Abstract: Developing suitable photocatalysts for the oxygen evolution reaction (OER) is still a challenging issue for efficient water splitting due to the high requirements to create a significant impact on water splitting reaction kinetics. Herein, $n$-type Bi$_2$WO$_6$ with flower-like hierarchical structure and $p$-type Cu$_2$O quantum dots (QDs) are coupled together to construct an efficient S-scheme heterojunction, which could enhance the migration efficiency of photogenerated charge carriers. The electrochemical properties are investigated to explore the transportation features and donor density of charge carriers in the S-scheme heterojunction system. Meanwhile, the as-prepared S-scheme heterojunction presents improved photocatalytic activity towards water oxidation in comparison with the sole Bi$_2$WO$_6$ and Cu$_2$O QDs systems under simulated solar light irradiation. Moreover, the initial O$_2$ evolution rate of the Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction system is 2.3 and 9.7 fold that of sole Bi$_2$WO$_6$ and Cu$_2$O QDs systems, respectively.

Keywords: photocatalysis; S-scheme heterojunction; water oxidation; quantum dots

1. Introduction

Sunlight provides an abundant renewable energy source to overcome the energy crisis that humans face in the future. Among all the strategies, solar energy conversion from sunlight into chemical energy has shown up as a sustainable and efficient route utilizing semiconductor photocatalysts [1,2]. As we know, water oxidation to dioxygen is a multi-electron transfer reaction in a photocatalytic water splitting process, which is a critical step and involves the difficult breaking of the O–H bond as well as the formation of an O–O bond [3,4]. Continuous efforts have been dedicated to the development of efficient water oxidation catalysts (WOCs), consisting of desirable semiconductor photocatalysts and cocatalysts with proper band structure and electrophilic ability, which could improve the light absorption capability and charge transportation with overall promoted photocatalytic performance for water oxidation [5,6].

Among various semiconductor photocatalysts, ternary metal oxide, $n$-type Bi$_2$WO$_6$, as one of the simplest members of the Aurivillius family, is comprised of accumulated layers of perovskite-like [WO$_4$]$^{2-}$ octahedral sheets and [Bi$_2$O$_3$]$^{2+}$ sheets [7–9]. Density functional theory (DFT) calculations show that the conduction band (CB) of Bi$_2$WO$_6$ is comprised of W 5d orbitals; the valence band (VB) mainly originates from hybridizing O 2p with Bi 6s orbitals, which not only enables the VB to be highly dispersed, but also facilitates the migration of photogenerated holes for specific oxidation reactions. In addition, the band gap of Bi$_2$WO$_6$ is about 2.8 eV, and the valence band edge is at +2.95 V vs. NHE (normal hydrogen electrode), which is high enough to trigger the water oxidation reaction for oxygen production. These unique properties reveal that Bi$_2$WO$_6$ can be utilized as a visible-light-driven photocatalyst for organic synthesis, CO$_2$ reduction,
and environmental remediation [10–12]. Nevertheless, similar to many semiconductors, the poor utilization efficiency of solar energy and high recombination rate of pure Bi$_2$WO$_6$ give rise to depressed photocatalytic activity and thereby cannot meet the rising demand of commercial applications [13–15].

Compared with mono-component photocatalysts, the hybrid heterojunction photocatalysts that hybridize at least two different functional catalysts into one system have attracted increasing attention in recent decades. In particular, the advanced Z- or S-scheme heterojunctions have been extensively investigated and reported; they synchronously realize efficient separation, transportation, and utilization of photoinduced charge with strong redox abilities by means of recombining weak electrons and holes at low potentials between the two semiconductors [16,17]. Therefore, to enhance the photocatalytic efficiency of Bi$_2$WO$_6$, it is feasible to couple Bi$_2$WO$_6$ with other cocatalysts for constructing an S-scheme heterojunction system [18–20]. For example, Liu et al. constructed Bi$_2$WO$_6$/CoAl-LDHs (layered double hydroxides) S-scheme heterojunction to obtain enhanced photo-Fenton-like catalytic performance, which profited from the synergistic effect of an internal electric field and S-scheme heterojunction [20]. Recently, quantum dots-modified semiconductor functional materials have received tremendous attention [21–23]. The quantum dots (QDs) can significantly increase the photon conversion efficiency by generating multiple excitons from a single photon owing to their unique quantum effect, but also easily match well with the band alignment of the host semiconductor [24]. Taking carbon QDs as an example, Kang et al. utilized carbon QDs to decorate Bi$_2$WO$_6$ for constructing the desirable band structure conditions induced by compensatory photo-electronic effects, thereby realizing overall water photo-splitting [25]. Moreover, the high specific surface area (SSA) supplies numerous active sites which are favorable for the adsorption of reactants and thus enhancing the observed photocatalytic activity. A major merit of these QDs decorated semiconductors is that more micro-heterojunction and a faster charge transfer process can be sustained due to the intimately contacted nature of the interface and the short charge-carrier transport paths. Among numerous semiconductors, Cu$_2$O QDs have shown up as a good candidate for tailoring photo-response and promoting charge carrier migration properties because of the well-aligned overlapped band structures of Bi$_2$WO$_6$ and Cu$_2$O [26]. In fact, Cu$_2$O is widely applied as an effective co-catalyst in photocatalytic or electrocatalytic systems for a hydrogen evolution reaction (HER) owing to its high conduction band potential, exhibiting good photocatalytic H$_2$ production activity [27,28].

In this study, we successfully decorated Cu$_2$O QDs onto the surface of Bi$_2$WO$_6$ micro-flowers (MFs) with a uniform dispersion to form multiple S-scheme micro-heterojunctions for enhancing the efficiencies of solar light utilization and photogenerated charge migration. The incorporation of Cu$_2$O QDs improved the adsorption ability of visible light and effectively facilitated the transportation of photoinduced charge carriers, and thus enhanced the photocatalytic activity for oxygen production under simulated solar light irradiation. This work suggests that the coupling of nanosized p-type Cu$_2$O QDs and the three-dimensional Bi$_2$WO$_6$ MFs has a great potential for application in photocatalytic water oxidation.

2. Materials and Methods

2.1. Synthesis of Flower-Like Hierarchical Bi$_2$WO$_6$ MFs

In a typical procedure, 1.32 g of Na$_2$WO$_4$·2H$_2$O was dissolved into 40 mL of purified water to form a transparent solution. Meanwhile, 1.96 g of Bi(NO$_3$)$_3$·5H$_2$O was firstly mixed with 80 mL of HNO$_3$ (0.3 M). After that, the Na$_2$WO$_4$ solution was dropped into the Bi(NO$_3$)$_3$ solution with vigorous magnetic stirring, and a white precipitate was formed quickly. Subsequently, 20 mL of NaOH solution (0.2 M) was added dropwise with stirring for 12 h. Finally, the mixture was transferred to a Teflon-lined autoclave and kept at 160 °C for 8 h. A light-yellow precipitate Bi$_2$WO$_6$ MFs was centrifuged, washed by purified water and dried in air at 60 °C.
2.2. Synthesis of Cu$_2$O QDs/Bi$_2$WO$_6$ Heterojunction

Firstly, 0.025 g of hexadecyl trimethyl ammonium bromide (CTAB) was dissolved into 20 mL of purified water to form transparent solution. Then, 0.1 g of the as-prepared Bi$_2$WO$_6$ sample was added into the above CTAB solution with stirring for 30 min. Meanwhile, 0.008 g of copper acetate (Cu(Ac)$_2$) and 0.016 g of ethylenediaminetetraacetic acid disodium (EDTA-Na) were dissolved into 5 mL of purified water. Subsequently, the Cu solution was mixed with the Bi$_2$WO$_6$ solution. Then, 10 mL of NaOH solution (0.05 M) was added dropwise into the mixed solution with stirring for 30 min. Afterwards, 10 mL of ascorbic acid (AA) solution (0.33 g) was dropped into the above solution with vigorous stirring for 1 h. The generated Cu$_2$O/Bi$_2$WO$_6$ was washed with absolute ethanol and distilled water several times to remove the surfactant, and dried overnight in a vacuum oven. The final products were named 1.5 wt% Cu$_2$O/Bi$_2$WO$_6$, 3wt% Cu$_2$O/Bi$_2$WO$_6$, and 6 wt% Cu$_2$O/Bi$_2$WO$_6$, where the 1.5, 3 and 6 wt% were the mass ratios of Cu$_2$O to Bi$_2$WO$_6$ in the mixed solution according to the theoretical stoichiometric ratio of added copper and bismuth elements. For comparison, a control sample was prepared without the addition of Bi$_2$WO$_6$ and labeled as Cu$_2$O.

2.3. Characterizations

X-ray diffraction (XRD) patterns of the prepared heterojunctions were performed using a Bruker D8 diffractometer (Billerica, MA, USA). The morphology and microstructure of the obtained catalysts were observed using a JSM5510LV (Tokyo, Japan) field emission scanning electron microscopy (SEM) and a JEOL 2100 (Tokyo, Japan) transmission electron microscopy (TEM). Raman spectra were recorded on an ISA dispersive Raman spectroscopy at 514 nm. Fourier transform infrared spectra (FTIR) were determined using a Bruker spectrometer (Billerica, MA, USA) with an ATR correction mode. X-ray photoelectron spectroscopy (XPS) was examined by a Thermo Escalab 250 instrument (Waltham, MA, USA) with Al-Kα radiation to determine the surface chemical species. UV–vis absorption spectra were conducted by a Cary 4000 UV-vis spectrometer (Waltham, MA, USA). Electron paramagnetic resonance (EPR) analyses were carried out using a Bruker EMS-plus instrument (Billerica, MA, USA) to detect the free radicals by using 5,5-dimethyl-1-pyrroline (DMPO) as a spin-trapping agent.

2.4. Photoelectrochemical Tests

Photoelectrochemical measurements were conducted using a CHI660E electrochemical workstation (Shanghai, China) with a three-electrode system in 0.05 M Na$_2$SO$_4$ electrolyte (20 mL, pH = 6.8). A catalyst deposited fluorine-doped tin oxide (FTO) electrode was served as a photoanode, while a Pt wire and a saturated calomel electrode (SCE) were applied as the counter electrode and reference electrode, respectively. For the photoanode preparation, 40 mg of the prepared photocatalysts were added into 2 mL of ethanol with 40 µL Nafion solution (5 wt%) and mixed homogeneously using a vortex oscillator. After that, the resulting mixture was dip-coated onto the prewashed FTO glass to obtain a film electrode with a controlled electrode area of 1 cm$^2$. The solar light source ($I_0 = 100$ mW cm$^{-2}$) was simulated using a 200 W Xenon lamp coupled with an AM 1.5G filter. Electrochemical impedance spectroscopy (EIS) tests were measured at a scan frequency range of 0.1 to 100 kHz under a voltage amplitude of 10 mV and a potential bias of 0.298 V vs. SCE.

2.5. Photocatalytic Activities

The photocatalytic reactions were performed in a Teflon lining reactor under the simulated solar light. 0.05 g of samples were added into 200 mL of the solution with La$_2$O$_3$ (0.2 g) and AgNO$_3$ (0.03 M). Before irradiation, the mixture was stirred for 30 min in the dark and then purged with N$_2$ to removal O$_2$. The concentration of O$_2$ in the reactor was measured by using gas chromatograph (Tet, GC-2030, Tokyo, Japan) with a thermal conductivity at an interval of 30 min.
3. Results and Discussion

Figure 1a displays a possible formation procedure of Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction through a facile hydrothermal and deposition route. Firstly, when the cationic surfactant CTAB is introduced, the CTAB can be adsorbed and anchored at the surface of Bi$_2$WO$_6$ MFs. The characteristic flower-like hierarchical Bi$_2$WO$_6$ with high SSA provides a structural framework for the uniform growth of nanoparticles on the sheets slowly with directed high-density. On the other hand, the EDTA and Cu(Ac)$_2$ are mixed with the purified water to form a blue Cu complex. Subsequently, the mixture is added drop-wise into the Bi$_2$WO$_6$/CTAB solution. As a result, the Cu complex is deposited on the surface of flower-like hierarchical Bi$_2$WO$_6$. With the addition of NaOH, Cu(II) ions from the Cu complex are slowly released to generate Cu(OH)$_2$ nanoparticles. As expected, the negatively charged nanoparticles could be attracted and grafted by the positive CTAB to restrain the agglomeration effect. When the weak reductive AA is added, the formed Cu(OH)$_2$ nanoparticles can be reduced to Cu$_2$O QDs on the surface of Bi$_2$WO$_6$ MFs, which further maintains the stability of the nanosized Cu$_2$O QDs without apparent aggregation. In Figure 1b, the XRD patterns of Bi$_2$WO$_6$ with different contents of Cu$_2$O QDs are present. As displayed, the XRD pattern of the as-prepared Bi$_2$WO$_6$ is in good agreement with the standard diffraction pattern of orthorhombic Bi$_2$WO$_6$ (JCPDS No. 73-2020) [29], where the obvious peaks at 28.3°, 32.9°, 47.2°, 55.9°, 58.6°, 69.1°, 76.1°, 78.5°, and 87.7° can be indexed to the (113), (020), (220), (313), (226), (040), (333), (046), and (246) crystal planes, respectively. Moreover, the patterns for Cu$_2$O/Bi$_2$WO$_6$ heterojunctions are similar to those of pure Bi$_2$WO$_6$, while no characteristic peaks belong to Cu$_2$O are observed, which is ascribed to the low loading mass and high dispersion of Cu$_2$O QDs in the Bi$_2$WO$_6$ matrix.

![Figure 1](image-url)

**Figure 1.** (a) Preparation illustrator and (b) XRD patterns of Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction.

SEM images of the bare Bi$_2$WO$_6$ MFs are displayed in Figure 2a,b, where the uniform flower-like hierarchical Bi$_2$WO$_6$ with 2–3 µm diameter are observed clearly. It is found that the hierarchical structure of Bi$_2$WO$_6$ is assembled by ultrathin sheets with 40 nm of
thickness, as present in Figure 2c,d, inferring high porosity and huge surface area, which benefits the exposure of more active sites.

![Figure 2. FESEM images of the pure flower-like Bi2WO6 samples with (a,b) wide scope and (c,d) higher resolutions.](image)

After introducing the Cu2O QDs, as shown in Figure 3a,b, it is clearly observed that the size of the Bi2WO6 hierarchical flowers displays a negligible change, while the nanosheets comprised of the flowers are mechanically exfoliated and the surface of the flower-like hierarchical structure becomes smoother, which is possibly due to the vigorous stirring during the Cu2O QDs deposition process. Meanwhile, with the increasing of Cu initial amount, the Cu2O nanoparticles are observed and anchored at the surface of the hierarchical Bi2WO6 MFs. As displayed in Figure 3c, the 3 wt% Cu2O QDs are uniformly deposited on the surface of Bi2WO6 MFs, while once the amount of Cu(II) precursor reaches to 6 wt%, large Cu2O nanoparticles are detected in Figure 3d,e, which indicates that the excess Cu(II) precursor is harmful for the dispersion of Cu2O QDs and causes the aggregation.

TEM and HRTEM images of the Cu2O QDs/Bi2WO6 heterojunction are presented in Figure 4. The micro-size Bi2WO6 MFs with 2–3 μm diameter is observed, which is agreement with the results of SEM, as displayed in Figure 4a, where the large thickness of the sample hampers the penetration of electron beams, leading to the black area. In general, quantum dots are defined as semiconductor nanocrystals with particle sizes ranging from 1 to 20 nm, which possess unique electronic properties owing to the apparent quantum confinement effect. It can be clearly observed that the Cu2O nanoparticles with ~20 nm of diameter are uniformly dispersed at the surface of Bi2WO6 MFs in Figure 4b,c. Owing to the smaller size, the Cu2O QDs can easily anchor at the surface of micro-sized Bi2WO6 to form micro-heterojunctions, which shorten the charge-carrier transfer pathways through the intimately contacted interface. The clear lattice fringe of 0.307 nm ascribed to the (110) crystal facet of Cu2O is detected in Figure 4d. These results demonstrate the successful construction of heterojunctions between Bi2WO6 and Cu2O.
Figure 3. FESEM images of the Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunctions with different Cu amounts: (a) 1.5 wt%, (b,c) 3 wt%, and (d,e) 6 wt%.

Figure 4. TEM (a,b) and HRTEM (c,d) images of the 3 wt% Cu$_2$O QDs/Bi$_2$WO$_6$ sample.

FTIR spectra of Bi$_2$WO$_6$ MFs, Cu$_2$O, and Cu$_2$O/Bi$_2$WO$_6$ are displayed in Figure 5a. The peaks at 818 and 703 cm$^{-1}$ are attributed to the symmetric and asymmetric vibration of W–O, respectively [30]. The peaks centered at 1599, 2924 and 2845 cm$^{-1}$ are due to the stretching vibration of O–H and C–H, respectively, which could be because of the usage of organic surfactants (CTAB, EDTA) during the synthesis procedure of the heterojunction system [31]. Besides, the characteristic peak of Cu$_2$O is not found in the samples of Cu$_2$O/Bi$_2$WO$_6$. To further investigate the composition of samples, Raman spectroscopy
of the samples was performed, as shown in the Figure 5b. The characteristic peaks at 796 and 827 cm\(^{-1}\) can be ascribed to the antisymmetric and symmetric Ag stretch modes of the O–W–O band, respectively [32,33]. The peak at 714 cm\(^{-1}\) is associated with the antisymmetric bridging mode of the tungstate chain. In addition, the obvious vibration peak at 308 cm\(^{-1}\) is assigned to translational modes involving simultaneous motions of WO\(_6^{6-}\) and Bi\(^{3+}\) [34]. For the pure Cu\(_2\)O, the intense peaks at low frequencies of 213 and 260 cm\(^{-1}\) originate from the stretching vibration of Cu\(_2\)O, which is consistent with the previous reports [35,36]. In the case of Cu\(_2\)O/Bi\(_2\)WO\(_6\), the characteristic peak at 308 cm\(^{-1}\) shifted to 296 cm\(^{-1}\), and the two peaks at 796 and 827 cm\(^{-1}\) became a broad peak at 809 cm\(^{-1}\) due to the cover of Cu\(_2\)O on the surface of the Bi\(_2\)WO\(_6\) MFs.

Figure 5. (a) FTIR spectra and (b) Raman spectra of the as-prepared Cu\(_2\)O/Bi\(_2\)WO\(_6\) samples: a. Bi\(_2\)WO\(_6\), b. 1.5 wt\% Cu\(_2\)O/Bi\(_2\)WO\(_6\), c. 3 wt\% Cu\(_2\)O/Bi\(_2\)WO\(_6\), d. 6 wt\% Cu\(_2\)O/Bi\(_2\)WO\(_6\), and e. Cu\(_2\)O QDs.

The XPS spectra were conducted to detect the chemical environment of elements in the catalyst, and all characteristic peaks were calibrated using C 1s (binding energy at 284.6 eV) as a reference. In Figure 6a, elements of W 4f, Bi 4f, O 1s, and Cu 2p were detected in the full survey spectrum of the 3 wt\% Cu\(_2\)O/Bi\(_2\)WO\(_6\), demonstrating the coexistence of these elements in the sample. As presented in Figure 6b, two distinct peaks located at 159.8 and 165.1 eV are assigned to the characteristic peaks of Bi 4f\(_{7/2}\) and Bi 4f\(_{5/2}\) in the trivalent oxidation state, respectively. In the previous report, the binding energy of Bi 4f\(_{7/2}\) in Bi\(_2\)WO\(_6\) MFs locates in the range of 158 to 159 eV while that for Bi\(_2\)O\(_3\) appears between 159 and 160 eV. Therefore, the peak located at 159.8 eV could be assigned to Bi\(^{3+}\) in Bi\(_2\)WO\(_6\) MFs [37,38]. In Figure 6c, the high resolution deconvoluted W 4f spectrum reveals two broad peaks at 38.2 and 36.0 eV corresponding to W 4f\(_{5/2}\) and W 4f\(_{7/2}\), respectively, suggesting the valence state of W element is +6 in the sample of Cu\(_2\)O/Bi\(_2\)WO\(_6\) heterojunction [39]. Moreover, as seen from Figure 6d, there are two obvious characteristic peaks at 953.3 and 933.5 eV, attributed to Cu 2p\(_{1/2}\) and Cu 2p\(_{3/2}\), respectively, revealing the feature of Cu\(^{+}\) in Cu\(_2\)O [40,41]. In contrast, the CuO state generally has a main characteristic peak locates at a binding energy of higher than 933 eV and characteristic shake-up satellite peaks at around 937–945 eV [42–45]. The shake-up peaks are often detected at around 9–10 eV higher than the main peaks, which results from the vigorous photoelectrons synchronously interacting with a valence electron and then being excited to a higher binding energy level [46]. However, in Figure 6d, the peak belonging to Cu\(^{2+}\) at 933.7 eV with the shake-up peaks at 937–945 eV is not observed, revealing that the copper species in Cu\(_2\)O/Bi\(_2\)WO\(_6\) hybrids are mainly presented as Cu\((l)\) [47–49].
Figure 6. XPS spectra of the 3 wt% Cu$_2$O/Bi$_2$WO$_6$: full spectrum survey (a), Bi 4f (b), W 4f (c), and Cu 2p (d).

UV–vis absorption spectra of various heterojunctions and the corresponding band gap energies calculated from the Tauc’s plots by $(\alpha h \nu) = A(h \nu - E_g)^{1/2}$ are presented in Figure 7, which reveals the sunlight response and absorption capability of Cu$_2$O, Bi$_2$WO$_6$ MFs, and various Cu$_2$O/Bi$_2$WO$_6$ hybrids. The absorption edge of Bi$_2$WO$_6$ MFs is about 460 nm, which suggests that the pure Bi$_2$WO$_6$ can only absorb UV and near-visible light. However, the absorption spectrum of Cu$_2$O sharply rises at the beginning of 650 nm, displaying strong visible light response ability, which makes it a desirable candidate for utilization of solar energy. When depositing Cu$_2$O QDs on the surface of Bi$_2$WO$_6$, the obtained Cu$_2$O/Bi$_2$WO$_6$ hybrid system exhibits improved absorption ability for visible light, as displayed in Figure 7a. The corresponding band gap energies are calculated and displayed in Figure 7b, where the band gap energy of Cu$_2$O/Bi$_2$WO$_6$ hybrids decreases with the introduction of Cu$_2$O. Meanwhile, it is observed that the band gap of the 6 wt% Cu$_2$O/Bi$_2$WO$_6$ hybrid is narrowed to 2.05 eV, which is obviously different from those of the 1.5 wt% and 3 wt% Cu$_2$O/Bi$_2$WO$_6$ hybrids. This result suggests that the excess amount of Cu precursor did not result in the formation of Cu$_2$O QDs but Cu$_2$O microstructures on the surface of Bi$_2$WO$_6$. It demonstrates that the optimal amount of Cu precursor exists in the formation of QDs-MFs micro-heterojunction structure. On the other word, the excessive Cu precursor leads to the enhancement of sunlight response property.
Figure 7. UV–visible absorption curves (a) and Tauc’s plots (b) of the prepared Bi$_2$WO$_6$ and different Cu$_2$O/Bi$_2$WO$_6$ heterojunctions.

To investigate the transportation behavior and efficiency of photoinduced charge carriers at the heterojunction interface, the photoelectrochemical properties of these samples were investigated. In Figure 8a, electrochemical impedance spectroscopies (EIS) of these samples in the manner of a Nyquist diagram were recorded in the dark and under light irradiation. In general, the radius of each semicircle is correlated to charge-transfer resistance ($R_{ct}$) at the interface of electrode/electrolyte; a smaller semicircle implies a lower $R_{ct}$ value [50–52]. As shown in Figure 8a, Cu$_2$O exhibits significantly smaller $R_{ct}$ under light irradiation (l) in comparison with being in darkness (d), indicating that the electrical resistance at the electrode/electrolyte interface is decreased due to the production of photogenerated charge carriers. In the case of the flower-like Bi$_2$WO$_6$ MFs, a larger semicircle is recorded, suggesting that the Bi$_2$WO$_6$ possesses poor electrochemical performance in charge-transfer process [53,54]. With the formation of the Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction, the $R_{ct}$ of Bi$_2$WO$_6$ is intensively reduced, which apparently improves the photoelectrochemical property of Bi$_2$WO$_6$ and is favorable for the transportation of the photogenerated charge carriers.

Figure 8. (a) Nyquist plots, Mott–Schottky curves of (b) Bi$_2$WO$_6$, (c) Cu$_2$O, and (d) Cu$_2$O/Bi$_2$WO$_6$. 
To gain deeper insights into the characteristics of the prepared heterojunctions, flat band potential and carrier concentrations are deduced from the Mott–Schottky (M–S) curves [55,56]. The electrode potentials vs. SCE are converted to the reversible hydrogen electrode (RHE) potentials based on the following Nernst equation [57]:

\[ V_{\text{RHE}} = V_{\text{SCE}} + 0.059 \times \text{pH} + V^0_{\text{SCE}} \]  

(1)

where \( V_{\text{SCE}} \) is the experimental potential measured against the SCE, \( V_{\text{RHE}} \) represents the converted potential vs. RHE, and \( V^0_{\text{SCE}} = 0.245 \) V at 25 °C. The Mott–Schottky (M–S) plots are depicted in Figure 8b–d, in which the flat band potentials at the electrode/electrolyte interface are calculated according to Equation (2) [36]:

\[ \frac{1}{C^2} = \left( \frac{2}{\varepsilon_r \varepsilon_0 N_d A^2} \right) [(V - V_{fb}) - kT/e] \]  

(2)

where \( C \) is the specific capacity, \( \varepsilon_r \) and \( \varepsilon_0 \) are the dielectric constant of the samples and the electric permittivity of vacuum \( (8.85 \times 10^{-12} \text{ N}^{-1} \text{ C}^2 \text{ m}^{-2}) \), respectively; \( N_d \) represents the carrier density of the catalysts, \( A \) is the efficient area of electrode, \( V \) and \( V_{fb} \) are the applied working potential and the flat band potential, respectively; \( k \) is the Boltzmann constant, \( T \) donates the absolute temperature, and \( e \) is the electron charge \( (1.602 \times 10^{-19} \text{ C}) \).

In Figure 8d, a positive slope of M–S plot is observed, inferring a \( n \)-type semiconductor of \( \text{Bi}_2\text{WO}_6 \). In contrast, the negative slope of the M-S plot indicates a \( p \)-type behavior of \( \text{Cu}_2\text{O} \) in Figure 8c, which is consistent with the previous reports [36,58]. Meanwhile, the flat band potentials of \( \text{Cu}_2\text{O} \) and \( \text{Bi}_2\text{WO}_6 \) are calculated to be 0.74 and \(-0.18 \) V vs. RHE at \( \text{pH} = 6.8 \), respectively. In Figure 8d, an inverted “V-shape” curve is detected in the \( \text{M}–\text{S} \) plot of \( \text{Cu}_2\text{O}/\text{Bi}_2\text{WO}_6 \), which is attributed to a characteristic curve of the \( p-n \) junction. It demonstrates that two distinct electronic behaviors (\( p \)- and \( n \)-type) are exhibited in the \( \text{Cu}_2\text{O}/\text{Bi}_2\text{WO}_6 \) photoelectrode. Moreover, a slight shift of \( x \) intercept in \( \text{Cu}_2\text{O}/\text{Bi}_2\text{WO}_6 \) occurs, implying the band realignment of \( \text{Cu}_2\text{O} \) and \( \text{Bi}_2\text{WO}_6 \).

The photocatalytic water oxidation performances of these prepared samples are presented in Figure 9. As shown in Figure 9a, the \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) heterojunctions display significantly enhanced \( \text{O}_2 \) evolution activities in comparison with the sole \( \text{Bi}_2\text{WO}_6 \) and \( \text{Cu}_2\text{O} \) QDs under simulated solar light irradiation. The incorporation of \( \text{Cu}_2\text{O} \) QDs improves the adsorption ability for visible light (Figure 7) as well as electrical conductivity of the prepared \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) heterojunctions (Figure 8a), thereby resulting in the enhancement of photocatalytic activity towards water oxidation under solar light irradiation, as the 1.5 wt% \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) heterojunction shown in Figure 9a. Meanwhile, the 3 wt% \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) heterojunction exhibits the best photocatalytic water oxidation performance, up to 50 \( \mu \text{mol} / \text{L} \) within 3 h, which is 2.1 and 6.1 times higher than that of pure \( \text{Bi}_2\text{WO}_6 \) and \( \text{Cu}_2\text{O} \) QDs, respectively. Furthermore, the initial \( \text{O}_2 \) evolution rate of the 3 wt% \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) heterojunction reaches 329 \( \mu \text{mol h}^{-1} \text{ g}^{-1} \), which is 2.3 and 9.7 fold that of sole \( \text{Bi}_2\text{WO}_6 \) and \( \text{Cu}_2\text{O} \) QDs system, respectively (Figure 9b), and is also superior to the reports in the literature (Table 1). However, excessive Cu(II) dosage (6wt%) is harmful for the dispersion of \( \text{Cu}_2\text{O} \) QDs and causes the aggregation, leading to deteriorated catalytic performance. For the stability of the heterojunction system, as the recycling tests shown in Figure 9c, the photocatalytic performance of the 3 wt% \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) hybrid fades to some extent due to the excess deposition of \( \text{Ag}^+ \) ions at the surface of heterojunction, but it still maintains good long-term stability and reuse potentiality. As a result, in Figure 9d, the 3 wt% \( \text{Cu}_2\text{O} \) QDs/\( \text{Bi}_2\text{WO}_6 \) hybrid exhibits a sustainable photocatalytic \( \text{O}_2 \) production capacity from water splitting.
Figure 9. (a) Photocatalytic water oxidization performance and (b) initial O$_2$ evolution rate of these as-synthesized Cu$_2$O/Bi$_2$WO$_6$ heterojunctions. (c) Recycling curves and (d) stability test of the 3 wt% Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction.

Table 1. Comparison of photocatalytic O$_2$ evolution performance between the 3 wt% Cu$_2$O/Bi$_2$WO$_6$ heterojunction and literature reports.

| Catalysts                  | Light Source                  | O$_2$ Evolution Rate in First Hour (μmol h$^{-1}$ g$^{-1}$) | Stability | Ref. |
|----------------------------|-------------------------------|------------------------------------------------------------|-----------|------|
| BpCo-COF-1                 | 300 W Xe lamp (λ > 420 nm)    | 152                                                        | 4 h       | [59] |
| IrO$_x$-am@TiO$_2$         | LED-405 lamp                  | 143.6                                                      | 4 h       | [60] |
| Mn-BiFeO$_3$               | 300 W Xe lamp (λ > 420 nm)    | 255                                                        | 6 h       | [61] |
| BP/BiVO$_4$                | 300 W Xe lamp (λ > 420 nm)    | 102                                                        | 3 runs, 9 h | [62] |
| BiFeO$_3$                  | 300 W Xe lamp (λ > 420 nm)    | 82.2                                                      | 5 h       | [63] |
| O$_x$-BiVO$_4$/rGO        | 300 W Xe lamp (λ > 420 nm)    | 180                                                        | 3 runs, 15 h | [64] |
| Sol-10BP/BiOBr            | 300 W Xe lamp (λ > 420 nm)    | 89.5                                                      | 4 runs, 16 h | [65] |
| V$_{Bi}$-rich Bi$_2$WO$_6$ | 300 W Xe lamp (λ > 420 nm)    | 100.13                                                   | 9 h       | [66] |
| KCu$_2$Nb$_2$O$_{10}$/CoFe-PB | 300 W Xe lamp (λ > 420 nm) | 89                                                        | 4 runs, 12 h | [67] |
| S-BiOCl                   | 200 W Xe lamp (λ > 420 nm)    | 142                                                      | 5 runs, 25 h | [68] |
| 3 wt% Cu$_2$O/Bi$_2$WO$_6$ | 200 W Xe lamp (λ > 420 nm)    | 329                                                      | 4 runs, 12 h | This work |

For the 3 wt% Cu$_2$O QDs/Bi$_2$WO$_6$ S-scheme heterojunction, the EPR results are displayed in Figure 10, where the signals attributed to the hydroxyl radicals (·OH) and superoxide radicals (·O$_2^-$) are detected. As shown in Figure 10a, the characteristic four peaks caused by the existence of DMPO–OH$^-$ adduct are observed, apparently, which demonstrates that water molecular adsorbed on the surface of photocatalyst could efficiently react with the photoinduced holes and form ·OH [69]. On the other hand, in Figure 10b, the characteristic six peaks are clearly found, which is ascribed to the superoxide radical [70]. It is demonstrated that both of ·OH and ·O$_2^-$ can be efficiently produced over the Cu$_2$O QDs/Bi$_2$WO$_6$ hybrids under the solar light irradiation.
As described in Figure 11b, the separated photoinduced holes at the VB of Bi$_2$WO$_6$ photocatalytic water oxidization on the Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction under simulated sunlight production. The retained electrons at the CB of Cu$_2$O are quenched by Ag$^+$ ions. Therefore, the construction of Cu$_2$O and oxidative holes at the VB of Bi$_2$WO$_6$ are efficiently retained simultaneously. Unfortunately, the VB potential of Cu$_2$O is situated at +0.83 eV, which is quite low and makes it hard to guarantee enough oxidative potential to oxidize water and produce gaseous O$_2$ [71]. Therefore, it is concluded that the Cu$_2$O QDs/Bi$_2$WO$_6$ hybrids might tend to construct a novel S-scheme band structure, as presented in Figure 11a. The photoinduced electrons at the CB of Bi$_2$WO$_6$ are likely to quench the holes at the VB of Cu$_2$O. Subsequently, the stronger reductive electrons at the CB of Cu$_2$O and oxidative holes at the VB of Bi$_2$WO$_6$ are efficiently retained simultaneously. As described in Figure 11b, the separated photoinduced holes at the VB of Bi$_2$WO$_6$ react with the adsorbed H$_2$O at the surface of hybridized system to generate O$_2$, and the retained electrons at the CB of Cu$_2$O are quenched by Ag$^+$ ions. Therefore, the construction of an S-scheme heterojunction is conducive to inhibiting the recombination efficiency of the photoinduced charge carriers, giving rise to more photogenerated holes taking part in the photocatalytic reactions, thereby enhancing the photocatalytic efficiency towards O$_2$ production.

Based on the above results, two types of II or S-scheme heterojunction can be built between Cu$_2$O QDs and Bi$_2$WO$_6$. Once the type II heterojunction is constructed, the trend of photoinduced charge carriers is for photogenerated holes at the VB of Bi$_2$WO$_6$ to migrate to the VB of Cu$_2$O; correspondingly, the photoinduced electrons at the CB of Cu$_2$O transfer to the CB of Bi$_2$WO$_6$. Consequently, photoinduced holes and electrons gather at the CB of Bi$_2$WO$_6$ and VB of Cu$_2$O, respectively. Unfortunately, the VB potential of Cu$_2$O is situated at +0.83 eV, which is quite low and makes it hard to guarantee enough oxidative potential to oxidize water and produce gaseous O$_2$ [71]. Therefore, it is concluded that the Cu$_2$O QDs/Bi$_2$WO$_6$ hybrids might tend to construct a novel S-scheme band structure, as presented in Figure 11a. The photoinduced electrons at the CB of Bi$_2$WO$_6$ are likely to quench the holes at the VB of Cu$_2$O. Subsequently, the stronger reductive electrons at the CB of Cu$_2$O and oxidative holes at the VB of Bi$_2$WO$_6$ are efficiently retained simultaneously. As described in Figure 11b, the separated photoinduced holes at the VB of Bi$_2$WO$_6$ react with the adsorbed H$_2$O at the surface of hybridized system to generate O$_2$, and the retained electrons at the CB of Cu$_2$O are quenched by Ag$^+$ ions. Therefore, the construction of an S-scheme heterojunction is conducive to inhibiting the recombination efficiency of the photoinduced charge carriers, giving rise to more photogenerated holes taking part in the photocatalytic reactions, thereby enhancing the photocatalytic efficiency towards O$_2$ production.

Figure 10. EPR spectra of DMPO-OH· (a) and DMPO-O$_2$· (b) of the 3 wt% Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction.

Figure 11. Proposed mechanisms of (a) construction of the novel S-scheme band structure and (b) photocatalytic water oxidization on the Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction under simulated sunlight irradiation.
4. Conclusions

In summary, we successfully prepared Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunctions by coupling hierarchical Bi$_2$WO$_6$ MFs with Cu$_2$O QDs to construct efficient S-scheme heterojunctions, which could facilitate the migration of photoinduced charge carriers. The electrochemical properties are investigated to explore the transportation performance and donor density of charge carriers in the S-scheme heterojunction system. The results indicate that the synthesized S-scheme heterojunction shows improved photocatalytic activity for water oxidation compared with the sole Bi$_2$WO$_6$ and Cu$_2$O QDs systems under simulated solar light illumination. The initial O$_2$ evolution rate of the heterojunction system is 2.3 and 9.7 fold that of sole Bi$_2$WO$_6$ and Cu$_2$O QDs system, respectively. Furthermore, it is evidently demonstrated that both of ·OH and ·O$_2^−$ can be generated efficiently over the Cu$_2$O QDs/Bi$_2$WO$_6$ heterojunction under the simulated solar light illumination.

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