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Dimension-matched plasmonic Au/TiO₂/BiVO₄ nanocomposites as efficient wide-visible-light photocatalysts to convert CO₂ and mechanism insights

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Dimension (D)-matched plasmonic Au/TiO₂/BiVO₄ nanocomposites have been successfully constructed by firstly preparing BiVO₄ nanoflakes via an ion exchange process from BiOCl nanosheets, followed by coupling (001) facet-exposed anatase TiO₂ nanosheets and then modifying plasmonic Au nanorods. The well-designed 1D/2D/2D nanocomposites exhibit exceptional visible-light photocatalytic activities for CO₂ conversion, by ~30-fold and ~60-fold enhancement compared to the resulting BiVO₄ nanoflakes and the previously-reported BiVO₄ nanoparticles, respectively. Based on the steady-state surface photovoltage spectroscopy, transient-state surface photovoltage responses, wavelength-dependent photocurrent action spectra and fluorescence spectra related to the produced •OH amounts, it is confirmed that the exceptional photocatalytic activity is comprehensively attributed to the fabricated 2D nanoflakes to increase the specific surface area of BiVO₄, to the coupled TiO₂ nanosheets as a new proper-energy platform to accept photogenerated electrons from BiVO₄ and plasmonic Au so as to greatly enhance the charge separation, and to the modified plasmonic Au with the extended wide-visible-light absorption to 660 nm to take as the co-catalyst for the transferred electrons to induce reduction reactions. Moreover, the dimension matching in the fabricated nanocomposite is much favorable for the photogenerated charge transfer and separation. Furthermore, it is suggested by isotope experiments of ¹³CO₂ and D₂O, along with electrochemical measurements, the produced H atoms are dominant active radicals to initiate the conversion of CO₂.

Introduction

The increasing depletion of world-wide energy caused by the rapid consumption of fossil fuels raises an event of concerns about the energy shortage and global warming.^[1] Nowadays, 81% of the energy comes from the burning of mineral resources. This huge usage will make it speedy dried up, and also result in excessive emission of carbon dioxide (CO_2) into the atmosphere, leading to the environmental detrimentally greenhouse effect.^[2] In this regard, developing renewable energy and converting greenhouse gas CO_2 into hydrocarbon fuel is a desirable pathway to address both energy crisis and environmental issues.^[3-4] Although some traditional

techniques have been intensively investigated toward the objective, however, these techniques are always accompanied with low mechanical strength, less stability, catalyst poisoning, and electrode corrosion.^[5-6] Hence, it is necessary to develop alternative techniques to overcome the disadvantages mentioned above. Semiconductor photocatalytic technology is a promising approach to solve the energy and environmental challenges mainly due to its mild reaction conditions, good duration and no collateral contamination.^[7-8] Therefore, it is a feasible way to address the issues of excessive emission of CO₂ with clean energy production.

Since there are *ca.* 46% visible light in the solar spectrum, it is essential to develop visible-light responsive photocatalysts with narrow bandgap, such as Fe_2O_3 , WO_3 and $BiVO_4$.^[9-11] Hereinto, $BiVO_4$ is a promising photocatalyst owing to its nontoxicity, high chemical stability and appropriate bandgap structure.^[12-13] However, the photocatalytic activity of $BiVO_4$ is still unsatisfactory mainly due to the rather small specific surface area, sluggish charge separation and limited visiblelight absorption. Therefore, it is of great significance to improve the photocatalytic activities of CO_2 reduction synergistically by increasing specific surface area, enhancing charge separation and extending visible-light absorption.

In general, the specific surface area of $BiVO_4$ is comparatively small, attributed to the resulting large particle size. This is because of its small solubility product constant in



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the aqueous solution which leads to the rapid nucleation and crystallite growth.^[14] Although various strategies like creating pores and decreasing particle size have been developed to increase the surface area of BiVO₄ with some success, the resulting surface area is still unsatisfactory and/or accompanied by poor structure stability.^[15-16] In addition, the porous structure may be collapsed during the photocatalytic reactions, consequently leading to reduced surface area and declined activity. These factors lead to the limited improvement of photocatalytic activities of BiVO₄. In recent years, two-dimensional (2D) nanostructured materials have drawn much attentions due to their relative large surface area and good charge transportation capacity.^[17-18] This naturally spurs us to obtain 2D nanostructured BiVO₄ for efficient photocatalysis. However, it is difficult to directly prepare 2D BiVO₄ via traditional methods due to its too small solubility product constant. Thus, it is highly desired to develop a new method to prepare 2D BiVO₄. Notably, BiOCl, another bismuthbased material is sheet-like and unstable. In this case, it is expected that 2D BiVO₄ with large specific surface area would be obtained by a controllable ion exchange process from BiOCI nanosheets as precursors. Unfortunately for this, it has seldom been reported up to date, which is of great significance for efficient photocatalysis on BiVO₄.

Similar to other visible-light responsive oxides like Fe₂O₃, BiVO₄ usually displays a sluggish charge separation.^[19] This is mainly because its conduction band bottom position is positive, indicating that its photogenerated electrons are not energetic enough to induce reduction reactions thermodynamically.^[20] As for this, it is much meaningful to prolong the lifetime of excited proper-energy-level electrons under visible-light irradiation for efficient photocatalysis on BiVO₄. Fortunately, we have confirmed in our previous work that coupling with wide bandgap oxide nanoparticles such as TiO₂, ZnO and SnO₂ as new platforms for accepting the electrons at high-level potential could effectively prolong the charge lifetime and enhance the charge separation, consequently leading to the improved photocatalytic activities for degrading pollutants.^[21-22] It is clearly demonstrated that TiO₂ is a suitable energy platform for BiVO₄ since it is a chemically stable and low cost with a proper conduction band bottom level. However, the interfacial contacts between zerodimension nanoparticles are weak, affecting the charge transfer and separation to a certain degree. In other words, the dimension matching between different parts for constructing effective heterojunction should be considered. However, it is often neglected. Thus, to fabricate an efficient 2D BiVO₄-based photocatalyst, a 2D anatase TiO₂ nanosheet should be designed to couple with. In recent years, (001) facetexposed anatase TiO₂ 2D nanosheet (001T) has attracted great attention because of its high photocatalytic activity.^[23] This stimulates us to prepare 2D/2D TiO₂/BiVO₄ heterojunctions for improving the interfacial connection to promote the charge transfer and separation. Noticeably, related works have seldom been reported to date. Therefore, it is much interesting to emphasize the dimensional match importance of different parts in the fabricated heterojunctions for efficient photocatalysis.

It is noticed that the visible-light absorption of BiVO₄ is limited with the threshold of ~ 570 nm. In fact, it is feasible to begin from ~530 nm when TiO₂ is used to modify it.^[20] Thus, it is highly desired to extent the visible-light utilization range of BiVO₄. Recently, plasmonic metals like Au and Ag have driven much attention because of their strong and wide visible-light responses, especially for Au.^[24-25] Zhu and coworkers demonstrated that the photocatalytic oxidation of formaldehyde could be achieved over plasmonic Au/TiO2 under visible-light irradiation, in which the hot electrons excited by surface plasmonic resonance (SPR) Au could overcome the Schottky barrier to transfer to the conduction band of TiO₂ and subsequently initiate the photocatalytic reaction on TiO₂ surfaces.^[26] Naturally, it is expected that it is much feasible to couple with plasmonic Au to the preprepared TiO₂/BiVO₄ nanocomposite for wide visible-light responsive photocatalysis. Simultaneously, the coupled Au would still exhibits good catalytic functions to the transferred electrons for inducing reduction reactions. For SPR Au, its visible-light response depends on its morphology, and generally its nanorods display much wide visible-light absorption compared to its spherical nanoparticles.^[27] Moreover, it is anticipated that the 1D nanorods are much well matching to the fabricated 2D/2D heterojunctions relative to nanoparticles. Therefore, dimension-matched the 0D 1D/2D/2D plasmonic Au/TiO₂/BiVO₄ nanocomposites are newly proposed for efficient visible-light driven CO₂ conversion by photocatalysis. Unfortunately, it has been not reported to the best of our knowledge, and it is obviously of significance to efficient photocatalysis for producing solar fuels.

In addition, the mechanism and pathway of photocatalytic CO₂ conversion to produce fuels are still ambiguous. Generally speaking, CO₂ reduction could take place directly by photogenerated electrons, or indirectly by the produced H radicals with photogenerated electrons. As for the direct reduction process, it requires the photogenerated electrons possess enough thermodynamic energy (about -1.9 V vs NHE).^[28] However, the required energy of photogenerated electrons possibly decreases to a certain degree if CO₂ easily adsorbs onto the photocatalyst surfaces.^[29] Therefore, it is possible for the chemically-adsorbed CO₂ to be reduced by the low-energy photogenerated electrons below -1.9 V. Relatively, it is much easier for photogenerated electrons to reduce H₂O to produce H (about 0 V vs NHE). In this case, the produced H radicals would initiate the conversion of CO₂. However, there is still lacking of evidences to support the above two aspects. Therefore, it is meaningful to clarify the related process mechanism.

Experimental section

Synthesis of BiVO₄ nanoparticles. In a typical synthesis, 4.85 g of Bi(NO₃)₃·5H₂O was dissolved in 100 mL of HNO₃ aqueous solution with a concentration of 2 mol/L under vigorous magnetic stirring. Then, 1 g of PEG and 1.17 g of NH₄VO₃ were

added to the above mixture, and pH was adjusted to 7 with $NH_3 \cdot H_2O$. Then, the mixture solution was ultrasonicated for 30 min followed by continuous stirring for 1 h. Finally, the solution was centrifuged and washed with deionized water and absolute ethyl alcohol by turns and kept at 60 °C in an oven. The sample was named as BV-NP.

Synthesis of BiVO₄ nanoflakes. The BiVO₄ nanoflakes were prepared by the conversion of bismuth oxychloride nanosheets. In a typical procedure, 0.26 g of BiOCI nanosheets were dispersed in 30 mL water, after stirring for 10 min, sonicated for 5 min. Then 20 mL of 6.09 g·L⁻¹ NaVO₃ was added dropwise to the above solution and stirred for 30 min. Finally, the mixture solution was transferred into a 100 mL Teflon-lined autoclave, sealed and heated at 150 °C for 8 h. After the system was cooled down to room temperature, the resulting product was washed with deionized water for several times, and then dried at 60 °C in an oven. The sample was named as BV-NF.

Synthesis of (001) facet-exposed anatase TiO₂ nanosheets. In a typical procedure, 5 mL of Ti(OBu)₄ was mixed with 20 mL of absolute ethanol under vigorous stirring. After that, hydrofluoric acid solution (0.9 mL, 40%) was added. The resulting solution was stirred for 1 h, transferred in a Teflon lined stainless-steel autoclave, and then kept at 160 °C for 24 h. After the system was cooled to room temperature, the white precipitate was collected, washed with ethanol and deionized water for several times by turns and named as 001T. Synthesis of Au nanorods. There are two primary steps in this procedure. The first step is to prepare Au seeds. 364 mg CTAB and 1 mg HAuCl₄·3H₂O were dissolved in 10 mL of deionized water. 10 min later, 0.6 mL (10 mM) NaBH₄ was added to the above solution under vigorous magnetic stirring. The asobtained Au seeds were used in the growth of nanorods. The second step is to prepare Au nanorods. 364 mg CTAB, 2 mg HAuCl₄·3H₂O and 100 µL (4 mM) AgNO₃ solution were mixed in 10 mL deionized water. After stirring for 10 min, 70 µL (78.8 mM) of ascorbic acid was added to the solution and immersed in water bath at 27-30 °C, then 12 μ L of Au seed was added and the reaction was allowed to proceed for 1 h. Finally, the as-synthesized Au nanorods were purified by centrifugation to remove free CTAB, and named as AuNR.

Synthesis of AuNR-loaded 001T/BV-NF nanocomposite. The nanocomposites were prepared by the wet chemical method. In the typical synthesis, a proper amount of (001) facet-exposed anatase TiO_2 nanosheets and $BiVO_4$ nanoflakes were dispersed in 30 mL of absolute ethyl alcohol (the mole ratio of TiO_2 to $BiVO_4$ is 5%), and a certain ratio of AuNR (the mole ratio of AuNR to $BiVO_4$ is 2%) were mixed to the above solution under magnetic stirring for about 1 h. Finally, the mixture was dried in water bath at 80 °C for 6 h and calcined at 450 °C in air for 2 h, and the sample was represented by AuNR/001T/BV-NF.

Characterization. The X-ray powder diffraction (XRD) patterns of the samples were recorded by using a Bruker D8 advance diffractometer with CuK α radiation. The UV-Vis diffuse reflectance spectra (UV-Vis DRS) of the samples were acquired on a Model Shimadzu UV2550 spectrophotometer

with BaSO₄ as a reference. The morphology of the samples was analyzed by scanning electron microscopy (SEM) on a Hitachi S-4800 instrument (Tokyo, Japan). Transmission electron microscopy (TEM) images of the samples were performed by a JEOL JEM-2010 electron microscope with an acceleration voltage of 200 kV. The N₂ adsorption-desorption isotherm were carried out by Micromeritics Tristar II 3020 system (U.S.A). The SS-SPS and TS-SPV measurement for samples were implemented on home-built equipment, which has been described in detail elsewhere.^[20,21]

Other experimental sections including fluorescence spectra related to the formed hydroxyl radicals, CO_2 -TPD, in-situ DRIFTS, electrochemical reduction, PEC measurement and photocatalytic activities for CO_2 conversion are described in detail in Electronic Supplementary Information.

Results and Discussion

2D flake-like structured BiVO₄ was prepared via an ion exchange approach from BiOCI nanosheets.^[30] The obtained BiVO₄ nanoparticles (BV-NP) and BiVO₄ nanoflakes (BV-NF) are both identical to that of pure monoclinic BiVO₄ (JCPDC no. 14-688) confirmed by XRD patterns (Figure S1a). No obvious difference in optical absorption is observed for BV-NP and BV-NF, which corresponds to a band gap of 2.16 eV characterized by the DRS spectra (Figure S1b). The morphology of BV-NF was investigated by the SEM images. It can be seen that the flakelike BiVO₄ is uniform with a mean width of 200-500 nm, and average thickness of 20 nm is clearly observed from the outward side (Figure S1c). Nitrogen adsorption-desorption isotherm was employed to examine the surface area, and it turns out that the surface areas of BV-NP and BV-NF are 1.1 and 11.6 m² g⁻¹, respectively (Figure S1d). Apparently, BV-NF exhibits large surface area compared with the conventional nanoparticles. To explore the properties of charge carriers, fluorescence spectra related to the formed hydroxyl radicals (•OH) was employed by means of the coumarin fluorescent method, in which the coumarin easily reacts with •OH to produce luminescent 7-hydroxycoumarin. In general, the stronger is the fluorescent signal, the larger is the produced •OH amounts, and the higher is the photogenerated charge.^[31] It can be seen that the produced $\bullet OH$ amounts of BV-NF are much higher than those of BV-NP (Figure S1e), indicating that the flake-like structured BiVO₄ exhibits high charge separation. The visible-light photocatalytic activities of BV-NP and BV-NF for CO_2 reduction were evaluated with H_2O as the reducing agent (Figure S1f), in which CH₄ as the predominant product was detected. It clearly shows that BV-NF exhibits much high photoactivities compared with BV-NP, which is in good agreement with the produced •OH amounts.

To further enhance the charge separation of BV-NF, 2D (001) facet-exposed TiO_2 coupled BV-NF (001T/BV-NF) nanocomposite was prepared, along with general anatase TiO_2 nanoparticle coupled one (T/BV-NF) as the reference. The XRD patterns for BV-NF, T/BV-NF and 001T/BV-NF are displayed in Figure S2a. One can see that there are very-weak characteristic peaks of anatase TiO_2 detected on T/BV-NF and 001T/BV-NF

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nanocomposites, which is due to its tiny amount. Simultaneously, the bandgap and optical properties of BV-NF doesn't change after coupling with TiO₂ (Figure S2b). Moreover, the TEM images of 001T/BV-NF (Figure S3) indicate that the surfaces of BV-NF are covered by sheet-like 001T, forming an intimate heterojunction, since the lattice fringes of (200) plane with the inter-planar distance of 0.26 nm and the spacing of the (001) lattice plane with 0.24 nm are attributed to BiVO₄ and TiO₂, respectively. Definitely, the intimate connection of 2D heterojunction is stable and plays a vital role in the charge transfer and separation.



Figure 1 SS-SPS responses (a), Photoelectrochemical of linear sweep voltammetric (LSV) scan responses under visible light illumination and dark (b), electrochemical impedance spectra (EIS) (c) and photocatalytic activities for CO₂ conversion under visible light irradiation for 4 hours (d) of BV-NF, T/BV-NF and 001T/BV-NF. PEC and EIS measurements were carried out with a three-electrode system in 0.5M Na₂SO₄ electrolyte, with the tested film as the working electrode, Ag/AgCl as the reference electrode.

The steady-state surface photovoltage spectroscopy (SS-SPS) is a well-accepted photophysical technique, which reveals the surface structural characteristics, surface states, along with generation. separation and recombination the of photogenerated charge carriers by means of the changes in the surface potential of a semiconductor before and after illumination. In general, the strong SPS response usually indicates the high charge separation. As seen from Figure 1a, BV-NF shows a rather low SPS response. However, T/BV-NF nanocomposite exhibits an enhanced SPS response. This is attributed to the introduced TiO₂ as a proper-energy platform to accept electrons. In particular, the 2D 001T/BV-NF heterojunction displays much higher SPS response, indicating high charge separation. As for the constructed 2D/2D nanocomposite, it is much favorable for the charge transportation, transfer and separation owing to the intimate connection of the geometrical dimensional matching. Photoelectrochemical experiments of linear sweep voltammetric (LSV) scans for BV-NF, T/BV-NF and 001T/BV-NF electrodes in 0.5M Na₂SO₄ electrolyte were carried out under visible-light illumination from the back side (Figure 1b). As

expected, T/BV-NF electrode shows an increased photocurrent density compared with BV-NF one, and the photocurrent signal of 001T/BV-NF electrode is much larger than that of T/BV-NF. This is further supported by the electrochemical impedance spectra (Figure 1c). T/BV-NF exhibits a decreased capacitive arc radius compared with BV-NF, and 001T/BV-NF shows the smallest arc radius, implying that the charge transfer from BiVO₄ to TiO₂ is promoted. As a result, the photocatalytic activities for CO2 conversion of T/BV-NF and 001T/BV-NF nanocomposites achieve about 3-fold and 9-fold enhancement compared with that of BV-NF, respectively (Figure 1d). Notably, it shows 3-fold increase in photoactivity when TiO₂ morphology is changed from 0D particles to 2D nanosheets. In addition, according to the nitrogen adsorptiondesorption isotherm, 001T/BV-NF exhibits nearly the same surface area compared with the T/BV-NF one (Figure S4). This implies that the improved photocatalytic performance of 001T/BV-NF is mainly due to the matched 2D/2D structure of TiO₂ and BiVO₄, rather than the surface area increase.



Figure 2 HRTEM image of AuNR/001T/BV-NF (a) and DRS spectra of 001T/BV-NF, AuNP/001T/BV-NF and AuNR/001T/BV-NF (b).

In order to investigate the effects of multi-dimensional nanostructured gold on the visible-light absorption and photocatalytic activities, plasmonic Au nanoparticles (AuNP)-Au nanorods (AuNR)-loaded 2D 001T/BV-NF and nanocomposites were prepared. As shown in Figure S5, there is a diffraction peak at 38.2° in XRD patterns, which is assigned to gold. SEM image of AuNR modified 001T/BV-NF shows a uniform dispersion of AuNR on 001T/BV-NF surface (Figure S6a). In addition, the elemental composition of AuNR/001T/BV-NF nanocomposites was analyzed by EDS, indicating the presence of Bi, V, O, Ti, Au elements in the nanocomposite, as shown in Figure S6b, implying the successful preparation of Au/TiO₂/BiVO₄ nanocomposite. TEM and HRTEM images were employed to investigate the morphological and structural features of Au modified 001T/BV-NF nanocomposites. It is confirmed from Figure 2a and Figure S7, both AuNP and AuNR form intimate ternary heterojunctions with BiVO₄ nanoflakes and TiO₂ nanosheets since the lattice spacing with 0.204 nm is attributed to the (200) facet of Au. It is clear that AuNP is spherical with ~10 nm in diameter, while the AuNR with a length of ca. 20 nm and a width of 8 nm. Figure 2b shows the DRS spectra of 001T/BV-NF nanocomposites with Au modification. It is clear that the optical absorption behavior of BiVO₄ doesn't change after modifying Au. However, there are obvious long-wavelength

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absorption peaks in the spectra, resulting from the surface plasmon resonance (SPR) of Au. It can be seen that AuNP shows a distinct SPR peak at 600 nm, while the SPR one of AuNR shifts to 660 nm. Thus, it is confirmed that the SPR effects of Au could extend the visible-light absorption of $BiVO_4$, especially for the AuNR.

The photogenerated charge separation was explored by the SPS technique (Figure 3a). One can notice that Au-loaded 001T/BV-NF nanocomposites exhibit strong SPS signals compared with 001T/BV-NF one. It is worth noting that there are two types of SPS signals for Au modified ones. The peaks located at ~450 and ~600 nm are attributed to the inherent charge separation of BiVO₄ and injection of hot electrons from SPR Au, respectively. In addition, the SPS response of AuNR-loaded one is much stronger than that of AuNP-loaded one, indicating the AuNR is much favorable to modify the resulting 001T/BV-NF for visible-light absorption and charge separation.

The TS-SPV method is an advanced technique to reveal the dynamic behaviours of photoinduced charge carriers. Generally speaking, for a nanosized semiconductor, its built-in electric field could be neglectable so that its effect on the carrier separation is much small. Thus, the charge separation is mainly affected by the diffusion process, always with the lifetime within the microsecond timescale. As shown in Figure 3b, the slow-time SPV signal of 001T/BV-NF is enhanced after Au modification, especially for the AuNR-modified one. Moreover, it is confirmed that the charge carrier lifetime of 001T/BV-NF is prolonged after AuNR modification by 300 µs.

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Figure 3 SS-SPS responses (a), TR-SPV responses (b), Fluorescence spectra related to the formed hydroxyl radicals under visible light excitation (c) and Photocatalytic activities for CO_2 conversion under visible light irradiation (d) of 001T/BV-NF, AuNP/001T/BV-NF and AuNR/001T/BV-NF. Inset Fig. 3a shows enlarged SPS responses from 500 to 800 nm.

To further investigate the photogenerated charge properties, photochemical experiments, including fluorescence spectra related to the amounts of produced hydroxyl radicals and EIS spectra for exploring interface resistance were carried out. As shown in Figure 3c and Figure S8, it is clear that Aumodified ones exhibit large •OH amounts and small capacitive arc radii compared with that of 001T/BV-NF, especially for AuNR-loaded one. This implies that the constructed 1D/2D/2D nanocomposite exhibits much better charge transportation, transfer and separation, which is agreeable with the above photophysical (above-mentioned SS-SPS and TS-SPV) results. It is attributed to the dimensional matching of different constituents in the fabricated nanocomposites. Thus, it is anticipated that the fabricated dimension-matching 1D/2D/2D nanocomposites would exhibit much high photocatalytic activities.

The photocatalytic activities for CO₂ reduction were evaluated under visible-light irradiation as shown in Figure 3d. The reduction products like CH₄ and CO, along with a certain amount of O_2 as the oxidation product, are detected. Apparently, the photocatalytic activities for 001T/BV-NF are improved after loading Au, and the AuNR-loaded nanocomposite displays higher photoactivity than the AuNPloaded one. Interestingly, the AuNP-loaded and AuNR-loaded nanocomposites achieve 2-fold and 3-fold photoactivity enhancements compared with 001T/BV-NF one, respectively. It is noted that the AuNR/001T/BV-NF one exhibits 30-time photoactivity enhancement compared to BV-NF. Βv comparison with some other published works (Table S1), it is clear that the photocatalytic activities of AuNR-loaded 001T/BV-NF in this work exhibit excellent performance for CO₂ conversion.^[32-35] In order to evaluate the stability of AuNR/001T/BV-NF, photocatalytic CO₂ reduction experiments were carried out under 8 hours continuous irradiation, as shown in Fig. S9. One can see that the amounts of evolved CH₄ and CO linearly become large with increasing the irradiation time indicating that the fabricated AuNR/001T/BV-NF nanocomposite is much stable.

Discussion

As described above, the flake-like $BiVO_4$ with large specific surface area exhibits much high photocatalytic activities compared with general nanoparticles. Remarkably, the photoactivities could be further improved by coupling with TiO₂, and it is much obvious with (001) facet-exposed one. This is mainly attributed to the matched 2D/2D structures between TiO₂ and BiVO₄ for the promoted charge transfer and separation. Moreover, the photocatalytic activities of 001T/BV-NF nanocomposites could be greatly improved by modifying with plasmonic Au, especially for the AuNR-loaded one. Thus, it is of great significance to reveal the mechanism of the enhanced charge separation on dimension-matched 1D/2D/2D AuNR-modified 001T/BV-NF nanocomposite, especially for the SPR effects.

Monochromatic photocurrent action spectra were thus performed, as shown in Figure 4a. One can learn that the photocurrent density of 001T/BV-NF gradually increases as the excitation wavelength decreases from 550 to 400 nm. Noticeably, it begins to sharply increase under 530 nm excitation, which is the threshold wavelength to facilitate the transfer of visible-light excited proper-energy electrons of BV-NF to 001T.^[20] In particular, the photocurrent density of

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001T/BV-NF greatly increases after loading Au, especially for the AuNR-loaded one. This indicates that it is much favorable for the photogenerated charge separation of 001T/BV-NF to load Au nanorods. Moreover, the obvious photocurrent response of AuNR-loaded one is observed even under 660 nm excitation, which is attributed to the hot electrons transfer to TiO₂ from SPR AuNR under visible-light irradiation. To further confirm this, the FS spectra related to the amounts of produced hydroxyl radicals was carried out under differentwavelength monochromatic light excitation (Figure 4b).



Figure 4 Normalized photocurrent action spectra (a) and Fluorescence spectra related to the formed hydroxyl radicals under 660 nm excitation (b) of 001T/BV-NF, AuNP/001T/BV-NF and AuNR/001T/BV-NF. Inset Fig. 4b shows FS signals under 590 nm excitation.

Based on the photoelectrochemical results, two typical monochromatic wavelengths of 590 and 660 nm were chosen. One can see that 001T/BV-NF shows a neglectable fluorescent response under 590 nm excitation owing to the threshold wavelength of 570 nm for exciting BiVO₄. Notably, the amount of produced hydroxyl radical is obviously increased after loading Au, and it is much larger for the AuNR-modified one even at 660 nm excitation. This is in good agreement with the above photoelectrochemical results, indicating that 1D AuNR is much beneficial for the extended visible-light response and the subsequent charge separation compared to OD AuNP. This further confirms that the geometrical dimension matching of different constituents in the fabricated 1D/2D/2D nanocomposite is crucial for the effective charge transfer and separation.



Figure 5 Electrochemical reduction curves in N₂-bubbled (a) and CO₂-bubbled systems (b) of 001T/BV-NF, AuNP/001T/BV-NF and AuNR/001T/BV-NF nanocomposites. The inset in (b) shows CO₂-TPD curves of the three samples as mentioned. Electrochemical performance was measured in 0.5 M Na₂SO₄ solution, and Hg/Hg₂Cl₂ (saturated KCl) electrode was used as the reference electrode.

To explore the mechanism of CO_2 conversion, electrochemical reduction measurements were carried out in different gas-bubbled systems. In the N₂-bubbled system

(Figure 5a), it is much favorable for H_2O reduction on the Auloaded 001T/BV-NF, especially for the AuNR one. However, it should be pointed out that the onset potentials of different BV-NF-based electrodes for H_2O reduction are similar to those in the CO₂-bubbled system (Figure 5b), implying that the reduction behavior of CO₂ is not preferred. This is attributed to the un-promoted adsorption of CO₂ after loading Au by means of the CO₂ temperature-programmed desorption curves (Figure 5b inset). Thus, it is deduced that the Au-loaded 001T/BV-NF prefers H_2O reduction to CO₂. Therefore, it is suggested that the produced H radicals from H_2O reduction are dominant active radicals to initiate the conversion of CO₂.

To further disclose the produced H atoms from the photocatalytic reduction of H_2O other than of H^+ and their roles in the subsequent conversion of CO_2 , isotopic D_2O and $^{13}CO_2$ labeling experiments were employed under identical photocatalytic reaction conditions. The photocatalytic products were identified and quantified with GC-MS technique. When H_2O is substituted with D_2O (Figure S10), C, CD, CD₂, CD₃, and CD₄ are detected, implying the important role of H in H_2O . In addition, a certain amount of CH₃OH as an effective hole capturer is deliberately added in the photocatalytic system, in which the photocatalytic activities for CO_2 conversion would be improved, simultaneously to effectively provide the source of H⁺ for being favorable to produce H radicals.^[36-37]



Figure 6 Amounts of CH₄ detected by GC analysis and ion peak intensity of CD₄ detected by GC-Mass spectrometry for AuNR/001T/BV-NF nanocomposite. The amount of CH₄ evolved in pure H₂O and methanol containing H₂O solution are denoted as a and b, respectively. The ion peak intensity of CD₄ in pure D₂O and methanol containing D₂O solution are denoted as a' and b'.

As expected (Figure 6), the amount of produced CH_4 in the presence of CH_3OH on AuNR/001T/BV-NF is much larger than that in H_2O by the GC test, and the amount of produced CD_4 in the presence of CH_3OH on AuNR/001T/BV-NF is also much larger than that in D_2O by the GC-MS test. Interestingly, it is noted that the activity-enhancement times after adding CH_3OH in H_2O and in D_2O are similar. The results reasonably indicate that the H atoms in the formed CH_4 are mainly originated from H_2O and CH_3OH and could capture the holes to promote charge separation. This is further supported by the in-situ DRIFTS (Figure S11a). One can see that the adsorption of methanol reach the equilibrium state in 30 min. Interestingly, under visible-light irradiation, as shown in Figure S11b, the intensity of methanol decreases while that of CO_2 increases significantly, indicating that methanol mainly acts as the

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sacrificial agent to capture photo-generated holes, which is consistent well with the isotope results. In addition, signals resulting from ¹³C, ¹³CH, ¹³CH₂, ¹³CH₃ and ¹³CH₄ by replacing CO₂ with ¹³CO₂ could be detected by the GC-Mass test (Figure S12). This further confirms that the produced CH₄ is from CO₂ resource.

On the basis of the above results and discussion, a schematic for the photogenerated charge transfer and separation and its induced reaction on the designed dimension-matched Au-loaded 001T/BV-NF nanocomposite under different visible-light wavelength ranges has been proposed (Figure 7). When the excitation wavelength range is from 400 to 530 nm, the produced proper-energy-level electrons of BiVO₄ would transfer to TiO₂, and then to Au as the co-catalyst for H production. When it is larger than 530 nm, the plasmonic Au-induced hot electrons with high thermodynamic energy will inject to the adjacent TiO₂ to produce H. The formed H by visible-light irradiation would continuously initiate the conversion of CO₂. Obviously, the synergistic mechanism in the SPR Au-loaded 001T/BV-NF results in the excellent photocatalytic activities for CO₂ conversion.



Figure 7 Schematic of the photogenerated charge transfer and separation and its induced reaction on the designed dimension-matched Au-loaded 001T/BV-NF nanocomposite under visible-light irradiation with wavelength of 530 -660 nm.

Conclusions

summary, dimension-matched AuNR/001T/BV-NF In nanocomposites as efficient photocatalysts to convert CO₂ have been successfully synthesized. It is clearly demonstrated that the exceptional photocatalytic activities are comprehensively attributed to the increased specific surface area by 2D-structured nanoflake, to the enhanced charge separation by coupling (001) facet-exposed TiO_2 as a new proper-energy-level platform to accept photogenerated electrons from BiVO₄ nanoflakes and SPR Au, to the extended visible-light absorption thanks to the SPR AuNR and to its cocatalyst role for the electrons transferred to TiO₂. In particular, the dimension matching in the fabricated nanocomposite is demonstrated to be much favorable for the photogenerated charge transfer and separation. In addition, it is confirmed that the produced H radicals are dominant active species to initiate the conversion of CO₂. Moreover, the resulting

AuNR/001T/BV-NF nanocomposite displays a wide visible-light response range from 400 nm to 660 nm, which is 34.8% of the solar spectrum and 78.9% of the visible light. This indicates that there is a great potential for solar fuel production by designing plasmonic-assisted $BiVO_4$ -based nanophotocatalysts. This work provides a feasible route to fabricate high-activity $BiVO_4$ -based nanophotocatalysts for solar fuel production.

Conflicts of interest

There are no conflicts to declare

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