdS/Cu2O/ZnO NRAs photoanode with different thicknesses of the CdS shell. The CdS/Cu2O/ZnO NRAs photoanodes with CdS deposition times of 10, 20, 30, and 40 min were denoted as 10 min CdS/Cu2O/ZnO, 20 min CdS/Cu2O/ZnO, 30 min CdS/Cu2O/ZnO, and 40 min CdS/Cu2O/ZnO, respectively.

**Characterization.** Powder X-ray diffraction (XRD) measurement was conducted on a PANalytical, PW3040/60 diffractometer with monochromatized Cu Kα radiation (λ = 0.15418 nm). The surface morphology and crystal microstructure of the as-prepared samples were examined using a field-emission SEM (FE-SEM, JEOL JSM-7001F) equipped with an energy-dispersive spectroscopy (EDS) device and TEM (JEM2010-HR). Surface electronic states and compositions of the sample were analyzed by XPS (ESCALab250). The UV–vis DRS of the samples were obtained over a UV–vis spectrophotometer (Cary 300) using BaSO4 as a reference.

**Water-Splitting Performances.** The electrochemical workstation (CHI 760D, China Chenhua) equipped with a single compartment quartz cell with a three-electrode system was adopted to evaluate the water-splitting performances of the as-prepared samples. The as-prepared photoanode (available working area was 2.25 cm²), saturated calomel electrode (SCE), and Pt sheet (1 × 1 cm²) were employed as the working electrode, reference electrode, and counter electrode, respectively. A 0.5 M Na2SO4 + 0.1 M Na2S aqueous solution (pH = 12.99) served as the electrolyte, and a 300 W Xe lamp equipped with a 420 nm cut-off optical filter was placed parallel to the photoelectrochemical system, where the distance was fixed at 8 cm from the quartz cell to the light source. For PCE calculations, the electrode potential versus SCE is converted to the RHE potential according to the Nernst equation: $E_{RHE} = E_{SCE} + 0.059pH + \frac{E^0_{SCE}}{2}$, where $E_{RHE}$ is the converted applied potential versus RHE, $E_{SCE}$ is the applied potential versus reference SCE, $E^0_{SCE}$ is the standard SCE electrode potential at 25 °C (0.244 V), and pH for the electrolyte is 12.99.

**Photoelectrocatalytic Degradation Measurements.** The photoelectrocatalytic ability of the photoanode was examined by degrading RhB solution. Generally, 50 mL of 0.5 M Na2SO4 + 0.1 M Na2S solution containing 4 mL of 0.1 mM RhB solution was used as the electrolyte. Before light irradiation, the photoanode was immersed and fixed vertically in the solution for 30 min in the dark to establish an adsorption/desorption equilibrium of dye molecules on catalysts. Moreover, a 300 W Xe lamp equipped with a 420 nm cut-off optical filter was introduced into the system, and a constant applied bias of 1.5 V was employed to impel the transfer of photoinduced electrons from the working electrode to the counter electrode. At a regular time interval of 20 min, 3 mL of the solution was collected and analyzed using a UV–vis spectrophotometer.
absorption spectrometer to determine the degradation rate \( \eta \) of RhB solution using the following equation

\[
\eta = \frac{(C_0 - C_t)/C_0}{t/0t}
\]

where \( C_0 \) is the initial concentration of RhB solution, \( C_t \) is the concentration of that at different intervals during the degradation process.

**ASSOCIATED CONTENT**

1. Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00507.

- SEM images; EDS spectrum; XPS spectra; plots of current density and carrier density; \( I-V \) curves; UV–vis absorption spectra (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: lzqgzu@gzhu.edu.cn. Tel: +86-20-39366908. Fax: +86-20-39366908.

**ORCID**

Zhao-Qing Liu: 0000-0002-0727-7809

**Notes**

The authors declare no competing financial interest.

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