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Au modified $BiVO_4$ microparticles for photocatalytic N_2 fixation*

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In this work, a visible light photocatalyst based on Au modified $BiVO_4$ microspheres was synthesized successfully through using a facile photodeposition method for visible light N_2 fixation. Compared with pure $BiVO_4$ microparticles (MPs), the obtained Au/$BiVO_4$ MPs show superior N_2 photofixation performance to $BiVO_4$, owing to the enhancements of both the visible light absorption and charge carrier separation. After optimization, the actual NH_4^+ generation rate of Au/$BiVO_4$ reaches 0.419 $mg\cdot L^{-1}$, which is approximately 2 times higher than that of the pure $BiVO_4$ one. The results presented herein provide new insights into rational design of highly active catalysts with Au NPs toward efficient, stable, and sustainable visible light N_2 fixation in mild conditions.

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Recently, visible light photocatalytic N_2 fixation has attracted much attention for its low cost, safety and environment friendly. With a rapid development of society and industry, the demand for chemical fertilizer, amino acid or other ammonia related products has been expanding. Nevertheless, how to realize an efficient N_2 fixation has become a global problem. Early as the 1970s, the invention of Haber-Bosch[1] method ended the history of human dependence on natural nitrogen sources, opening up a new era of artificial nitrogen fixation. However, the Haber-Bosch method is extremely resource intensive and polluting, thus it is urgent to seek a new method for N_2 fixation[2]. Solar energy is a renewable energy source with large storage. Thus, it is expected to develop a technique for N_2 fixation by utilizing solar energy as the excitation source[3].

$BiVO_4$ has emerged as a promising material for photocatalyst, showing visible light photocatalytic activity[4]. The monoclinic scheelite $BiVO_4$ with a bandgap of ~2.4 eV exhibits a higher photocatalytic activity than its crystal-structure counterparts[5]. Its lower bandgap energy enables light absorption up to 11% of the solar spectrum compared to 4% for the conventional ultra-violet (UV)-sensitive TiO_2. However, unmodified $BiVO_4$ photoanodes suffer from poor charge transport and sluggish nitrogen fixation kinetics[2,4], which significantly restricted the practical applications of $BiVO_4$ in photocatalysis[6]. Therefore, various strategies such as doping with nitrogen[7] or molybdenum[8], loading of cocatalysts, such as Co-Pi[9], Pd[10], black phosphorus (BP)[11], Au[12], or construction of a heterojunction[13], have been employed to alleviate these restrictions. Among them, noble metals have been reported to be effective cocatalysts for enhancing the photocatalytic and photoelectrochemical (PEC) performance of photocatalysts[10,12]. As the Fermi levels of these noble metals are lower than that of $BiVO_4$, the photo-excited electrons can be transferred from conduction band (CB) of $BiVO_4$ to noble metal particles, while photo-generated holes remain on the valence band (VB) of $BiVO_4$. It greatly reduces the recombination rate of photoexcited electron-hole pairs, resulting in a more efficient separation and a higher photocatalytic activity.

Here, a facile route was developed for synthesizing Au nanoparticles (NPs) modified $BiVO_4$ photocatalysts, which was capable for reducing N_2 in a water/methanol system under a visible light irradiation and ambient pressure. The Au NPs could dramatically enhance the visible-light harvesting as well as carrier separation in the Au/$BiVO_4$ hybrid, thereby improving total power conversion efficiency. Such a cooperative effect resulted in a higher photocatalytic activity for artificial photosynthesis of ammonia. Mechanistic insights into the high selectivity as well as the synergistic effect were proposed and discussed by terms of the experimental results.

$Bi(NO_3)_3\cdot 5H_2O$, NH_4VO_3, KOH, and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. The water used throughout all the experiments was purified through a Millipore system.

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The $BiVO_4$ powders were synthesized through a facile hydrothermal route. Typically, 2.43 g $Bi(NO_3)_3 \cdot 5H_2O$ and 0.25 g sodium dodecyl benzene sulfonate (SDBS) were dissolved in 10 mL of HNO_3 (4 mol/L) aqueous solution under continuous stirring for 30 min. Soon afterwards, the obtained homogeneous solution was added drop by drop into 20 mL of NaOH (2 mol/L) alkaline solution containing 0.58 g of NH_4VO_4 and 0.25 g of SDBS, followed by stirred for 30 min to form an orange suspension. Then, the pH value was adjusted to 7.0 with NaOH. Afterwards, the solution was transferred and sealed in a Teflon-sealed steel autoclave and kept at 200 °C for 24 h. After hydrothermal process, the autoclave was cooled to room temperature (RT). The precipitates were collected and washed alternately with deionized (DI) water and absolute alcohol for several times. Finally, the obtained sample was dried in an oven at 100 °C for 4 h, and then the light-yellow powders were obtained.

500 mg as-prepared $BiVO_4$ powders were dispersed in 100 mL DI water, different amounts of $HAuCl_4$ (0.01 g, 0.05 g, 0.1 g, and 0.2 g) were then added into these solutions individually with a continuing stirring for 30 min to get a precursor. The mixture was stirred under visible light with a 500 W Xe lamp for 5 h. After then, the sample was collected, washed and centrifuged by DI water/ethanol alternatively for several times. Finally, the obtained products were dried in air for 4 h, and then collected for characterization and other uses.

All photocatalytic measurements were carried out in a photoreduction reactor at atmospheric temperature and pressure for the fixation of molecular nitrogen. A 500 W Xe lamp was used as an irradiation source for providing visible light output, while a methanol aqueous solution (H_2O:CH_3OH=4:1) was used in the photocatalytic experiment. Prior to measurement, the mixture solution was purged with high-purity nitrogen for 20 min to remove the dissolved oxygen. Typically, 15 mg photocatalyst was dispersed into 15 mL methanol aqueous solution and stirred ultrasonically for 30 min to guarantee homogeneity. During the whole test, the reaction solution was bubbled with nitrogen with a flow rate of 70 mL/min under magnetic stirring. The production velocity of ammonia was monitored by Nessler's reagent spectrophotometry. Typically, 1 mL Nessler's reagent was dropped into 1 mL obtained reaction solution. The mixed solution was placed in dark for 20 min before ultra-violet visible (UV-Vis) measurements, which was carried out by a doubled-beam UV-Vis spectrophotometer (Shanghai Xinmao Instrument Co., Ltd., model Cary300). The adsorption peak intensity of indophenol at 430 nm was used for evaluating the production rate of ammonia or ammonium ions.

X-ray powder diffraction patterns (XRD, Bruker Co., Ltd., model D8 ADVANCE) were recorded in the region of 2θ=10°—70° using Cu Kα radiation (λ=0.154 18 nm) with a step scan of 2.0°/min at RT using a counter diffractometer. The morphology and structure of as-prepared samples were examined with scanning electron microscopy (SEM, Hitachi Co., S-4800). UV-Vis diffuse reflectance spectra (DRS) of $BiVO_4$ were recorded by using an integrating sphere with a $BaSO_4$ reference, and then the absorbance plots were converted from reflection by the Kubelka-Munk method.

The PEC performance of the obtained products was carried out by using a three-electrode quartz cell connected with a CHI660E electrochemical workstation (CHI Instruments, Shanghai, China). Herein, a Pt foil, a saturated calomel electrodes (SCE) and a 0.1 mol/L Na_2SO_4 solution (pH=6.8) were employed as the counter electrode, reference electrode and electrolyte, respectively. In order to prepare a working electrode, 10 mg photocatalyst ($BiVO_4$ or Au/$BiVO_4$ powders), 10 μL nafion solution (5wt%), 20 μL DI water and 20 μL ethanol were mixed ultrasonically to form a homogeneous suspension. Then, 20 μL of the above suspension was deposited onto a 2 cm×3 cm fluorine doped tin oxide (FTO) glass and placed on a hot plate at 60 °C to evaporate the liquids. Both the quantity and area of these electrodes were kept the same to realize a valid PEC measurement. Finally, a series of PEC measurements, including the transient photocurrent responses, electrochemical impedance spectra (EIS) and Mott-Schottky (M-S) plots, were carried out under a full-spectrum irradiation or in dark.

Fig.1 shows the XRD patterns of the $BiVO_4$ microparticles (MPs) loaded with various Au contents. The diffraction peaks of the sample were in conformity to the standard card of $BiVO_4$ (JCPDS 14-0688), indicating that the all prepared photocatalysts possessed the same crystal structure. It was confirmed that the photocatalysts displayed a single monoclinic scheelite structure[14], while no any other phases or impurities were detected for the as-prepared sample. The observed diffraction peaks of $BiVO_4$ were strong and sharp, indicative of a high crystallinity.

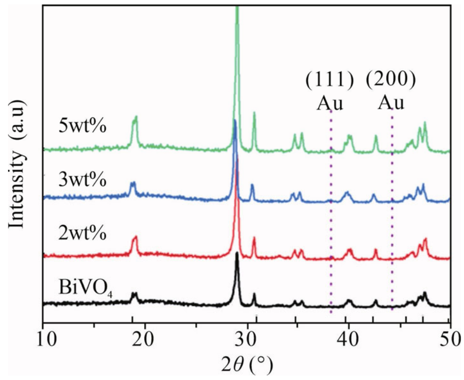
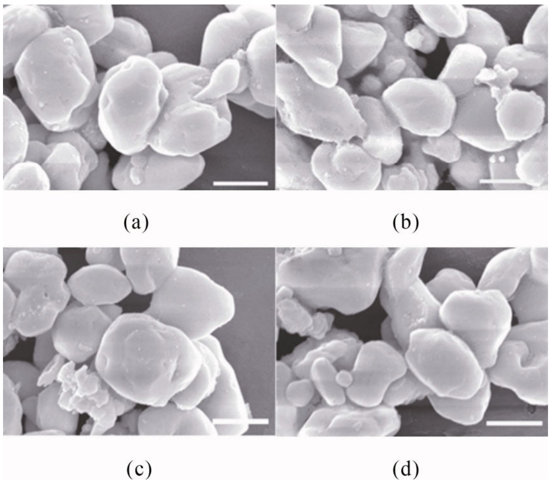


Fig.1 Typical XRD patterns of Au/$BiVO_4$ with various Au loading contents, with reference to a standard JCPDS card (No. 14-0688)

The surface morphology of $BiVO_4$ MPs with various loading amounts were shown in Fig.2. The as-prepared $BiVO_4$ photocatalyst was made up of MPs with an average size of ~1.5 μm, which was suitable for deposition of Au NPs. As could be seen, the Au NPs were difficult to be distinguished from the field emission scanning electron microscopy (FESEM) image even at a large magnification rate of 50 000, suggesting that the average size of these Au NPs was lower than 10 nm. It suggested that the photodeposition was a good method for preparing the ultrathin Au NPs. Besides, there weren't any changes in the surface morphology of $BiVO_4$ MPs even after a modification of ultrathin Au NPs.


(a) (b)

(c) (d)

Fig.2 SEM images of (a) pure $BiVO_4$, (b) 2wt% Au/$BiVO_4$, (c) 3wt% Au/$BiVO_4$ and (d) 5wt% Au/$BiVO_4$ (The scale is 500 nm.)

The UV-Vis absorption spectra of Au/$BiVO_4$ samples were depicted in Fig.3(a). The absorption edge of pure $BiVO_4$ appeared at ~509 nm, corresponding to its band-gap of 2.44 eV. It was also found that the Au/$BiVO_4$ samples displayed a higher absorption than $BiVO_4$ over a visible light range of 500—800 nm, which might be attributed to the surface plasmonic resonance effect from Au NPs[12], leading to the enhanced visible light photocatalytic activity. Besides, the M-S plots of the samples are collected to define their CB positions (Fig.3(b)). The derived flat-band potentials (V_{fb}) of $BiVO_4$ and Au/$BiVO_4$ were about −0.53 V and −0.82 V (versus SCE), respectively. Apparently, the more negative the V_{fb} value, the larger band bending at interface is the photoanode. It would be favourable for enhancing the PEC performance.

Otherwise, the EIS results revealed that 3wt% Au/$BiVO_4$ samples the smallest semicircle in the Nyquist plots (Fig.3(c)), suggesting the lowest charge-transfer resistance occurred at the solid electrode/electrolyte interfaces. Obviously, it suggested that an Au modification was favourable for the charge transport/ separation of photoinduced carriers[15]. Moreover, transient *J-t* plots indicated that Au/$BiVO_4$ exhibited a greatly enhanced photocurrent density than pure $BiVO_4$ particles (Fig.3(d)), revealing the promoted separation or transfer of photogenerated carriers inside the Au/$BiVO_4$ sample.

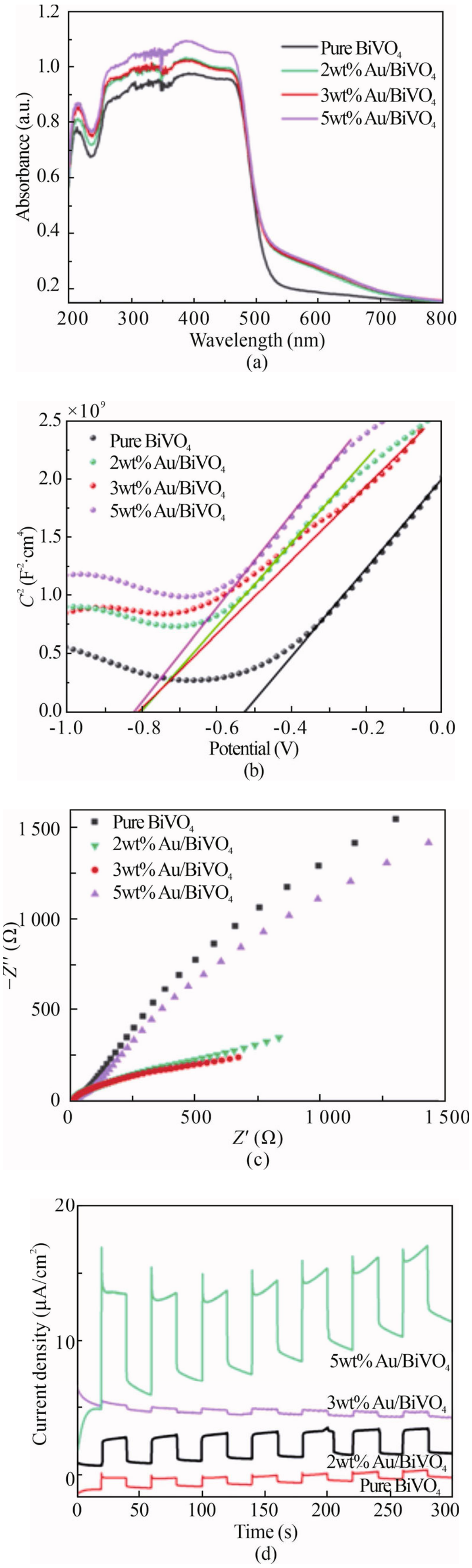


Fig.3 (a) UV-vis absorption spectra, (b) M-S plots measured in dark, (c) Nyquist plots under irradiation, and (d) transient *J-t* plots of Au/$BiVO_4$ samples with various loading amounts

The N_2 reduction reaction was carried out in a designed photoreduction reactor with magnetic stirring under constant N_2 gas bubbling, while a 500 W Xe lamp was used as the irradiation source. The irradiation intensity on the reactor surface was calibrated to be 100 mW/cm^2. The reactions involved during the N_2 photoreduction process could be described as follows.

Photocathode:

$$N_2 + 4H_2O + 6e^- + 4H^+ \rightarrow 2NH_4^+ + 4OH^- , \qquad (1)$$

Photoanode:

$$CH_3OH + 2h^+ \rightarrow CH_2O + 2H^+ . \qquad (2)$$

As a result, the visible-light photocatalytic N_2 fixation activities of $BiVO_4$ photocatalysts with different Au loading amounts were shown in Fig.4. The $BiVO_4$ MPs were active to catalyze the splitting of nitrogen with methanol as the hole scavenger, giving a nitrogen fixation rate of 0.219 mg·L^{-1}, while Au exhibited much improved photocatalytic activity for nitrogen fixation compared to pure $BiVO_4$. The highest photocatalytic rate for nitrogen fixation was observed on 3wt% Au/$BiVO_4$ (0.419 mg·L^{-1}), of which the ammonia yield was higher than that of 2wt% Au/$BiVO_4$ (0.374 mg·L^{-1}). However, the photocatalytic nitrogen fixation rate decreased to 0.398 mg·L^{-1} with increasing Au content to 5%, which might be attributed to the agglomeration of ultrathin Au NPs. Besides, the performance degradation of Au/$BiVO_4$ with excessive loading might be associated with an enhanced light shedding from Au NPs. Totally, the above results demonstrated a higher activity of 3% Au/$BiVO_4$ than the one with other loading amounts for photocatalytic nitrogen fixation.

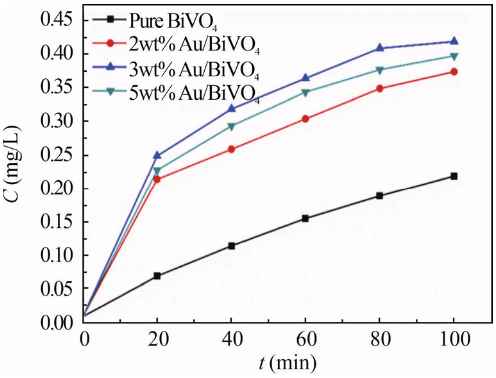


Fig.4 Quantitative determination of ammonia generated from the as-prepared $BiVO_4$ and Au/$BiVO_4$ under visible light irradiation

Therefore, the mechanism of ultrathin Au NPs decorated $BiVO_4$ MPs could be illustrated as follows. Au NPs could cause the surface plasmon effect, leading to an enhancement of visible light absorption. A Schottky barrier would be built at the Au/$BiVO_4$ interface, leading to more efficient separation of photoinduced electron-holes. The Au NPs acted as the photocatalytic reaction sites, which was favourable for collecting the photogenerated electrons from $BiVO_4$ for reducing N_2 molecules.

In conclusion, an Au modified $BiVO_4$ photocatalyst was synthesized successfully as a cost-effective photocatalyst for visible-light-driven photofixation of nitrogen. The plasmonic Au NPs were capable to produce a great deal of hot electrons as well as accelerate the carrier separation. The synergistic effect of the above two reactions could break the strong triple bonds of N_2 molecules to form ammonia. The performance of Au/$BiVO_4$ could be optimized by adjusting the Au loading amounts. As a result, the 3% Au/$BiVO_4$ photocatalyst shows outstanding performance for N_2 fixation with considerable ammonia evolution rate (0.419 mg·L^{-1}) and excellent stability. Our results presented herein provide new insights into a rational design of nanostructured $BiVO_4$ photocatalysts toward efficient, stable and sustainable visible-light-driven photocatalytic N_2 fixation.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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