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In situ surface-trap passivation of CuBi₂O₄ photocathodes for unbiased solar water splitting†

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Passivating surface traps plays a crucial role in mitigating the efficiency loss of solar water-splitting electrodes. However, the associated surface-trap passivation approaches require the introduction of an overlayer, complicating the fabrication process and increasing the capital cost of photoelectrodes. Herein, using CuBi₂O₄ as a prototype, an *in situ* surface-trap passivation strategy is developed, which yields a beneficial 90 mV anodic shift in hydrogen-evolution onset. Detailed mechanism investigations prove that the intentionally added Mg²⁺ ions in the precursor gradually segregate as MgO and enrich at the grain boundaries/surface of the CuBi₂O₄ multicrystalline, porous film during annealing, *via* which surface traps stemming from dangling bonds are spontaneously passivated; measurements of photovoltage generation characteristics and carrier lifetime validate the favorable roles of the MgO passivator in CuBi₂O₄ photocathodes. A bias-free water-splitting device is assembled using MgO-passivated CuBi₂O₄ and Mo-doped BiVO₄ as the photocathode and photoanode respectively in a tandem configuration, delivering a solar-to-hydrogen conversion efficiency of approximately 0.41%.

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Introduction

Photoelectrochemical (PEC) water splitting, which directly captures and converts renewable solar energy to green hydrogen, is a promising approach to mitigate the increasingly urgent energy crisis and severe environmental pollution stemmed from excessive consumption of fossil fuels.^{1–7} To enable large-scale application of PEC water splitting, numerous efforts have been devoted to seeking and developing high-efficiency, earth abundant and stable semiconductor electrodes in the past few decades.^{8–13} Metal oxides have attracted much attention due to their high crustal abundance and stability in ambient environments.^{14–18} However, most of the metal oxides, such as TiO₂ (~3.0 eV),^{19,20} WO₃ (~2.6 eV),^{21,22} BiVO₄ (~2.4 eV),^{23–28} and Fe₂O₃ (~2.1 eV),^{29–34} show n-type semiconducting characteristics and thereby could serve as water-oxidation photoanodes. Comparatively, metal oxides with p-type conductivity and suitable for construction of water-reduction photocathodes are relatively limited, prohibiting the development of high-

performance all oxide-based bias-free solar water splitting systems/devices.

Recently, a p-type metal oxide of CuBi₂O₄ was identified as a promising photocathode candidate, due to its favorable bandgap of about 1.8 eV, sufficiently positive flat band potential at about 1.2 V *vs.* the reversible hydrogen electrode (RHE) and air processibility.^{35–37} In principle, CuBi₂O₄ could produce a water-reduction photocurrent of 19 mA cm⁻² under AM 1.5 G 1-sun conditions, yet the reported performances of CuBi₂O₄ photocathodes are far from the theoretical value.^{38,39} This phenomenon can be rationalized by the highly mismatched light penetration depths (about 280 nm for the 550 nm photon) and charge carrier diffusion lengths (10–50 nm) of CuBi₂O₄.^{40–43} By shortening the migration lengths of minority carriers and increasing the volume ratio of the space-charge region to the electrode bulk, nanostructuring could be an available strategy to address the above issue for CuBi₂O₄ photocathodes.⁴⁴ However, unfavorable surface traps/states with energy levels in the band gap may develop for CuBi₂O₄ photocathodes upon nanostructuring, due to the increased densities of dangling bonds and defects, and contribute to Fermi level pinning thereby enhancing charge carrier recombination. Therefore, the beneficial effects of nanostructuring are generally cancelled out by the detrimental influences of surface traps/states, making nanostructured CuBi₂O₄ photocathodes less efficient for water reduction.

The above challenge faced by nanostructured CuBi₂O₄ photocathodes could be circumvented by depositing a thin passivation overlayer, as has been extensively investigated for

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α -Fe₂O₃ photoanodes.^{45,46} Although this surface-trap passivation scheme is effective, it usually involves the use of complicated post-treatment processes such as atomic layer deposition, chemical bath deposition and physical vapor deposition. If the surface traps/states on nanostructured CuBi₂O₄ photocathodes could be *in situ* passivated/ameliorated during the electrode fabrication/formation procedure, it would be more intriguing and cost-effective. Herein, by introducing appropriate amounts of Mg²⁺ ions into the precursor solution, *in situ* developed MgO segregations during the annealing step locate at the surface/grain boundaries of CuBi₂O₄ and serve as effective surface-trap passivators. The resulting MgO-passivated CuBi₂O₄ photocathode shows improved H₂ evolution activity at more anodic potentials when compared to the pristine one, and meanwhile allows combination with the Mo-doped BiVO₄ photoanode to drive bias-free overall water splitting under light illumination.

Results and discussion

All CuBi₂O₄ photocathodes were synthesized *via* a metal-organic decomposition method; varied amounts of Mg(NO₃)₂·6H₂O were added into the precursor solution to form Mg-modified CuBi₂O₄ photocathodes. The fabrication process of Mg-modified CuBi₂O₄ photocathodes is schematically illustrated in Fig. 1a. Fig. 1b shows the PEC water reduction performances of CuBi₂O₄ and Mg-modified CuBi₂O₄ (with 1%, 3%, 5%, 7%, 10% of Mg) photocathodes in a KB₁ electrolyte (pH 9.2) under AM 1.5 G simulated sunlight irradiation. As depicted by the *J*-*V* characteristics, when the introduced amounts of Mg are less than 3%, the water reduction activities of CuBi₂O₄ and Mg-modified CuBi₂O₄ photocathodes are essentially identical. Adding more Mg (5%, 7% and 10%) offers CuBi₂O₄ photocathodes with largely improved performances; among them, 5% and 7% of Mg-modified CuBi₂O₄ photocathodes deliver the highest onset potentials at about 1.15 V *vs.* RHE, and the latter electrode also shows the highest saturation photocurrent density of -0.2 mA cm⁻² at 0.7 V *vs.* RHE. The photocurrent

densities (at 0.7 and 1 V *vs.* RHE) and photocurrent onsets of CuBi₂O₄ and Mg-modified CuBi₂O₄ photocathodes are summarized in Fig. 1c and d. As 7% of introduced Mg affords the CuBi₂O₄ photocathode the highest photocurrent density along with a 90 mV positive shift in onset potential, it is denoted as Mg-CuBi₂O₄ hereafter and subjected to further characterization studies.

XRD patterns collected on CuBi₂O₄ and Mg-CuBi₂O₄ electrodes are shown in Fig. 2a and S1.† Besides signals from FTO substrates, all other diffraction peaks are readily assigned to tetragonal CuBi₂O₄ (JCPDS 42-0334). Interestingly, no observable shift of XRD peaks can be detected in Mg-CuBi₂O₄ electrodes compared to the pristine CuBi₂O₄ film, indicating that introduced Mg does not occupy Cu or Bi sites in the lattice of CuBi₂O₄. On the other hand, no MgO or its related phase/component can be resolved by XRD, possibly due to its low content in the Mg-CuBi₂O₄ composite electrode (Fig. S2†). Raman spectra of both CuBi₂O₄ and Mg-CuBi₂O₄ electrodes show sharp characteristic peaks of CuBi₂O₄ at 134, 261, 400, and 577 cm⁻¹ (Fig. 2b), confirming the formation of well crystalline CuBi₂O₄ films; again, no Raman peaks belonging to MgO can be probed in the Mg-CuBi₂O₄ electrode. Therefore, it is hypothesized that the introduced low-content Mg in the Mg-CuBi₂O₄ electrode may exist in the form of MgO nanoparticles and distribute uniformly in the matrix of the CuBi₂O₄ film. Light harvesting efficiency measurements on CuBi₂O₄ and Mg-CuBi₂O₄ electrodes reveal their almost identical photon capturing abilities in the tested wavelength range, suggesting a minor contribution of MgO to the light absorption process of CuBi₂O₄ (Fig. 2c). In addition, both CuBi₂O₄ and Mg-CuBi₂O₄ electrodes display an absorption edge of *ca.* 682 nm, corresponding well to the bandgap of tetragonal CuBi₂O₄ (1.85 eV, Tauc plot in inset of Fig. 2c).

XPS characterization studies were carried out to investigate the compositions and chemical bond information of CuBi₂O₄ and Mg-CuBi₂O₄ electrodes. As shown in Fig. 2d, both electrodes display spin-orbit doublets at 953.7 and 933.8 eV along with two shake-up satellite peaks in the Cu 2p spectra,

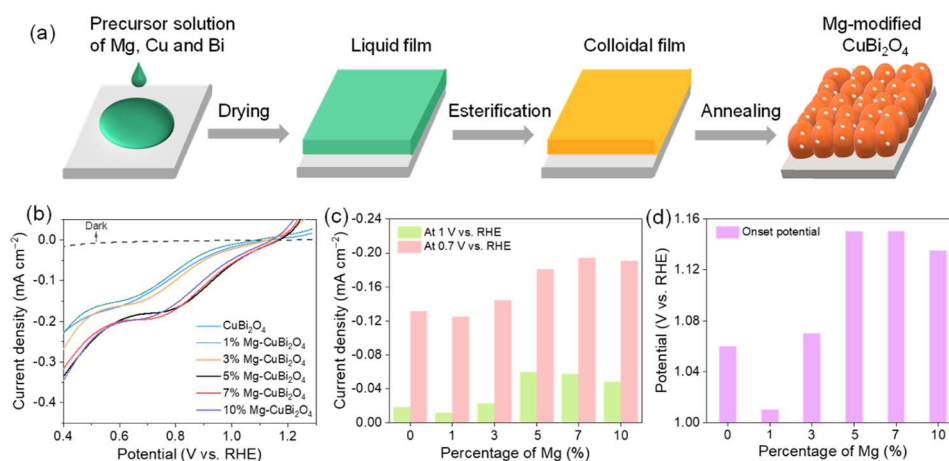


Fig. 1 (a) Schematic illustration of the synthetic process of Mg-modified CuBi₂O₄ photocathodes. (b) *J*-*V* curves of CuBi₂O₄ and Mg-modified CuBi₂O₄ photocathodes in KB₁ (pH = 9.2); the corresponding (c) photocurrent densities at 0.7 and 1 V *vs.* RHE and (d) onset potentials.

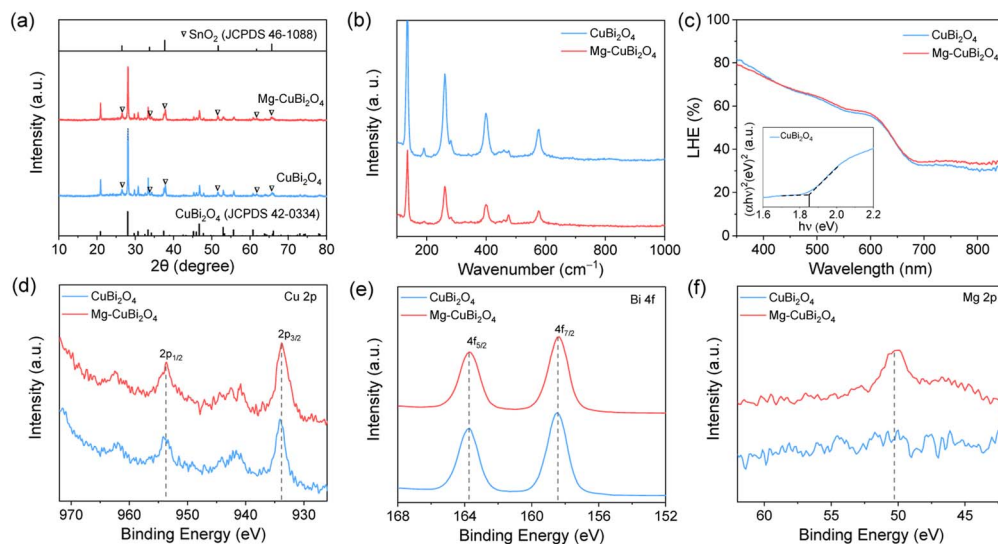


Fig. 2 (a) XRD patterns (triangles: peaks of FTO), (b) Raman spectra and (c) UV-vis absorption spectra (inset: Tauc plots, $(\alpha h\nu)^2$ as a function of $h\nu$) of CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ photocathodes. XPS spectra of (d) Cu 2p, (e) Bi 4f and (f) Mg 2p orbits in CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ samples.

suggesting an almost identical environment and oxidation state (+2) of Cu in them. In the Bi 4f region (Fig. 2e), both electrodes exhibit binding energies of 163.7 and 158.4 eV, which can be assigned to $4f_{5/2}$ and $4f_{7/2}$ of the Bi element with a valence state of +3. The O 1s spectra of the two electrodes can be deconvoluted into two peaks at 531.3 and 529.3 eV (Fig. S3†), which correspond to adsorbed hydroxyl species and lattice oxygen, respectively. As expected, a Mg signal is only detected on the $\text{Mg-CuBi}_2\text{O}_4$ electrode (Fig. 2f), the position of which (at ~ 50.6 eV) points to the presence of MgO. The above XPS analyses demonstrate that the chemical states of Cu, Bi and O in CuBi_2O_4 are not altered upon the introduction of Mg, and these Mg species form MgO instead of dopants in the CuBi_2O_4 film matrix.

As revealed by SEM observations, both CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ electrodes have porous structures, with particle sizes in the range of 100–300 nm (Fig. 3a and b and S4†). Such a film morphology is favorable for the collection of minority charge carriers. The firmly interconnected film particles along with high crystallinity, on the other hand, facilitate efficient transport of majority carriers in CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ electrodes.^{47–49} In sharp contrast to the pristine CuBi_2O_4 electrode which exhibits a relatively smooth particle surface, a large quantity of white spots appear on the $\text{Mg-CuBi}_2\text{O}_4$ electrode. These nanoparticles could be *in situ* generated MgO segregations, the formation and distribution of which are confirmed by the energy dispersive X-ray spectroscopy (EDS) elemental mapping characterization studies.

To further investigate the characteristics of CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ electrodes, and probe the nature and distribution of the segregated nanoparticles in $\text{Mg-CuBi}_2\text{O}_4$, HR-TEM and EDS analyses were performed on CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ particles peeled from the corresponding electrodes. As depicted by Fig. S5†, sphere-like CuBi_2O_4 particles with a smooth surface are observed, and the measured lattice spacing of 0.190 nm

agrees well with the (4 2 0) plane of tetragonal CuBi_2O_4 . Bright diffraction spots are obtained in the selected area electron diffraction pattern, demonstrating the high crystallinity of CuBi_2O_4 particles, which is also consistent with XRD and

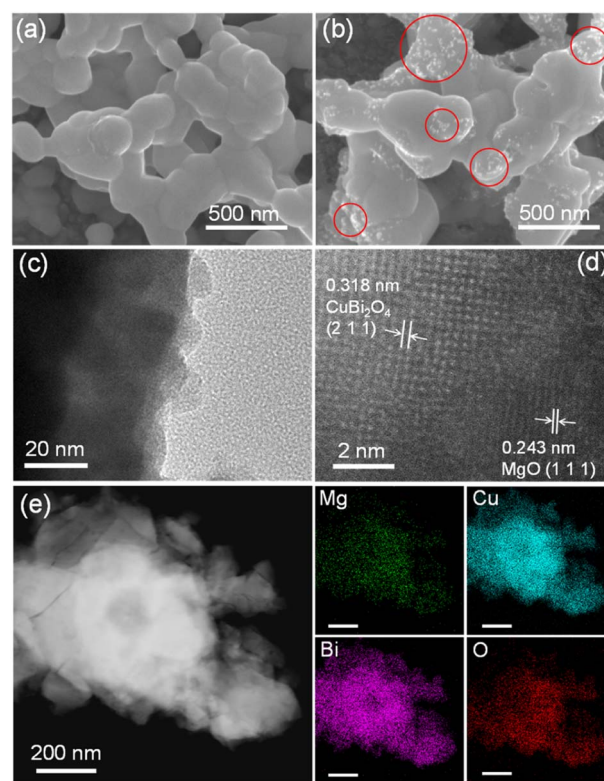


Fig. 3 SEM images of (a) CuBi_2O_4 and (b) $\text{Mg-CuBi}_2\text{O}_4$ films (several MgO particles are marked by red circles). (c) TEM (inset: SAED) and (d) HR-TEM images of $\text{Mg-CuBi}_2\text{O}_4$. (e) EDS elemental mappings of the $\text{Mg-CuBi}_2\text{O}_4$ sample (scale bar: 200 nm).

Raman characterization studies. In terms of $\text{Mg-CuBi}_2\text{O}_4$, particles with sizes of several to several tens of nm are observed to distribute randomly on the surface of $\text{Mg-CuBi}_2\text{O}_4$ particles (Fig. 3c), and the calculated interplanar spacing of 0.243 nm accords well with the (1 1 1) plane of MgO (Fig. 3d). Therefore, the introduced Mg in the $\text{Mg-CuBi}_2\text{O}_4$ electrode exists in the form of MgO nanoparticles, which distribute uniformly on the $\text{Mg-CuBi}_2\text{O}_4$ particle surface as demonstrated by EDS elemental mapping analyses (Fig. 3e and S6†).

To understand how the presence of segregated MgO nanoparticles affects the water reduction performance of the CuBi_2O_4 photocathode, charge separation efficiencies (η_{sep}) of CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ photocathodes were measured. As shown in Fig. 4a, the η_{sep} values of the $\text{Mg-CuBi}_2\text{O}_4$ photocathode are higher than those of the pristine CuBi_2O_4 photocathode at all applied potentials. Specially, η_{sep} of the $\text{Mg-CuBi}_2\text{O}_4$ photocathode increases from 0.5% at 1.1 V vs. RHE to 5.4% at 0.6 V vs. RHE, while those for the CuBi_2O_4 photocathode are 0.1% at 1.1 V vs. RHE to 3.2% at 0.6 V vs. RHE, respectively. The larger ΔOCP (difference of open-circuit potential in the dark and under light) of the $\text{Mg-CuBi}_2\text{O}_4$ photocathode (0.213 V) than that of the pristine CuBi_2O_4 photocathode (0.086 V) further confirms the enhanced charge separation and band bending of $\text{Mg-CuBi}_2\text{O}_4$ compared to CuBi_2O_4 (Fig. 4b). Furthermore, the measurement of ΔOCP also provides a means to extract charge carrier recombination lifetimes and thereby understand the quality of the electrode/electrolyte junction. Under open-circuit

conditions, upon switching from the quasi-equilibrium of illumination to the dark equilibrium, the charge carrier recombination is largely dominated by the built-in electric field (band bending) of the space charge layer. The larger the band bending is, the faster the charge carrier recombination occurs at the transient of light-off. The charge carrier recombination lifetime is quantified using the following equation:

$$\tau = -\frac{k_B T}{e} \left(\frac{d\Delta\text{OCP}}{dt} \right)^{-1}$$

where τ is the charge carrier recombination lifetime, k_B is the Boltzmann constant, T is the temperature and e is the elementary charge.⁵⁰ As shown in Fig. 4c, the calculated carrier recombination lifetime for the pristine CuBi_2O_4 photocathode is ca. 100 ms at the transient of light-off under open-circuit conditions. Comparatively, under the same conditions the carrier recombination lifetime of the $\text{Mg-CuBi}_2\text{O}_4$ photocathode is ca. 26 ms. Therefore, the faster ΔOCP decay kinetics of the $\text{Mg-CuBi}_2\text{O}_4$ photocathode demonstrates the better quality of the electrode/electrolyte junction (or larger band bending) than that of the pristine CuBi_2O_4 photocathode. The substantially enhanced photovoltage generation of the $\text{Mg-CuBi}_2\text{O}_4$ electrode at above-bandgap excitation than that of the pristine CuBi_2O_4 electrode further supports this hypothesis (Fig. 4d).

Using Mott-Schottky analysis, the possible effects of Mg as an acceptor-type dopant have been excluded (Fig. S7†). It is therefore reasonable to propose that these segregated MgO

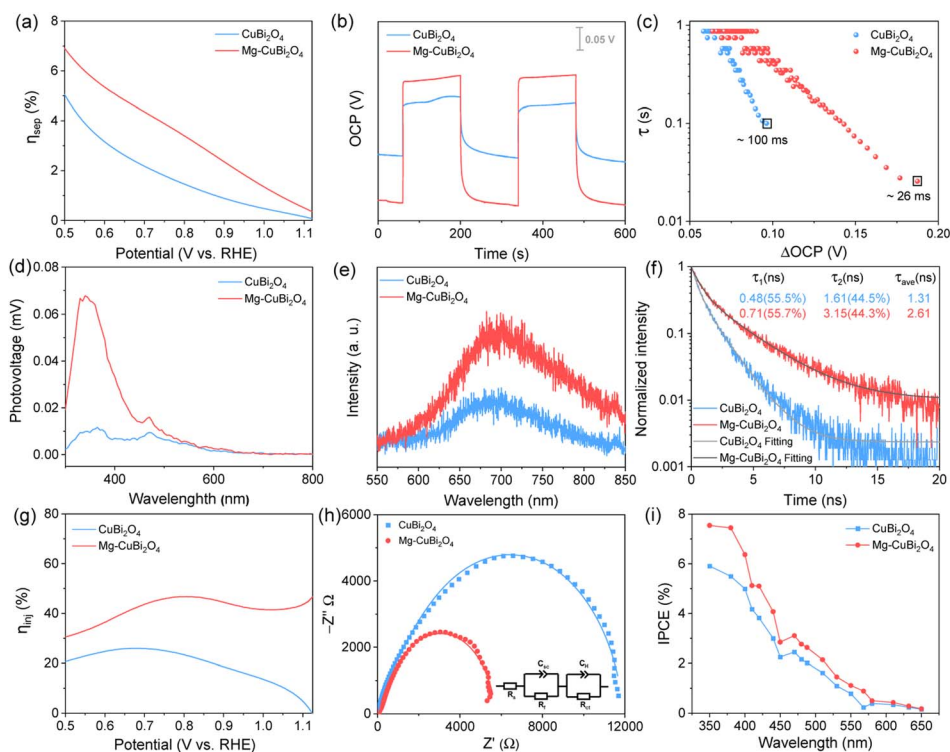


Fig. 4 (a) Charge separation efficiency (η_{sep}), (b) open-circuit potential (OCP) values, (c) carrier lifetime as a function of ΔOCP originated from OCP-decay curves when turning off light, (d) surface photovoltage curves, (e) steady-state PL spectra, (f) TRPL spectra, (g) surface charge injection efficiency (η_{inj}), (h) Nyquist plots (inset: the equivalent circuit for the samples), and (i) IPCE spectra of the CuBi_2O_4 and $\text{Mg-CuBi}_2\text{O}_4$ photocathodes.

nanoparticles may play a role in surface-trap passivation, *via* which Fermi level pinning is lessened and band bending (built-in electric field) in the Mg-CuBi₂O₄ photocathode is enhanced. Photoluminescence (PL) and time-resolved PL (TRPL) measurements were conducted to investigate the defects and trap states in CuBi₂O₄ and Mg-CuBi₂O₄ electrodes. Both CuBi₂O₄ and Mg-CuBi₂O₄ samples exhibit a PL emission peak at 692 nm, which agrees well with the bandgap of tetragonal CuBi₂O₄. Compared to pristine CuBi₂O₄, enhanced PL intensity is obtained on the Mg-CuBi₂O₄ sample (Fig. 4e). Meanwhile, the carrier lifetime of Mg-CuBi₂O₄ (2.61 ns) extracted from its exponentially decayed TRPL signal is about twice that of pristine CuBi₂O₄ (1.31 ns), as shown in Fig. 4f. The greatly enhanced PL intensity and prolonged PL lifetime of Mg-CuBi₂O₄ over CuBi₂O₄ suggest that the presence of segregated MgO nanoparticles indeed leads to a reduced density of trap states and a suppressed carrier recombination rate in the Mg-CuBi₂O₄ photocathode.

The surface water reduction behaviors of CuBi₂O₄ and Mg-CuBi₂O₄ photocathodes were evaluated by probing their charge injection efficiency (η_{inj}) curves (Fig. 4g). Substantially increased η_{inj} values are observed on the Mg-CuBi₂O₄ photocathode compared with the pristine CuBi₂O₄ photocathode, especially at more positive potentials. Specifically, at an applied potential of 0.6 V *vs.* RHE, the η_{inj} values for CuBi₂O₄ and Mg-CuBi₂O₄ photocathodes are 24.8% and 36.5%, respectively; at 0.8 V *vs.* RHE, the η_{inj} value for the Mg-CuBi₂O₄ photocathode is almost double that of the pristine CuBi₂O₄ photocathode (46.7% *vs.* 23.4%). Photo-assisted electrochemical impedance spectroscopy (PEIS) measurements were also performed to analyze the interfacial charge transfer behaviors of CuBi₂O₄ and Mg-CuBi₂O₄ photocathodes. The collected Nyquist curves shown in Fig. 4h reveal that the charge transfer resistance (R_{ct}) of the pristine CuBi₂O₄ photocathode is *ca.* 2 times as large as that of

the Mg-CuBi₂O₄ photocathode. The above η_{sep} , ΔOCP , η_{inj} and PEIS results together suggest that surface trap states stemming from surface dangling bonds of CuBi₂O₄ not only cause Fermi level pinning thereby suppressing charge carrier separation in the CuBi₂O₄ film bulk, but also retard water reduction kinetics at the CuBi₂O₄ surface, as schemed in Fig. S8a†. Using *in situ* developed MgO segregations, surface traps of the CuBi₂O₄ electrode are effectively passivated, giving rise to enhanced charge separation in the bulk and accelerated charge transfer kinetics at the surface of the CuBi₂O₄ electrode simultaneously, as illustrated in Fig. S8b.†

IPCE spectra of CuBi₂O₄ and Mg-CuBi₂O₄ electrodes were measured at 0.6 V *vs.* RHE in KB₁ solution. As shown in Fig. 4i, both IPCE curves of CuBi₂O₄ and Mg-CuBi₂O₄ electrodes exhibit a monotonic decrease trend from 350 to 650 nm, and the onset wavelength of *ca.* 650 nm matches closely with their light absorption curves. Compared to that on the pristine CuBi₂O₄ photocathode, the overall profile of the photocurrent action spectrum on the CuBi₂O₄ photocathode improves obviously, consistent with the *J-V* measurements in Fig. 1b. The *i-t* curves displayed in Fig. S9† reveal that the water reduction performance of the Mg-CuBi₂O₄ photocathode is always higher than that of pristine CuBi₂O₄ across the entire test, demonstrating the positive roles of segregated MgO nanoparticles in the Mg-CuBi₂O₄ photocathode; the rapid decrease of photocurrents at the initial stage may result from poor water reduction kinetics at the CuBi₂O₄ surface. In addition, the results of XRD and SEM demonstrated that the structure and morphology remain stable during the reaction (Fig. S10 and S11†).

Based on the above analyses, the roles played by spontaneously segregated MgO nanoparticles in the Mg-CuBi₂O₄ photocathode can be understood as follows. In an ideal case, the photogenerated electrons in the conduction band of p-type CuBi₂O₄ would migrate to the electrode surface to drive the

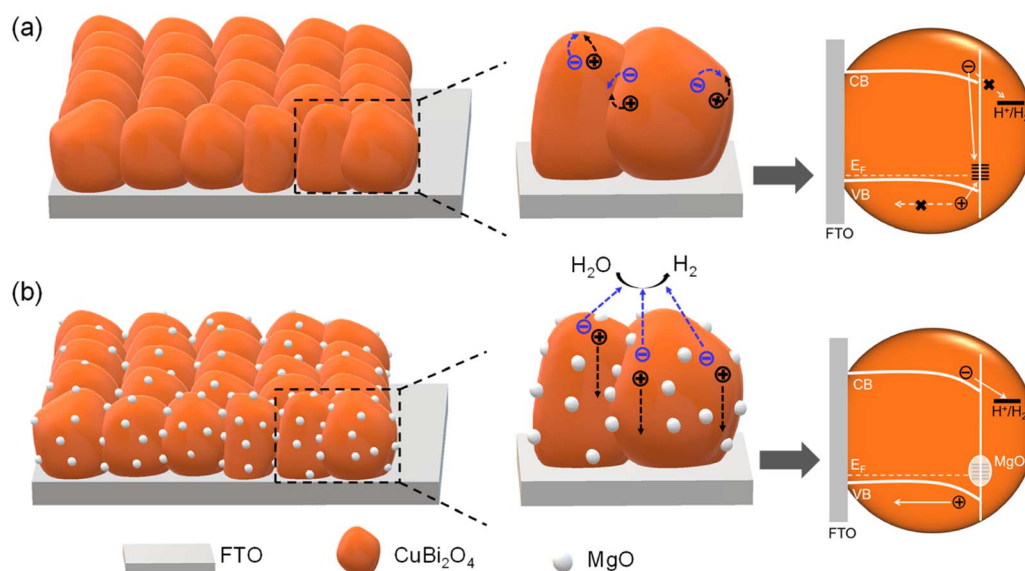


Fig. 5 Schematic diagram of the role of MgO in the PEC water reduction on CuBi₂O₄ photocathodes: carrier transport and energy bands of (a) CuBi₂O₄ and (b) Mg-CuBi₂O₄ photocathodes.

water reduction reaction under the action of the built-in electric field; the photogenerated holes in the valence band would transport to the counter electrode to oxidize water. In practice, to address the issue of mismatched light penetration depths and charge carrier diffusion lengths, nanostructured CuBi_2O_4 photocathodes are usually employed and excess dangling bonds are then created on the CuBi_2O_4 photocathode surface and form trap states. Under this condition, the built-in electric field (band bending) is deteriorated and photogenerated electrons are easily captured by surface trap states, which lead to increased carrier recombination, delayed photocurrent onset and suppressed saturation photocurrents on nanostructured CuBi_2O_4 photocathodes (Fig. 5a). By introducing Mg^{2+} ions in the precursor solution, MgO nanoparticles segregate and enrich at the grain boundaries/surface of the CuBi_2O_4 photocathode during the single-pass fabrication procedure. These spontaneously segregated MgO nanoparticles would eliminate (part of) the dangling bonds thereby reducing the trap-state density on the CuBi_2O_4 photocathode surface. Under this condition, an enhanced built-in electric field (band bending) and accelerated charge transfer kinetics are achieved on the $\text{Mg-CuBi}_2\text{O}_4$

photocathode, leading to increased saturation photocurrents and a positively shifted onset potential (Fig. 5b). When used as the passivator, MgO has the following advantages. First, its large bandgap (about 7.8 eV) ensures that MgO will not interfere with the light absorption of CuBi_2O_4 . Second, MgO exhibits good chemical and electrochemical stability, which would sustain its functions during long-term operation. Third, as an oxyphilic element, Mg would be strongly bonded to oxygen, thus efficiently reducing the density of surface dangling bonds on the CuBi_2O_4 photocathode.

Due to its favorable hydrogen-evolution onset potential, the $\text{Mg-CuBi}_2\text{O}_4$ photocathode was series-connected with a classical Mo-doped BiVO_4 photoanode to assemble a bias-free tandem water-splitting device (Fig. 6a). Overlap between the J - V characteristics of $\text{Mg-CuBi}_2\text{O}_4$ and Mo:BiVO_4 electrodes yields a maximum reachable photocurrent of 0.33 mA cm^{-2} (Fig. 6b), which is increased by 37.5% compared to that of the CuBi_2O_4 - $\parallel\text{Mo:BiVO}_4$ device (Fig. S12[†]). Under AM 1.5 G simulated sunlight and bias-free conditions, a photocurrent of *ca.* 0.28 mA cm^{-2} is generated on the $\text{Mg-CuBi}_2\text{O}_4\parallel\text{Mo:BiVO}_4$ device, demonstrating its ability to drive unbiased overall water splitting (Fig. 6c).

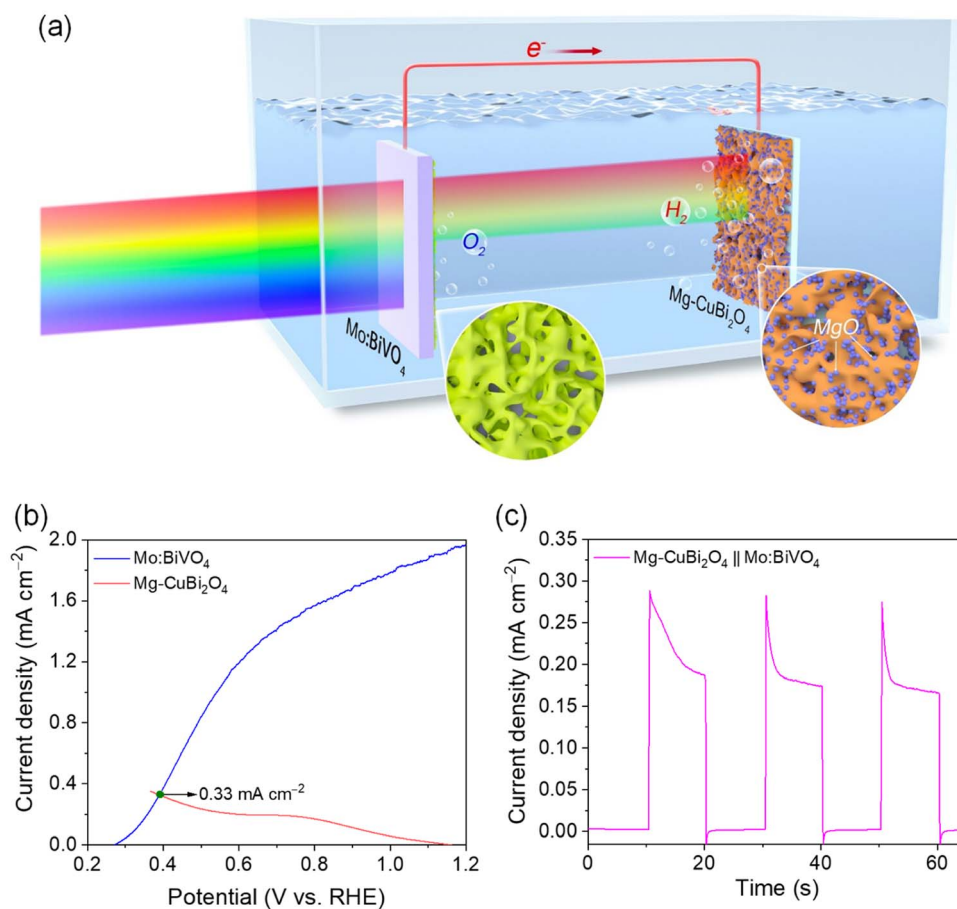


Fig. 6 Performances of the p-n tandem cell: (a) schematic diagram of the $\text{Mg-CuBi}_2\text{O}_4\parallel\text{Mo:BiVO}_4$ tandem cell in operation; (b) J - V curves of a single Mo:BiVO_4 photoanode and a single $\text{Mg-CuBi}_2\text{O}_4$ photocathode; (c) i - t curve of the p-n tandem cell consisting of Mo:BiVO_4 and $\text{Mg-CuBi}_2\text{O}_4$ under continuous illumination at zero bias voltage.

Conclusions

In summary, an *in situ* surface-trap passivation approach for the CuBi_2O_4 photocathode is proposed. It is demonstrated that spontaneously segregated MgO nanoparticles on the CuBi_2O_4 photocathode surface partially eliminate surface-trap states, resulting in increased bulk charge separation and improved interfacial charge transfer characteristics. The as-derived MgO(7%)-passivated CuBi_2O_4 photocathode yields a photocurrent onset of 1.15 V vs. RHE, which is *ca.* 90 mV anodic shift of the pristine CuBi_2O_4 photocathode. When the MgO-passivated CuBi_2O_4 photocathode is combined with a Mo-doped BiVO_4 photoanode to construct a bias-free tandem water-splitting device, a solar-to-hydrogen conversion efficiency of 0.41% is achieved, 37.5% greater than that assembled with a pristine CuBi_2O_4 photocathode. This study identifies MgO as a novel yet effective large-bandgap material for passivating surface traps thereby boosting the performances of water-splitting photoelectrodes. Moreover, the concept of *in situ* surface-trap passivation would flourish the passivating strategies for semiconductor-based devices and inspire cost-effective device manufacturing processes.

Experimental

Materials

Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.99\%$, Aladdin Chemistry Co., Ltd); copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\geq 99\%$, Sinopharm Chemical Reagent Co., Ltd); magnesium(II) nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$, Xilong Chemical Co., Ltd); concentrated nitric acid (HNO_3 , 65–68%, Sinopharm Chemical Reagent Co., Ltd); glacial acetic acid (CH_3COOH , $\geq 99.5\%$, Sinopharm Chemical Reagent Co., Ltd); absolute ethanol ($\text{C}_2\text{H}_6\text{O}$, $\geq 99.7\%$, Sinopharm Chemical Reagent Co., Ltd); boric acid (H_3BO_3 , $\geq 99.5\%$, Nanjing Chemical Reagent Co., Ltd); potassium hydroxide (KOH, $\geq 99.7\%$, Sinopharm Chemical Reagent Co., Ltd) and deionized water were used without further purification.

Preparation of CuBi_2O_4 and Mg-modified CuBi_2O_4 photocathodes

CuBi_2O_4 and Mg-modified CuBi_2O_4 photocathodes were synthesized *via* the metal-organic decomposition method (Fig. 1a). $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in glacial acetic acid (0.1 mol L^{-1}), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in absolute ethanol (0.05 mol L^{-1}) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in absolute ethanol (0.05 mol L^{-1}) were used as precursor solutions. For the preparation of the CuBi_2O_4 film, a certain amount of Cu and Bi solutions were mixed according to a stoichiometric ratio of Cu : Bi = 1 : 2. Then the mixed solution was dropped on FTO substrates ($1 \text{ cm} \times 2 \text{ cm}$), dried at $45 \text{ }^\circ\text{C}$ and then calcined at $600 \text{ }^\circ\text{C}$ in a muffle furnace for 60 min to form CuBi_2O_4 . Mg-modified CuBi_2O_4 electrodes were synthesized by adding 1%, 3%, 5%, 7% and 10% of magnesium (with respect to Bi) to the precursor solutions.

Preparation of Mo-doped BiVO_4 photoanodes

Mo-doped BiVO_4 photoanodes were prepared by a sol-gel method. 1.25 mmol Bi_2O_3 and 1.5 mL HNO_3 were dissolved in 23.5 mL ethylene glycol to obtain 0.1 mol L^{-1} Bi. 2.5 mmol NH_4VO_3 and 1.5 mL HNO_3 were dissolved in 23.5 mL ethylene glycol to form 0.1 mol L^{-1} V. 0.357 mmol $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was added in 23.5 mL ethylene glycol to produce 0.1 M Mo. The precursor solution of Mo-doped BiVO_4 was prepared by mixing 0.2 mmol anhydrous citric acid, 1 mL precursor solution of Bi, and 1 mL precursor solution of V. The mixed solution was dropped on FTO substrates (exposed $1 \text{ cm} \times 1 \text{ cm}$), dried at $90 \text{ }^\circ\text{C}$ for 20 min, then heated at $120 \text{ }^\circ\text{C}$ for 20 min, and then calcined at $520 \text{ }^\circ\text{C}$ for 1 h to synthesize Mo: BiVO_4 photoanodes. The NiFeO_x cocatalyst was loaded on Mo: BiVO_4 photoanodes by a photo-assisted electrodeposition method. Electrolyte for deposition was potassium borate buffer solution (KOH: 0.2 M; H_3BO_3 : 0.4 M) containing 1.5 mmol L^{-1} $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1.5 mmol L^{-1} $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. The applied potential was $-0.14 \text{ V vs. Ag/AgCl}$ by the *i-t* testing method. The total time of deposition was 6 min, during which the light was turned off for 20 s after every 30 seconds of illumination.

Characterization of photoelectrodes

The crystal structures of all the photoelectrodes were detected by X-ray diffraction (XRD, Rigaku Ultima III) with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The light absorption spectra of films were recorded on a UV-visible (UV-vis) spectrophotometer (Shimadzu, UV-vis 2550; PerkinElmer, Lambda 950). The structure of the material and Raman vibrational spectra were measured using a LabRAM ARAMIS Raman spectrometer (HORIBA Scientific). The chemical states of elements were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250). The morphologies and elemental distribution of photocathodes were surveyed using a scanning electron microscope (FEI Nova NanoSEM 230 and ZEISS ULTRA 55). High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analysis were investigated using a transmission electron microscope (JEOL 2100F TEM and an FEI double-aberration corrected Titan G2 60-300S/TEM). Surface photovoltage was surveyed using a surface photovoltage spectrometer (CEL-SPS1000). Photoluminescence (PL) and time-resolved photoluminescence (TRPL) decay spectra were observed using a fluorescence spectrometer (Andor-SR-500i).

Electrochemical characterization studies

PEC performances were measured in a three-electrode cell using an electrochemical workstation (CHI-760E, Shanghai Chenhua). The PEC cell consists of a working electrode (photocathode), a reference electrode (Ag/AgCl electrode) and a counter electrode. The electrolyte was a potassium borate buffer solution (KOH: 0.2 M; H_3BO_3 : 0.4 M). The potential vs. Ag/AgCl was converted to that vs. the reversible hydrogen electrode (RHE). Photocurrents were tested under AM 1.5 G simulated sunlight (100 mW cm^{-2}), from a simulator (Newport Sol3A

Class AAA; CEL-AAAS50, Beijing Zhongjiao Jinyuan Technology Co., Ltd). The light intensity was adjusted using a standard silicon cell (Newport 91150).

Author contributions

Yingfei Hu: investigation, methodology, validation, formal analysis, writing – original draft. Jun Wang: methodology, formal analysis, writing – review & editing. Huiting Huang: data curation, methodology, formal analysis, writing – review & editing. Jianyong Feng: formal analysis, supervision, project administration, writing – original draft. Wangxi Liu: data curation, methodology, formal analysis. Hangmin Guan: resources, formal analysis. Lingyun Hao: resources, formal analysis. Zhaosheng Li: supervision, project administration, funding acquisition, writing – review & editing. Zhigang Zou: supervision, project administration, funding acquisition.

Conflicts of interest

The authors declare no competing financial interest.

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