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Bi2Fe4O9 thin films as novel visible-light-active photoanodes for solar water splitting

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We report the chemical solution deposition (CSD) of a phase-pure Bi2Fe4O9 thin film for use as a photoanode in photoelectrochemical (PEC) water splitting. The energy levels of Bi2Fe4O9 films have been measured and n-type characteristics have been confirmed. With band gaps determined as 2.05 eV (indirect) and 2.80 eV (direct) and valence and conduction bands straddling the water oxidation and reduction potentials, this material is highly promising as a photocatalyst for solar water splitting. The photocurrent of a planar photoanode reached 0.1 mA/cm2 at 1.23 VNHE under AM1.5 G illumination. The addition of H2O2 as a hole scavenger increased the photocurrent to 0.25 mA/cm2, indicating hole injection is one limiting factor to the performance. The performance was enhanced by nearly 5-fold when the Bi2Fe4O9 photoanode is coupled to a Co-Pi surface co-catalyst. The photoanode also shows excellent stability with no change in photocurrent over three hours of continuous illumination. These results indicate that this material represents a promising addition to the growing selection of low-cost, stable photocatalysts for use in solar water splitting.

Novel materials for efficient solar-to-fuel conversion have been pursued extensively since the first report of water oxidation using TiO2[1](#_ENREF_1), [2](#_ENREF_2). Along with TiO2, other binary transition metal oxides such as Fe2O3[3](#_ENREF_3) and WO3[4](#_ENREF_4), have been explored and found to show many desirable properties for the production of solar fuels. However, these materials usually have some limitations either from large optical band gaps or short carrier diffusion lengths[5](#_ENREF_5), [6](#_ENREF_6). For example, the application of TiO2 is significantly limited by a large band gap of *ca* 3.2 eV, which means only 3 – 4% of solar light can be used to generate photoexcited carriers. Efforts have been made to address these challenges such as doping to reduce the band gap[7](#_ENREF_7) or nanostructuring to overcome the short carrier diffusion lengths[8](#_ENREF_8). Meanwhile, increasing research attention has been paid to the development of ternary metal oxides for application as photoanodes. The materials of interest include narrow-band-gap BiVO4[9](#_ENREF_9) and CuWO4[10](#_ENREF_10) as well as those with polar structures such as BaTiO3[11](#_ENREF_11) and PbZrxTi1-xO3[12](#_ENREF_12).

It is worth noticing that many compounds containing Bi3+ have been found to be narrow-band-gap semiconductors. In addition these Bi3+ containing compounds can show high PEC activity under visible light due to the strong hybridization between O-2p and Bi-6s orbitals[13](#_ENREF_13), [14](#_ENREF_14). It has also been found that hybridized energy bands can increase the separation of photoexcited holes and electrons and further improve the PEC conversion efficiency[15](#_ENREF_15). Therefore, in addition to BiVO4, other Bi-based compounds, CuBi2O4[16](#_ENREF_16), BiFeO3[17](#_ENREF_17), and Bi2WO6[18](#_ENREF_18) have attracted interest as possible visible-light photocatalysts.

Bi2Fe4O9 has attracted attention for a number of applications such as semiconductor gas sensors and catalyst for ammonia oxidation to NO[19](#_ENREF_19). Like many other Bi-based compounds, Bi2Fe4O9 exhibits a narrow indirect band gap with reported values ranging from ca. 1.9 to ca. 2.1 eV[20](#_ENREF_20), [21](#_ENREF_21). Nanoparticles of Bi2Fe4O9 have been reported to be highly visible-light-active photocatalysts with a near-infrared absorption. These particles show good photocatalytic activity for organic contaminant degradation[22](#_ENREF_22). However, to date there has been no reported studies on the use of Bi2Fe4O9 thin films as photoelectrodes for PEC applications.

In this work, we prepare Bi2Fe4O9 thin films using chemical solution deposition (CSD) and study the photoelectrochemical performance of the as-produced thin films. The Bi2Fe4O9 electrode exhibits photoanodic behaviour with high PEC activity and good stability under simulated sunlight. A photocurrent density of 0.1 mA/cm2 at 1.23 VNHE was obtained under AM1.5G irradiation. A value of 0.05 mA/cm2 was obtained when the UV light was blocked, demonstrating the ability of Bi2Fe4O9 to harvest visible light for photochemical reactions. The addition of a hole scavenger (H2O2) in the PEC process increased the photocurrent to 0.25 mA/cm2 at 1.23 VNHE and lowered the onset potential. Based on these results, we propose that Bi2Fe4O9 is a promising photoanode for PEC applications.

Bi2Fe4O9 thin films were deposited using a simple CSD using a stoichiometric 1:2 molar ratio of bismuth nitrate and iron nitrate as precursors in a sol which also contained 2-methoxyethanol and acetic anhydride. Five layers of the sol were spin coated onto fluorine-doped tin oxide coated glass substrates, with staged drying and annealing up to a maximum of 650 ℃ (full methods in Supplementary Information). Figure 1a shows a typical surface scanning-electron microscope (SEM) micrograph for the Bi2Fe4O9 thin films showing smooth films with grains from 50 – 200 nm. Figure 1b shows a cross-section of a typical film indicating that the film is *ca.* 150 nm thick and consists of several small crystallites. X-ray diffraction pattern of the as-produced film (Figure 1c) confirms that a phase-pure sample of Bi2Fe4O9 has been produced with an orthorhombic structure (ICDD 74-1098; space group: *Pbam*) and lattice constants of a = 7.950 Å, b = 8.428 Å, and c = 6.005 Å. All additional peaks in the diffraction pattern can be attributed to the substrate.

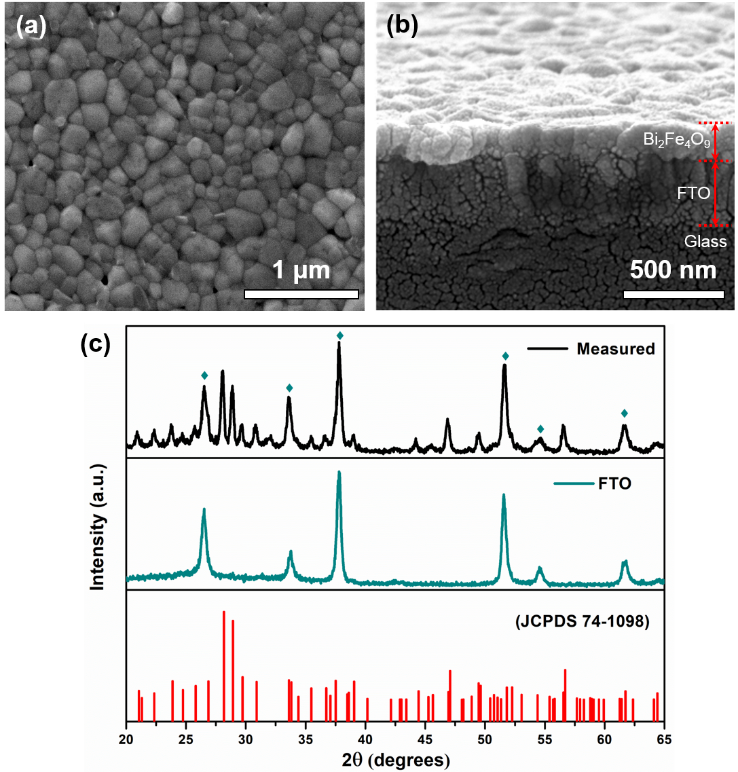


Figure 1. a) Top-down and b) cross-section SEM images of the Bi2Fe4O9 film. c) XRD pattern of the Bi2Fe4O9 film (measured), with the measured pattern of the FTO substrate, and reference spectrum for Bi2Fe4O9 (JCPDS 74-1098) for comparison. Sample peaks corresponding to the FTO substrate are indicated. All other peaks index to Bi2Fe4O9.

X-ray photoelectron spectroscopy (XPS) was undertaken to characterize the elemental composition and chemical states of the Bi2Fe4O9 film. The XPS spectra of a typical sample is shown in Figure 2, with the XPS full survey spectrum shown in Figure 2a. All obtained binding energies were normalized using the C 1s peak at 284.6 eV. A detailed view of the bismuth 4f spectrum is given in Figure 2b and shows two distinct peaks: the Bi 4f7/2 peak at 158.9 eV and the Bi 4f5/2 peak at 164.2 eV. Both these peaks and their positions are characteristic of the presence of bismuth in the +3 oxidation state, as expected for Bi2Fe4O9.

The Fe 2p core level, shown in Figure 2c, consists of two peaks located at 723.7 eV (Fe 2p1/2) and 710 eV (Fe 2p3/2). The Fe 2p3/2 peak was deconvoluted into two peaks located at 711.1 eV and 709.6 eV, corresponding to Fe3+ and Fe2+, respectively. The formation of Fe2+ is attributed to the presence of oxygen vacancies commonly occurring in the deposition processes of perovskite thin films[23](#_ENREF_23), [24](#_ENREF_24), which is further confirmed in the O 1s spectrum: the deconvolution of the O 1s line results in peaks at 529.5 eV and 531.5 eV. The peak at 529.5 eV belongs to M‑O-M bonds and that at 531.5 eV is due to a high number of defect sites with a low oxygen coordination, i.e. due to the presence of oxygen vacancies in accordance with the presence of Fe2+.

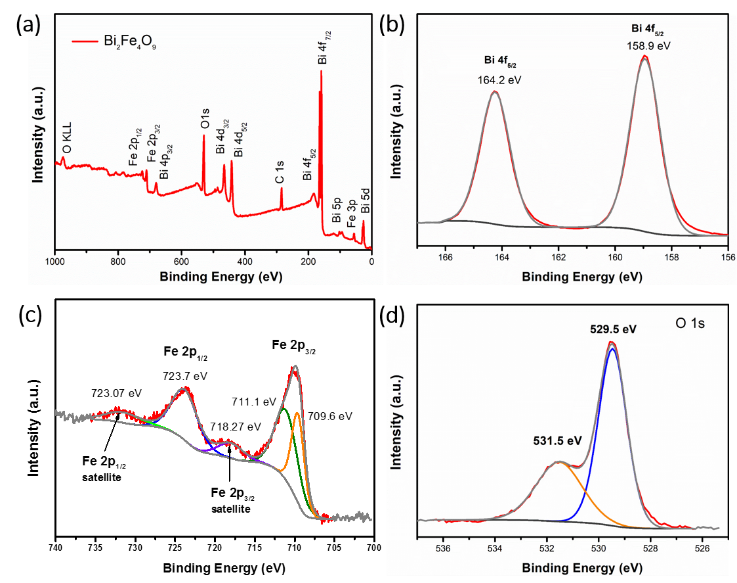


Figure 2. (a) Survey spectrum, (b) Bi 4f, (c) Fe 2p and (d) O 1s XPS spectra of Bi2Fe4O9 film showing fitted peaks.

The UV-vis absorption spectrum of the Bi2Fe4O9 films shown in Figure 3a demonstrates light absorption over a wide range of frequencies from the UV into the visible, consistent with the reported band gap of around 2 eV. It has been reported in previous studies that the Bi2Fe4O9 nanoparticle samples had near-infrared light absorption, which was ascribed to the splitting of Fe 3dtransitions[25](#_ENREF_25). For our thin film samples a broad, shallow absorption peak can be observed between 650 nm to 800 nm, and a distinct absorption edge starts from ~ 600 nm and increases with the decreasing wavelength. The good visible light absorption of the material indicates the possibility of photoactivity under visible-light illumination.

The linear regions in the derived Tauc plots (Figure 3b) indicate indirect and direct band gaps of 2.05 and 2.80 eV respectively, in close agreement with the calculated band structure for Bi2Fe4O9[26](#_ENREF_26). The band gap associated with the indirect transition is close to ideal for solar water splitting[27](#_ENREF_27), giving an indication that the material will be able to drive photochemical processes under visible light. However, the indirect transition means that there will be limited light absorption across the thin sample and gives some indication as to why nanoparticles have been of interest to date: the absorption cross section and scattering associated with nanoparticles can add to the effective pathlength and increase absorption. Despite this, the presence of a direct transition at an only slightly higher energy of 2.8 eV means that there is still strong absorption within the visible region, as seen in the absorption spectrum (Figure 3a).

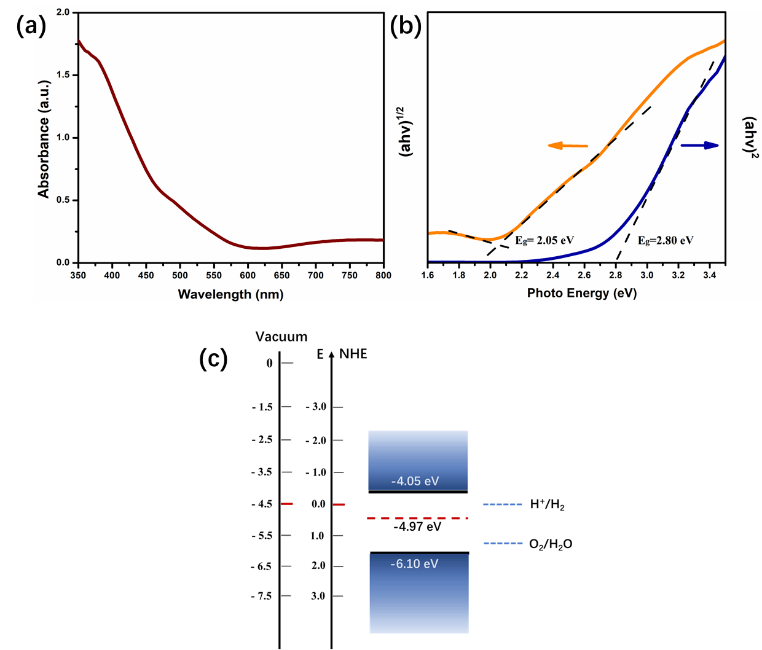


Figure 3. a) UV-vis absorbance spectra and b) derived Tauc plots corresponding to the allowed direct (right scale) or allowed indirect (left scale) band gap. c) Energy levels of Bi2Fe4O9 electrode. Red dashed line shows the measured Fermi level. The redox potentials of water splitting are also shown

To understand the variety of photochemistry that can be driven on the surface of a photocatalyst the band structure of the system must be understood, particularly in the case of a relatively new material as reported here. In order to obtain the energy levels of the Bi2Fe4O9 films, UV ambient pressure photoemission spectroscopy[28](#_ENREF_28) (UV-APS) and Kelvin probe measurement have been carried out to determine the valence-band edge and the Fermi energy level (EF). The measured valence-band edge by UV-APS is -6.10 eV and the measured EF value is -4.97 eV. Note that the constant EF value was measured over 100s indicating a stable electronic property of the Bi2Fe4O9 films. Based on these values and the measured indirect optical band gap energy of 2.05 eV, a band diagram was constructed (shown in Figure 3c), indicating Bi2Fe4O9 is slightly n-doped and has a valence band edge below the water oxidation potential, suitable for photocatalytic water oxidation. The n-type characteristic of the material was also confirmed by surface photovoltage measurements[29](#_ENREF_29), [30](#_ENREF_30), which show a negative shift in work function upon illumination (Fig. S3, ESI).

The photoanodic activity of Bi2Fe4O9 films were investigated using PEC in a standard three electrode configuration. Figure 4a shows the photocurrent-voltage (I-V) curves of a Bi2Fe4O9 photoelectrode illuminated using full AM1.5G and visible light only (λ > 420 nm) chopped irradiation. The data shows a steady increase in photocurrent with increasing applied anodic potential and the photocurrent at 1.23 VNHE reached 0.1 mA/cm2 under full sun illumination. Despite the large number of previous studies of PEC water oxidation using bismuth ferrite films with composition BiFeO3, this has produced consistently lower photocurrent values than our Bi2Fe4O9 thin films. For example, Yu *et al.*[*31*](#_ENREF_31) produced for BiFeO3 films deposited by pulsed laser deposition (PLD) and obtained ~ 0.09 mA/cm2 at 1.23 VNHE under 1 sun, which was higher than that reported by Quynh[32](#_ENREF_32) who also prepared BiFeO3 by PLD giving ~0.06 mA/cm2 at 1.1 VNHE under 1 sun. A BiFeO3 film deposited on epitaxial SrRuO3/SrTiO3 substrate by sputtering has been reported to have a much lower value of ~0.01 mA at 1 VNHE[17](#_ENREF_17). It is worth noting that the Bi2Fe4O9 photoanode reported here was prepared by a low-cost deposition method and is a planar film without nanostructuring. It therefore offers a large scope to further optimise the synthesis and morphology of this material to produce improved photocurrent in the future, along similar lines as the well-studied photoanode material: Fe2O3. This has demonstrated photocurrents over 2 mA/cm2 through the production of optimised nanostructured films, while planar films – more directly comparable to the Bi2Fe4O9 photoanode reported herein – generally produce negligible photocurrents, or those in the low μA/cm2 range[33](#_ENREF_33).

To confirm the visible-light response of the Bi2Fe4O9 thin films, photocurrent was measured with the UV portion filtered from the AM1.5G illumination (λ > 420 nm), which reached 0.05 mA/cm2 at 1.23 VNHE, confirming the potential for Bi2Fe4O9 to be a visible-light-active catalyst indicated by the UV-Vis spectra.

It can be seen from Figure 4a that the chopped light linear sweep voltammetry (LSV) curves showed obvious transient photocurrent peaks upon light switching. Such peaks are known to be associated with a variation in the rates of carrier extraction across the semiconductor interface[34](#_ENREF_34). To investigate this in more detail we have studied the impact of a hole-scavenger, H2O2, on the photocurrent of the system. Figure 4b shows a plot of current density vs applied potential under chopped illumination using two different electrolytes: 0.2 M Na2SO4 and 0.2 M Na2SO4-0.5 M H2O2. The onset potential for the photocurrent shifted negatively with the addition of H2O2 to the electrolyte solution (from 0.7 to 0.3 VNHE). This agrees well with the expectation, since H2O2 has a more negative oxidation potential than H2O (E0 = +0.68 VNHE for O2/H2O2 and E0 = +1.23 VNHE for O2/H2O), which means that the E0redox of the two electrolyte solutions are 0.34 VNHE (with H2O2) and 0.615 VNHE (without H2O2).

The transient photocurrents associated with the non-equilibrium extraction of holes and electrons have also been significantly reduced upon the addition of H2O2 and the photocurrent at 1.23 VNHE increased to 0.25 mA/cm2. Transient photocurrents under chopped illumination have been observed in a range of photoanode materials such as Fe2O3[34](#_ENREF_34) and BiVO4[35](#_ENREF_35). This phenomenon has been associated with a characteristic signature of hole accumulation at the photoanode/electrolyte interface[36](#_ENREF_36). The kinetics of the 4-hole oxidation of water to molecular oxygen means that there is an excess of generation of photoexcited holes over the rate of extraction to perform the electrochemical reaction. It is accepted that positive current transients upon turning the light on represent the accumulation of holes at the electrode/electrolyte interface. A negative current transient observed upon turning the light off represents the back reaction of electrons from the conduction band with the accumulated holes[34](#_ENREF_34). The addition of H2O2 as a hole scavenger promotes the reaction of accumulated holes at the electrode/electrolyte interface and suppresses back electron-hole recombination. The addition of a hole scavenger demonstrates that the photocurrents of Bi2Fe4O9 electrode can be further improved in the future by eliminating the hole injection barrier at the electrode/electrolyte interface, for example by combination with co-catalysts or reduction in surface trap states.

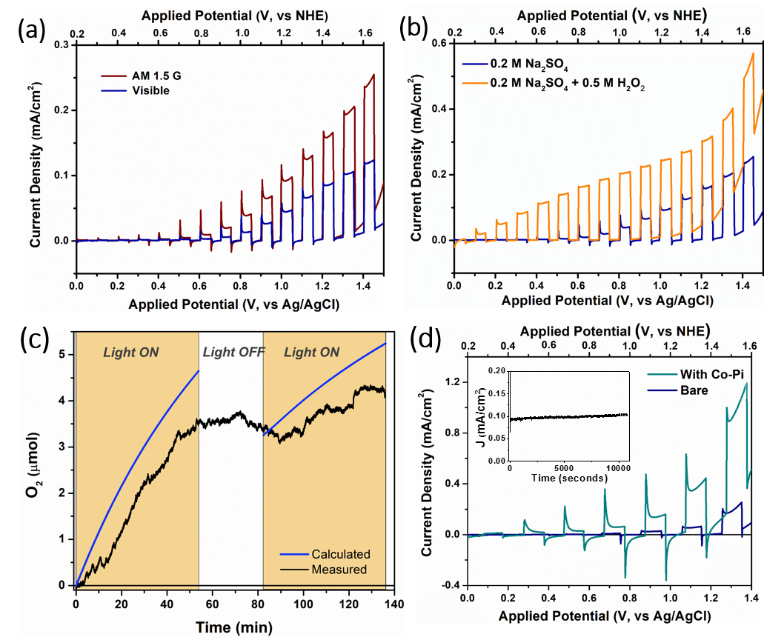


Figure 4. a) J-V curve for Bi2Fe4O9 underboth chopped 100 mW/cm2 AM 1.5 G and visible light irradiation (λ > 420 nm) in Na2SO4 electrolyte (pH 6.5). b) J-V curve under chopped illumination (1 sun AM 1.5 G) for Bi2Fe4O9 electrode without and with a hole scavenger (H2O2). c) Oxygen evolution measured by a Clark electrode in gas phase (black) and the amount of oxygen calculated (blue) from the chronoamperometry. d) Chopped J-V curve for Bi2Fe4O9 electrode without and with Co-Pi co-catalyst deposition. Inset: Photocurrent density (J) – time curves of Bi2Fe4O9 electrode measured at an applied potential of 1.2 VNHE for 3h in 0.2 M Na2SO4 solution under 1 sun illumination indicating good stability.

The ability of the photoanode to produce oxygen under illumination was measured using a Clark electrode (full details in ESI). It can be seen from Figure 4c that the measured oxygen content clearly increases over the periods of illumination, indicating successful photoelectrocatalytic water oxidation. Furthermore, the Faradaic efficiency (FE) for oxygen evolution was calculated by comparing this measured oxygen evolution to the theoretical maximum oxygen production, derived from the chronoamperometry (at 1.2 V vs. Ag/AgCl; full details of the calculation method are given in the ESI). This gave a FE of 82.1 ± 5.9 %. This is remarkably high compared to other ferrites (BiFeO3) that have shown FE close to 70%[37](#_ENREF_37), again indicating the promise of this system as a potential high-efficiency photoanode material.

Considering the issues with hole accumulation and associated recombination discussed above, co-catalyst deposition was investigated as a route to enhance the performance of the Bi2Fe4O9 photoanode. A CoOx overlayer (Co-Pi) was deposited on the surface of the Bi2Fe4O9 (details of method in ESI) and chopped light LSV was re-tested. As shown in Figure 4d, the deposition of the Co-Pi overlayer shifts the photocurrent onset potential ~ 200 mV to more negative potentials as well as the dark onset. Although transient photocurrent spikes are still present, indicating high levels of hole accumulation and recombination, the addition of the Co-Pi increases the photocurrent density by approximately a factor of 5, indicating it is a promising route to enhance the photoelectrocatalytic performance of this material, as found with other systems.

A key consideration for the use of photocatalytic materials is the stability of the system under illumination. We studied the stability of a Bi2Fe4O9 electrode by measuring the photocurrent over time (chronoamperometry) under an applied potential of 1.2 VNHE and full sunlight illumination in a 0.2 M Na2SO4 electrolyte, as shown in Figure 4d (inset). It can be seen from the *I-t* results that there is no loss of photocurrent during the 3-hour test, indicating the good stability of Bi2Fe4O9 films under illumination for use as a photoanode.

Conclusions

We present the first report of the use of Bi2Fe4O9 as a photoanode for photoelectrochemical water oxidation. Phase-pure Bi2Fe4O9 films have been synthesized via a simple CSD method using a stoichiometric Bi/Fe molar ratio of 1:2 for the precursor preparation. The Bi2Fe4O9 photoanode exhibits an indirect bandgap of 2.05 eV coupled with a direct transition at 2.8 eV leading to a strong visible light response. The measured band positions indicate suitability for water oxidation. PEC tests demonstrate high activity of the Bi2Fe4O9 electrode under AM1.5G and visible light illumination. By adding a hole scavenger, we have demonstrated that a hole injection barrier exists at the surface of the Bi2Fe4O9 electrode. This indicates that the PEC performance of the material can be further improved by combination with other photo- or electrocatalysts, or other tools such as modification of surface states to enhance carrier extraction, or nanostructuring to increase active surface area. We show that Bi2Fe4O9 combines strong light absorption, easy fabrication and good stability under illumination, making it a promising candidate for photoanodes in application of practical solar energy-driven PEC water splitting.

Conflicts of interest

There are no conflicts to declare

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