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Interfacial bonded CuCo₂O₄/TiO₂ nanosheets heterostructures

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Abstract

View Article Online DOI: 10.1039/C9CY01209E

Constructing high-performance, economical and environmentally friendly photocatalysts remains a challenge for the efficient conversion of solar energy. In this work, CuCo₂O₄ nanoparticles modified on TiO₂ nanosheets has been designed and fabricated via a facile hydrothermal method followed by an in situ calcination process. The resultant 10%-CuCo₂O₄/TiO₂ heterostructure exhibited superior photocatalytic activity under full spectra. The H₂ generation rate can reach 4830 µmol g⁻¹ h⁻¹ under 300 W Xe lamp irradiation, which is 32 times higher than that of pristine TiO₂ and the highest increase fold of binary TiO₂-based non-noble system reported so far. Its apparent quantum yield (AQY) value can reach 11.5% at 365 nm. Furthermore, we demonstrate that there are chemical bonds formed at the interface between well-dispersed CuCo₂O₄ and TiO₂ by XPS spectra and electronegativity theory, and the efficient separation of charge carriers due to the p-n junction adopting the interfacial Ti-O-Cu/Co bonds is crucial for the improved performance and photostability. This work develops possibilities to prepare feasible CuCo₂O₄-based heterostructures for energy conversion.

Keywords: CuCo2O4; TiO2 nanosheets; Hydrogen evolution; Interfacial chemical bonds

Introduction

Unsustainable fossil fuels and global environmental pollution caused by burning fossil fuels trigger an upsurge to develop new sources of energy. Hydrogen (H₂) is an ideal alternative for traditional fossil fuels due to its renewable, pollution-free and high-energy intensity features.¹⁻⁶ At present, H₂ production mainly depends on the reforming of coal and natural gas, which will inevitably aggravate the consumption of non-renewable energy and bring environmental pollution. How to produce H₂ rationally has become a research hotspot. Economical, efficient and pollution-free photocatalytic technology based on semiconductors has attracted significant attention. Photocatalytic technology can be used to degrade organic pollutants, reduce heavy metal ions and produce H₂ from water splitting.⁷⁻¹¹

Titanium dioxide (TiO₂) possesses many merits of stability, non-toxicity and abundant reserves, which is the most extensive investigated material in the field of photocatalysis. However, wide band-gap and fast recombination of photoinduced carriers still limit the practical application in solar conversion.¹²⁻¹⁷ Among many strategies, the morphology control has been commonly employed to enhance the activities of TiO₂, such as nanoparticle, nanowire, nanosheet and nanorod etc. Due to unique microstructures and peculiar physicochemical properties, two-dimensional TiO₂ exhibits great potential in photocatalysis. Compared with bulk structures, TiO₂ nanosheets possess larger specific surface areas and highly active surface atoms, which are conducive to the surface adsorption and reaction.¹⁸⁻²³ Nevertheless, poor separation of charge carriers is still the bottleneck restricting its practical application.

Modification of noble metal cocatalysts (e.g. Pt, Au, Ag etc.) as electron donor and acceptor is favor for improving H₂ production due to the formation of Schottky barrier and the decrease of H₂ evolution overpotential.²⁴⁻²⁷ However, the scarcity severely retards their practical application. Compared with

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noble metal, the space electron orbital of transition metals are easy to accept electron pairs and require relatively little energy. Besides, they have strong redox and coordination ability, and the excellent photoelectric properties make them the most promising materials in multiple fields.²⁸⁻³⁰ More recently, transition metal phosphides (TMPs) become an effective resolution to improve the photocatalytic activity of semiconductors. Song et al. used Ni₂P, NiCoP and FeP to improve the performance of TiO₂ nanoparticles.³¹ The H₂ production rates reached 1410, 1540 and 770 µmol h⁻¹ g⁻¹ under optimum condition, which was 12.5, 13.6 and 6.8 times higher than that of bare TiO₂. Yue et al. demonstrated that the efficient separation of photoinduced hole-electron between Cu₃P and TiO₂ can significantly enhances H₂ generation rate.³² Unfortunately, the efficiency of TMP for TiO₂ is still hard to achieve the level of that of noble metals. Therefore, it is necessary to explore novel and more efficient co-catalysts.

P-type semiconductor CuCo₂O₄ has attracted considerable attention in high performance electrode materials owing to high conductivity, corrosion resistance, nontoxicity, and low cost. Compared with single metal oxides CuO or Co₃O₄, ternary compounds CuCo₂O₄ possesses higher electrochemical activity and conductivity due to the lower activation energy of charge transfer in multivalent transition metal cations.³³⁻³⁶ Moreover, ternary compounds still reserve excellent properties of monometallic oxides.³⁷ Currently, CuCo₂O₄ is gradually emerging in the field of photocatalysis, such as degradation of methyl orange, reduction of hexavalent chromium and CO₂, but rarely reported in hydrogen evolution.³⁸⁻⁴¹

Based on the above understanding, a novel heterojunction of ternary $CuCo_2O_4$ nanoparticles modified 2D TiO₂ nanosheets was successfully fabricated using a facile hydrothermal method followed by an in situ calcination process. $CuCo_2O_4$ with an average size about 10 nm were well dispersed onto the TiO₂ nanosheets. Under 300 W Xe lamp irradiation, the 10%-CuCo₂O₄/TiO₂ sample exhibited

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superior photocatalytic activity in H_2 production (4830 μ mol g⁻¹ h⁻¹). The excellent activities of CuCo₂O4/TiO₂ mainly belongs to the formation of interfacial chemical bonding, lower overpotential and efficient separation of electron-hole pairs across the p-n junction between CuCo₂O₄ and TiO₂ nanosheets. Finally, the possible mechanism of charge transfer over CuCo₂O₄ and TiO₂ was proposed and discussed in detail.

Experimental section

Fabrication of TiO₂ Photocatalysts

 TiO_2 nanosheets were fabricated via a hydrothermal method. Typically, 3 mL of HF (40%) was slowly added into 27 mL of tetrabutyltitanate (TBT) under vigorous stirring. Then, the mixed solution was heated at 180 °C for 24 h in Teflon-lined stainless steel vessel. After cooling down, the white suspensions were washed with NaOH solution (1 M) to remove the fluoride ion, and then washed with ethanol and water. Finally, the obtained TiO₂ nanosheets were dried at 60 °C for 12 h.

Fabrication of CuCo₂O₄/TiO₂ Nanosheets

CuCo₂O₄/TiO₂ hybrids were synthesized through an in situ calcination reaction. In detail, a certain amount of Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O and (NH₄)₂CO₃ aqueous solution (1 M) were dissolved in 100 mL water in a three-neck flask and refluxed at 100 °C for 1.5 h after adding TiO₂ powder. Then, the precipitates were washed by ethanol and dried at 60 °C for 10 h. Finally, the CuCo₂O₄/TiO₂ composites were obtained after calcination at 300 °C for 3 h and denoted as x%- CuCo₂O₄/TiO₂ (x represents the mass fraction of CuCo₂O₄ in the composite calculated by the input amount of Cu²⁺ and Co²⁺). Besides, CuCo₂O₄ was prepared under the same conditions without adding TiO₂ nanosheets.

The preparation processes of CuCo₂O₄/TiO₂ and the detailed conditions are illustrated in Fig. 1.



Figure 1. Synthesis route of CuCo₂O₄/TiO₂ nanosheets.

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Characterization

The crystalline phases, morphologies and textural characteristics of the obtained samples were analyzed by X-ray powder diffraction (SmartLAB SE, Rigaku), transmission electron microscopy (Tecnai G2 F30) and N₂ adsorption/desorption isotherm (Quantachrome NOVA 2000e). The elemental composition and chemical state of the samples were measured by X-ray photoelectron spectroscopy (Kratos AXIS NOVA). The UV/vis spectrophotometer (Shimadzu UV-3600) was employed to analyze the photoresponse properties of the catalysts. Photoluminescence spectra and fluorescence decay spectra were acquired on Hitachi F-7000 and Edinburgh FLS-1000.

A series of photoelectrochemical performances consisting of I-t curves (0.5 V bias potential), electrochemical impedance spectroscopy (frequency ranging from 0.01 to 10⁵ Hz) and Linear sweep voltammetry (scan rate of 10 mV s⁻¹) were measured using a CHI660E electrochemical workstation in 0.5 M Na₂SO₄ electrolyte. The as-synthesized 4 mg samples on the ITO glass, the Pt wire and Ag/AgCl (saturated with KCl solution) electrode were functioned as working electrode, counter electrode and reference electrode, respectively.

Photocatalytic Activity Measurements

An on-line detection system (Lab Solar-IIIAG, Beijing Perfect Light Technology Co. Ltd, China) was employed to evaluate the activity of samples. A 300 W Xe lamp was used as the full spectrum light source (350- 780 nm). 20 mg sample was placed in a Pyrex top-irradiation vessel containing 100 mL of mixture solution (20% TEOA) as sacrificial agent. The distance from lamp to reactor is about 20 cm and the light intensity at this position is about 382 mW cm⁻². Before irradiation, the system was evacuated completely until the vacuum gauge reached in a stable state. The generated H₂ was detected by a gas chromatography (Tianmei, GC7900) with N₂ as carrier. In addition, Pt/TiO₂ catalysts obtained

by photo-deposition $H_2PtCl_6 \cdot 6H_2O$ (1 g/L) were also tested for photocatalytic H_2 evolution under same conditions.

The apparent quantum yield (AQY) was investigated with 365 nm band-pass filter under 300 W Xe lamp. The average irradiation intensity was 20.38 mW/cm² and the irradiation area was 24 cm². The QE is calculated based on the eqn. (1) below.

$$QE = \frac{\text{Number of evolved H}_2 \text{ molecules} \times 2}{\text{Number of incident photons}} \times 100\%$$
$$= \frac{2\nu t N_A}{ISt\lambda \frac{1}{hc}} \times 100\% \tag{1}$$

I, t, λ , N_A , v, S, c and h are corresponding to incident light density (W·cm⁻²), illumination time (s), incident light wavelength (nm), Avogadro constant, H₂ generation rate (mol·s⁻¹), illumination area (cm²), velocity of light and Planck constant.

Hydroxyl Radical Trapping Experiment

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Detection of the surface hydroxyl radical groups (•OH) by probe molecule terephthalic acid (TA) was performed under 300 W Xe lamp irradiation. The reaction (eqn. (2)) product 2-hydroxyterephthalic acid (TA-OH) could be measured at 425 nm by PL spectroscopy. First, the 20 mg different samples were immersed in 50 mL mixed solution (0.05 M TA and 0.02 M NaOH) and the dark adsorption process was carried out for 30 min. Then, under light irradiation, about 3 mL solution was withdrawn from the mixture every 10 min intervals and detected by Hitachi-F7000 florescence spectrophotometer with excitation at 315 nm.

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Results and discussion



Structures and Compositions of Photocatalysts

Figure 2. XRD patterns of samples.

As shown in Fig. 2, the signals centered at 19.1°, 31.3°, 36.9°, 44.9°, 59.2°, and 65.2° match to (111), (220), (311), (222), (400), (511), and (440) plane of the cubic spinel $CuCo_2O_4$ (JCPDF No. 01-1155),⁴² respectively. All binary composites exhibit the similar diffraction peaks at 25.2°, 37.9°, 48.0°, 53.9°, 62.7°, 70.3°, and 75.2°, corresponding to (101), (004), (200), (105), (204), (116), (215) crystal planes of anatase TiO₂ (JCPDF No. 21-1272).⁴³ Via partial enlarged detail, it can be found that the peak at 37.9° broadens gradually with the increase content of $CuCo_2O_4$, and when loading content reaches 20%, the diffraction peak of $CuCo_2O_4$ can be obviously observed, indicating that the binary $CuCo_2O_4/TiO_2$ composite has been successfully fabricated.



Figure 3. (a-e): TEM images of samples (TiO₂, and 6%, 8%, 10%, 20%- CuCo₂O₄/TiO₂), (f) and (g): magnification TEM image and size distribution histograms of 10%- CuCo₂O₄/TiO₂, (h-l) and (m): the

corresponding EDX mapping images and EDS spectrum of 10%-CuCo_2O_4/TiO_2.

The SEM images (Fig. S1) show that the surface of TiO_2 becomes rough and aggregated with the increase of $CuCo_2O_4$ loading content, which could be clearly seen in TEM images. It can be seen from Fig. 3 that the pristine TiO_2 has ultrathin rectangular nanosheets structure with thickness approximately 10 nm and 40-60 nm side length. The clear lattice fringes of 0.35 nm matches well with (101) plane of anatase TiO_2 . For 10%-CuCo₂O₄/TiO₂ (Figure 3d and i), the CuCo₂O₄ nanoparticles with average size about 8 nm are homogenously anchored on the surface of TiO_2 , but almost completely covers the surface of TiO_2 nanosheets in 20%-CuCo₂O₄/TiO₂ composite. This shielding effect severely inhibits the photocatalytic activity of the binary catalyst. The lattice

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spacing of 0.26 nm corresponds to (311) planes of cubic $CuCo_2O_4$. It can be seen $Cu^{DO[:10:10:20]/C9CY01209E}$ elements are evenly dispersed on the surface of TiO₂ based on the EDX mapping (Fig. 3h–i). Moreover, from EDS analysis (Fig. 3m), the atomic ratio of Cu : Co is about 1 : 2, which is accordance with the stoichiometric ratio of CuCo₂O₄.



Figure 4. N₂ adsorption-desorption isotherm plots and pore diameter distributions (insert) of samples.

The nitrogen adsorption-desorption test was performed to investigated the specific surface areas of the samples. As shown in Fig. 4, it can be categorized as type IV isotherms with H3 hysteresis loop for TiO₂ and 10%-CuCo₂O₄/TiO₂, indicating the presence of slit-like mesopores due to stacking of nanosheets.⁴⁴ The BET surface area (Table S1) of 10%-CuCo₂O₄/TiO₂ (102.04 m² g⁻¹) is greatly improved compared with that of TiO₂ (46.53 m² g⁻¹), which may be caused by more slit like pores produced in gas (CO₂) insitu pyrolysis process. This improvement of specific surface area provides more active sites and facilitates interfacial mass transfer in photocatalytic reaction.



Figure 5. High-resolution XPS spectra of samples (a) Ti 2p, (b) O 1s, (c) Co 2p and (d) Cu 2p.

The survey spectra (Fig. S2) exhibits the presence of Ti, Cu, Co and O elements in CuCo₂O₄/TiO₂. High-resolution Ti 2p XPS spectrum (Fig. 5a) shows two major peaks at 459.22 and 464.92 eV, attributed to the formation of Ti⁴⁺ state. Meanwhile, two tiny Ti³⁺ signals at 457.67 and 463.16 eV appears after loading CuCo₂O₄.⁴⁵ The O 1s XPS spectra of CuCo₂O₄/TiO₂ in Fig. 5b displays three characteristic peaks centered at 528.53, 530.53 eV and 532.63 eV, which are indexed to the lattice oxygen in CuCo₂O₄ and TiO₂ and the oxygen of adsorbed hydroxide ions, respectively.^{46,47} The high-resolution Co 2p spectrum (Fig. 5c) can be deconvoluted into two major characteristic peaks with spin-energy separation value about 15 eV, indicating Co²⁺ (782.74 and 798.41 eV) and Co³⁺ (781.47 and 796.57 eV) exist in composites, which are characteristic of spinel cobalt oxides.³⁸ The peaks at 785.97, 789.51 and 803.64 eV belong to the shake-up satellites, further confirming the presence of multivalent cobalt. As shown in Fig. 5d, Cu 2p peak can be fitted into two prominent peaks located at 935.13 and 955.15 eV, which is attributed to Cu²⁺ in composites.⁴⁸

For comparison, the single catalysts (TiO₂ and CuCo₂O₄) were also investigated by XPS analysis. Interestingly, the ratio of Co²⁺/Co³⁺ is obtained as 1.7, and Cu⁺ (931.97 and 951.80 eV) could be observed in CuCo2O4.49 However, the ratio of Co2+/Co3+ becomes 0.8 and only Cu2+ exists in CuCo₂O₄/TiO₂ hybrid. Meanwhile, part of the Ti⁴⁺ shows the conversion to Ti³⁺ after loading CuCo₂O₄, implying the following redox reaction (eqn. (3)) occurs on surface based chemical bonding during the annealing process.

$$Ti^{4+} + Co^{2+}/Cu^{+} = Ti^{3+} + Co^{3+}/Cu^{2+}$$
 (3)

Therefore, the theoretical calculation of electronegativity and comparative experiments were carried out to explain this phenomenon.⁵⁰ Electronegativity (EN) is the scale of the ability of an atom to attract electrons in compounds. According to eqn. (4), the EN of given elements with different oxidation state and coordination number can be calculated. χ_i , n^* , I_m , R and r_i are EN, effective principal quantum numbers, ultimate ionization energy, Rydberg constant and ionic crystal radius, respectively. The specific values are shown in Table. 1.

$$\chi_{i} = 0.105 n^{*} (I_{m} / R)^{1/2} / r_{i} + 0.863$$
(4)

Element	n*	I _m /eV	R/eV	r _i /Å	χi
Ti ⁴⁺	3.45	43.267	13.6	0.745	1.73028345
Ti ³⁺	3.45	27.4917	13.6	0.81	1.498850064
C0 ²⁺	3.45	17.083	13.6	0.79	1.376918106
Co ³⁺	3.45	33.5	13.6	0.685	1.69298601
Cu^+	3.45	7.72638	13.6	0.74	1.231973565
Cu^{2+}	3.45	20.2924	13.6	0.71	1.48622849

Table 1. Electronegativity Values Calculated by the eqn (4).

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EN values of Ti⁴⁺, Co²⁺ and Cu⁺ are calculated as 1.73, 1.38 and 1.23, indicating Ti⁴⁺ has $\frac{\text{DDI:10.1039}/\text{COCVOI209E}}{\text{electronic affinity than Co²⁺ and Cu⁺ when forming chemical bonds. Hence, it can be inferred the formation process of CuCo₂O₄/TiO₂ as follows in Fig. 6. During calcination reaction, CuCo(OH)₂CO₃ attached to TiO₂ could be decomposed and gradually produce CuCo₂O₄, accompanied by the formation of many oxygen vacancies, which react with lattice oxygen on the surface of TiO₂ to form chemical bonds. The different electronegativity leads to electron migration from Co/Cu to Ti across Ti-O-Co/Cu. Hence, it produced Ti³⁺ and high valence state Cu²⁺/Co³⁺. Meanwhile, the binding energy of lattice oxygen in TiO₂ (530.09 eV) and CuCo₂O₄ (529.07 eV) shows red and blue shifts, respectively.$



Figure 6. The synthesis mechanism of CuCo₂O₄/TiO₂ composite.

In order to prove the existence of interfacial chemical bond, the 10%-CuCo₂O₄/TiO₂ composite prepared by mechanical mixing were also characterized by XPS spectrum. As shown in Fig. S3, the univalent copper ion is not oxidized and the ratio of Co²⁺/Co³⁺ remains at 1.8, and there is no Ti³⁺ in hybrid via mechanical fabrication, further indicating the interfacial bonding due to unsaturated coordination atoms occurs during annealing process like Zheng et al.'s work.⁵¹ In addition, according to XPS valence band spectra (Fig. 7), the valance band position (E_{VB}) of TiO₂ and CuCo₂O₄ are obtained as 2.27 and 0.41 eV, respectively.



Figure 7. XPS valence band spectra of (a) $CuCo_2O_4$ and (b) TiO_2 .

Photocatalytic Activities and Stabilities



Figure 8. (a) Photocatalytic H₂ evolution amounts and (b) H₂ evolution rates of the samples, (c) AQY under 300 W Xe lamp irradiation with 365 nm band-pass filter, (d) cycling tests on 10%-CuCo₂O₄/TiO₂ composite, (e) XRD patterns of 10%-CuCo₂O₄/TiO₂ before and after use and (f)

 H_2 generation of different content Pt/TiO₂.

The photocatalytic H₂ evolution for all samples was evaluated with triethanolamine (TEOA) as the

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trapping agent under irradiation of 300 W Xe lamp. Fig. 8a and Fig. 8b display the H₂ evolution yield and the photocatalytic H₂ evolution rate (PHER) of all samples after 5 h irradiation, respectively. It can be seen that the PHER increases to the maximum after 4 h's irradiation and keeps the balance, which may be related to the activation of reaction sites and the dissolution of produced H_2 in water at the initial stage. Due to the fast recombination of photoinduced carriers, the TiO₂ and CuCo₂O₄ exhibit relatively low PHER of 151 and 42 µmol g⁻¹ h⁻¹, respectively. In contrast, the PHER increases significantly with modification of CuCo₂O₄. The optimum H₂ production activity of 4830 μ mol g⁻¹ h⁻¹ is obtained at 10% of CuCo₂O₄, which is about 32 times than single TiO_2 and the highest increase fold of binary TiO₂-based non-noble system reported so far (summarized in Table. 2). Its apparent quantum yield (AQY) value was calculated to be 11.5% at 365 nm (Fig. 8c). However, the shielding effect caused by excessive $CuCo_2O_4$ inhibits the photocatalytic activity of the binary catalyst. Additionally, the PHER of 10%-CuCo₂O₄/TiO₂ shows negligible decrease after four consecutive cycles (Fig. 8d), and there are no significant changes before and after in the XRD patterns (Fig. 8e), confirming excellent stability.

Photocatalyst	Light source	Scavenger	H ₂ yield	increase multiple	AQY	References
Cu ₃ P/TiO ₂	300 Xe	10%TEOA	7940 µmol h ⁻¹ g ⁻¹	11	4.6%	33
Ni ₂ P/TiO ₂	300 Xe	20%Methanol	1410 µmol h ⁻¹ g ⁻¹	12.5	-	32
NiCoP/TiO ₂	300 Xe	20%Methanol	1540 µmol h ⁻¹ g ⁻¹	13.6	-	32
FeP/TiO ₂	300 Xe	20%Methanol	770 µmol h ⁻¹ g ⁻¹	6.8	-	32
CuO _x /TiO ₂	300 Xe	20%Methanol	1523.2 μmol h ⁻¹ g ⁻¹	18.2	7.05%	49
Cu/TiO ₂	300 Xe	10% methanol	12779 μmol h ⁻¹ g ⁻¹	6.6	-	62
Co ₃ O ₄ -TiO ₂ (B)	350 Xe	20% methanol	6359µmol h ⁻¹ g ⁻¹	9.2	10.9%	63
CuCo ₂ O ₄ /TiO ₂	300 Xe	20%TEOA	4830 µmol h ⁻¹ g ⁻¹	32	11.5%	This work

Table 2. Summary of Reported TiO₂-Based Photocatalytic.

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For comparison, the photocatalytic activity of Pt/TiO_2 catalysts fabricated by photo-deposition reaction was measured under the same conditions. The highest PHER (Fig. 8f) achieves 5246 µmol g⁻¹ h^{-1} over 3%-Pt/TiO₂, which is slightly higher than that of 10%-CuCo₂O₄/TiO₂. What's more, the PHER of 10%-CuCo₂O₄/TiO₂ prepared by mechanical mixing is 1190 μ mol g⁻¹ h⁻¹ (Fig. S4), which is far less than that of the composite prepared by insitu calcination process. Based on the above results, it can be explained that this heterojunction and surface chemical bonding can significantly enhance photocatalytic activity. Considering application economy, it is obviously that $CuCo_2O_4$ is a suitable alternative to Pt for its high practical potential in photocatalysis.

Optical Properties of Photocatalysts



Figure 9. (a) UV-vis diffuse reflectance spectra of prepared samples inset is the photographs of samples under daylight (inset is the photographs of samples under daylight: (I) TiO₂, (II) 4% (III) 8%

(IV) 10%-CuCo₂O₄/TiO₂, (V) CuCo₂O₄) and (b) PL spectra of TiO₂ and 10%-CuCo₂O₄/TiO₂.

As shown in Fig. 9a, TiO₂ nanosheets exhibit excellent photoresponse to ultraviolet region but have little absorption above 400 nm. CuCo₂O₄ shows superior absorption to the full spectrum, possibly due to its own black color and narrow band gap. Therefore, the absorption of visible light of the hybrid catalysts increases with the addition of $CuCo_2O_4$, which is consistent with the color change of samples. Interestingly, a broad absorption peak appeared between 600 and 800 nm, attributed to the d-d

transition of Co and Cu ions species.^{52,53} As depicted in Kubelka-Munk plots (Fig. S5), the band gap energy (E_{a}) of TiO₂ and CuCo₂O₄ are calculated as 2.97 and 1.56 eV, respectively, which is in line with previous reports.41,54

The separation efficiency of photogenerated carriers were analyzed by steady-state and time-resolved photoluminescence (PL) spectra. Fig. 9b shows the steady-state PL spectra under excitation with 220 nm. The high PL intensity of pristine TiO₂ indicates the high recombination of charge carriers. The 10%-CuCo₂O₄/TiO₂ composite displays lower PL intensity, revealing that the coupled CuCo₂O₄ could effectively promotes the separation of electrons and holes through Ti-O-Cu/Co bonds, which increases useful carriers in photocatalysis. Furthermore, time-resolved PL study based on bi-exponential kinetic fitting exhibits the decay data in Fig. 10. The resulting emission lifetimes are 1.78 (τ_1) and 8.66 (τ_2) ns for 10%-CuCo₂O₄/TiO₂ hybrids, shorter than those of TiO₂ 1.87 (τ_1) and 10.04 (τ_2) ns. The average radiative lifetime $\langle \tau \rangle$ for bare TiO₂ nanosheets and 10%-CuCo₂O₄/TiO₂ hybrids is obtained to be 7.83 and 6.83 ns, respectively. The decreased fluorescent lifetime suggests a charge transfer nonradiative pathway across chemical bonding and efficient charge separation between TiO₂ and CuCo₂O₄.55



Figure 10. Time-resolved transient PL decay of (a) TiO₂ and (b) 10%-CuCo₂O₄/TiO₂.

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Figure 11. (a) I-t curves, (b) Nyquist plots, (c) bode phase spectra and (d) linear sweep voltammetry

curves of the samples.

To further investigate the modification effects of $CuCo_2O_4$ on TiO_2 in promoting the photocatalytic activity, charge separation and migration during the photocatalytic process, the photoelectric characteristics were performed in 0.5 M Na₂SO₄ solution. As shown in Fig. 11a, the 10%-CuCo₂O₄/TiO₂ exhibits higher photocurrent density of 3.91 µA at 0.5 V bias potential, which is 2.73 folds than that of pristine TiO₂ (1.43 µA), indicating improved separation efficiency of charge carriers. According to the smaller arc radius in EIS analysis (Fig. 11b), the interfacial charge transfer resistance of CuCo₂O₄/TiO₂ decreases significantly, which is due to intimate electronic interaction between TiO₂ and CuCo₂O₄.⁵⁶ There are two time constants (two semicircle) in the Bode diagram (Fig. 11c), corresponding to double layer at low frequency and the space charge region at high frequency. The charge transfer in space charge region plays a key role in photocatalysis. Hence, according to eqn.

Photoelectrochemical Measurements

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$$\tau_n = 1/2\pi f_n \tag{5}$$

As shown in LSV curve (Fig. 11d), $CuCo_2O_4/TiO_2$ presents a lower overpotential (-1.40 vs SCE) than that of bare TiO₂ (-1.54 V vs SCE) at -1 mA cm⁻² current density, suggesting hydrogen reduction process is easier to react on $CuCo_2O_4/TiO_2$ surface.⁵⁸ Based on the above results, the $CuCo_2O_4$ with superior conductivity significantly improves the photoelectric properties of TiO₂, which could be attributed to p-n junction with chemical bonding at the interface and the lower overpotential for H₂ production.





Figure 12. PL intensity of TA-OH generated by different samples under illumination.

For sake of clearly analyzing the charge transfer route, the hydroxyl radical (·OH) trapping

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experiment was carried out for an hour. From Fig. 12a, blank experiment shows that only negligible ·OH is produced in the absence of catalyst. Fig. 12b exhibits an intense emission signals at 425 nm, revealing pristine TiO₂ produces a large number of \cdot OH under solar irradiation. That is because E_{VB} position (2.27 eV vs NHE) is more positive than +1.99 eV (E_{.OH/OH}-), implying holes in the VB of TiO₂ can oxidize OH⁻ to •OH.⁵⁹ In Fig. 12c, CuCo₂O₄ with negative E_{VB} potential (0.41 eV vs NHE) is difficult to generate •OH. Interestingly, the •OH produced by binary CuCo₂O₄/TiO₂ (Fig. 12d) are much lower than those produced by TiO_2 , implying the oxidizability of holes reduces due to the transfer to negative energy band, which is similar to type II heterojunction.



Figure 13. Photocatalytic water splitting mechanism of CuCo₂O₄/TiO₂.

According to the above analysis, a proposed mechanism for the improved photoactivity of the CuCo₂O₄/TiO₂ hybrids towards H₂ evolution under light illumination is displayed in Fig. 13. Ultrathin lamellar and nanoparticle favor interphase transport of charge carriers. The coordinatively unsaturated metal atoms promote the hybridization between CuCo₂O₄ nanoparticles and TiO₂ nanosheets.⁶⁰ The E_{VB} of TiO₂ and CuCo₂O₄ are 2.27 and 0.41 eV, respectively. The E_{VB} of TiO₂ and CuCo₂O₄ are -0.70 and -1.15 eV, respectively. The intimate contact between n-type TiO_2 and p-type $CuCo_2O_4$ establishes

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a p-n junction with staggered band alignment.^{33,61} Moreover, the equilibrium Fermi level (E_{t}) produces (E_{t}) produc

Conclusions

In summary, the CuCo₂O₄ nanoparticles modified on TiO₂ nanosheets have been successfully fabricated via a facile hydrothermal method followed by an in situ calcination reaction. The 10%-CuCo₂O₄/TiO₂ sample exhibits superior photocatalytic activity in H₂ generation (4830 μ mol g⁻¹ h⁻¹), which is 32 folds than that of pristine TiO₂. This typical p-n junction material possesses unique properties of abundant surface reactive sites, improved current density, reduced charge transfer impedance, and lower overpotential for H₂ production. Moreover, the well dispersion of CuCo₂O₄ onto the surface of TiO₂ nanosheets adopting interfacial chemical bonding is beneficial to charger transfer and photostability in photocatalytic process. Finally, this work develops a new horizon for exploring non-noble metal CuCo₂O₄-based photocatalysts.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos.21676213, 21476183, and 51372201), the China Postdoctoral Science Foundation (No.2016M600809) and the Natural Science Basic Research Plan in Shaanxi Province of China

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