[Article]

doi: 10.3866/PKU.WHXB201812054

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Construction of Advanced Two-dimensional Heterostructure Ag/WO_{3-x} for Enhancing Photoelectrochemical Performance

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Abstract: Solar energy, which is clean, affordable and reliable, can help alleviate the current environmental pollution and energy crisis efficiently. In the past few decades, great progress has been made in harvesting and converting solar energy into chemical energy. Among various technologies, plasmon-induced photoelectrochemistry has been proposed as a promising alternative for solar energy conversion. The hot electrons generated from plasmon excitation and transfer from metal nanostructures to semiconductors is a potential new paradigm for solar energy conversion. However, the ultrafast decay of the hot carriers is unfavorable for the improvement of photocatalytic efficiency. Therefore, finding more efficient photocatalysts, with enhanced light absorption and a longer carrier lifetime, is of paramount importance for improving the conversion efficiency of solar energy, but their fabrication is challenging. In this work, a plasmonic metal/semiconductor heterostructure based on Ag nanoparticles embedded in two-dimensional (2D) amorphous sub-stoichiometric tungsten trioxide (a-WO_{3-x}), followed by annealing, was successfully fabricated. Firstly, the peculiar nanostructure of 2D a-WO_{3-x} was successfully constructed from WS₂ nanosheets with supercritical CO₂ (SC CO₂) at 200 °C. Secondly, the Ag/a-WO_{3-x} heterostructure was synthesized using an *in situ* reduction method. Finally, the obtained 2D heterostructure of Ag/WO_{3-x} was annealed at 400 °C in N₂ to further improve its stability and conductivity. X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were used to characterize the structure, morphology, and composition of the material, respectively. UV-Vis spectra were also measured to evaluate light adsorption. Characterization results show that the amorphous structure can effectively anchor metal nanoparticles, and the metal nanoparticles are uniformly dispersed in the amorphous region and have a small size. The as-prepared nanocomposites showed efficient photoelectrochemical (PEC) water splitting when serving as photoelectrode materials, and efficient PEC activity towards photo-oxidation degradation currents under excitation of Ag localized surface plasmon resonance (LSPR). The photocurrent response of the Ag/WO_{3-x} heterostructure was approximately five times greater than that of a-WO_{3-x}. Moreover, the PEC degradation efficiency of Ag/WO_{3-x} reached 96.7% for MO under Vis light illumination (after reaction for 120 min), while the PEC degradation efficiency of WO_{3-x} was only 63.6%. The high PEC performance of the composite photoanode can be ascribed to the local surface plasmon resonance (LSPR) effect of the Ag nanoparticles, which can enhance the light absorption and hot electron transformation. Moreover, the construction of local crystalline-amorphous interfaces can further promote the separation efficiency of the photogenerated electron-hole pairs, and thus increase conductivity. This work provides a positive strategy for the fabrication of advanced photocatalysts, and a new perspective on understanding of the synergistic effects of structural and electronic regulations.

Key Words: Two-dimensional material; Plasmonic metal/semiconductor heterostructure; PEC conversion

Received: December 30, 2018; Revised: January 24, 2019; Accepted: January 28, 2019; Published online: February 20, 2019.

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The project was supported by the National Natural Science Foundation of China (21773216, 51173170, 21571157) and the Innovation Talents Award of Henan Province, China (114200510019).

国家自然科学基金(21773216, 51173170, 21571157)和河南省创新人才(114200510019)资助项目

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构筑先进二维异质结构 $\text{Ag}/\text{WO}_{3-x}$ 用于提升光电转化效率

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摘要: 等离子体激元诱导的光电化学反应被认为是太阳能转换的有效替代方案。寻找具有增强的光吸收以及更长载流子寿命的高效光催化剂对于提高太阳能的转换效率至关重要, 但其制备却具有挑战性。我们制备了Ag纳米颗粒均匀负载的二维(2D)无定形三氧化钨(a-WO_{3-x}), 并对其进行退火处理, 所获得的纳米异质结用作光电极材料具有高效的光电转化效率, 并且其光氧化降解性能也显著提升。该光电阳极的高光电催化(PEC)性能归因于等离子体金属Ag纳米颗粒的局部表面等离子共振(LSPR)效应能够增强体系的光吸收和热电子转移。此外, 局部结晶-非晶界面的构筑可以进一步提高光生电子-空穴对的分离效率并增加体系的导电性。

关键词: 二维材料; 等离子体金属/半导体异质结构; PEC转换
中图分类号: O646

1 Introduction

Utilization of renewable solar energy in chemical transformations has been regarded as one of the most promising approach to satisfy the rising global energy demand and simultaneously solve the corresponding environmental problems¹⁻⁵. Among various forms for solar energy utilization, photocatalysis, which can promote the chemical reactions by the light-matter interaction, represents an efficient way to realize the converting of solar energy to chemical energy⁶. In view of the abundant and renewable nature of solar and water resources, hydrogen and oxygen production from photoelectrochemical (PEC) water splitting using semiconductor photocatalysts have caught the attention of researchers from academics and industry⁷⁻¹⁰. However, current photocatalysts suffer from insufficient light absorption, inefficient charge separation, and high charge recombination rate as well. Therefore, exploring photoelectrode materials with highly photoactive and longer carrier lifetime are urgently demanded.

Ideal solar-to-fuel photocatalysts must effectively harvest solar energy to enhance conversion efficiency. Recently, incorporating plasmonic metal nanoparticles into photocatalytic systems holds great promise for dramatically improving the efficiency of sunlight absorption and solar energy conversion, in which the localized surface plasmon resonance (LSPR) effect of the metal nanoparticles plays a significant role in promoting the photoactivity¹¹⁻¹³. To date, many semiconductors (such as TiO_2 , Fe_2O_3 , ZnO and WO_3 , etc.) and metals (such as Au, Ag, Cu, etc.) have been employed to prepare metal/semiconductor composite photocatalysts for plasmon-enhanced water splitting¹⁴⁻¹⁹. In the plasmonic metal/semiconductor systems, the hot electrons transferred from excited plasmonic metal can be directly injected into the conduction band of semiconductor for that they have higher energy than the interfacial Schottky barrier (ϕ_{SB}), and then contribute to the production of photocurrent²⁰⁻²². However, if simply mixing plasmonic metal nanoparticles with semiconductor, their interface interaction will be very weak and

moreover the metal nanoparticles cannot be well-controlled, resulting in the plasmon effect is greatly reduced²³. Thus, rational designing peculiar plasmonic metal/semiconductor heterojunction is necessary.

On the basis of our previous study²⁴, loading the plasmonic metal Ag nanoparticles into a peculiar 2D amorphous sub-stoichiometric tungsten trioxide (a-WO_{3-x}), in this work, we further annealed the obtained 2D heterostructure of $\text{Ag}/\text{a-WO}_{3-x}$ at 400 °C in N_2 to obtain the expected nanocomposites with local crystalline-amorphous interface (Scheme 1), moreover the plasmonic metals are uniformly dispersed and have intimate contact with the WO_{3-x} nanosheets.

2 Experimental

2.1 Supercritical CO_2 (SC CO_2)-assisted in inducing chemical reaction

WS_2 nanosheets with single or few layers can be prepared by exfoliating bulk WS_2 powder (99%, Sigma-Aldrich Reagent Inc., Product Number: 243639) with assistance of SC CO_2 ²⁵⁻²⁷. Then, amorphous nanosheets can be further obtained by supercritical reaction conditions at 473.2 K, 16 MPa.

2.2 Synthesis of $\text{Ag}/\text{WO}_{3-x}$ heterostructure

Ag nanoparticles were prepared by a facile in situ redox at room temperature. Ag nanoparticles were produced by quickly addition of sodium citrate solution (45.6 mg, GR, Sinopharm

Scheme 1 Schematic preparation process of the as-prepared heterostructure.

Chemical Reagent Co., Ltd) and AgNO_3 (6.8 mg, AR, Sinopharm Chemical Reagent Co., Ltd) solution to the aqueous solution. The mixture was stirred vigorously at room temperature, following by addition of a certain amount of ascorbic acid solution (200 μL , 0.1 $\text{mmol}\cdot\text{L}^{-1}$, AR, Sinopharm Chemical Reagent Co., Ltd). The reaction lasted for 1 h. Next in order to improve the stability of the as-prepared catalyst sample, the obtained sample was further annealed at a temperature of 400 $^{\circ}\text{C}$ in N_2 for 1 h.

2.3 Characterization

The morphology and structure of the materials were characterized by transmission electron microscopy (TEM) (JEM-2100, JOEL). X-ray diffraction (XRD) patterns of samples were measured on a Y-2000 X-ray Diffractometer with copper K α radiation ($\lambda = 0.15406 \text{ nm}$) operating at 40 kV and 40 mA. X-ray photoelectron spectroscopy was performed using a Thermo ESCALAB 280 system with Al/K (photon energy = 1486.6 eV) anode mono X-ray source. UV-Vis spectra (Shimadzu UV-240/PC) were measured to evaluate the light adsorption.

2.4 Photoelectrochemical (PEC) measurements

The PEC measurements were tested using an electrochemical workstation (CHI660E, Shanghai Chenhua Co., Ltd., China) with a typical three-electrode cell. The as-prepared sample was used as the working electrode, a Ag/AgCl electrode and Pt wire were used as reference and counter electrode, respectively. 0.5 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_4 was used as the electrolyte. The working electrodes were prepared by dropping the suspension onto the surface of a clean fluorine-doped tin oxide (FTO) conductive glass substrate. The light ON-OFF switches were set as 100 s when measuring the I - t curves of the absolute values under visible light. The bias for the measurement was set as 0.8 V. The reversible hydrogen potential can be converted from the

Ag/AgCl reference electrode potential as $E_{\text{RHE}} = E_{\text{vs Ag/AgCl}} + E_{\text{Ag/AgCl}}^0 + 0.059 \times \text{pH}$, where $E_{\text{Ag/AgCl}}^0$ is 0.1976 V at 25 $^{\circ}\text{C}$.

The incident photon-to-current conversion efficiency (IPCE) spectra was collected by a solar simulator (Newport 66984, USA) coupled with a filter (Newport 71260) and an aligned monochromator (Newport 1-800-222-6440). All the electrochemical measurements were carried out by an electrochemical workstation (CHI 660E). IPCE can be expressed by the equation: $\text{IPCE} = (1240 \times I) / (\lambda \times J_{\text{light}})$, where I ($\text{mA}\cdot\text{cm}^{-2}$) is the measured photocurrent density at a specific wavelength, λ (nm) is the wavelength of incident light, and J_{light} ($\text{mW}\cdot\text{cm}^{-2}$) is the measured irradiance at a specific wavelength.

The PEC degradation of methyl orange (MO) was performed in a 100 mL of two electrode quartz cell system with 300 W Xe lamp equipped with a UV cut-off filter (420 nm) on a CHI 660E Electrochemical Workstation, and the light intensity was kept as 100 $\text{mW}\cdot\text{cm}^{-2}$. 0.5 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_4 was used as electrolyte solution. The initial concentration of MO in the solution was 20 $\text{mg}\cdot\text{L}^{-1}$. The as-prepared sample (20 mg) was dispersed into the MO solution. The graphite electrode was connected to the working electrode, and a Pt wire was used as counter electrode. The absorbance of MO was measured at a wavelength of 464 nm. The PEC degradation of MO was performed with a voltage of 1.0 V *versus* Ag/AgCl . The system was illuminated after stirring in dark for 30 min to reach equilibrium of complete adsorption-deposition for the photoelectrode. Samples were then taken from the reactor every 15 min, and the concentration of MO was determined by a UV-Vis spectrophotometry.

3 Results and Discussion

The TEM image of the $\text{Ag}/\text{WO}_{3-x}$ heterostructure is shown in Fig. 1a, it can be seen that the as-prepared heterostructure has

Fig. 1 (a) TEM image of $\text{Ag}/\text{WO}_{3-x}$ heterostructure. (b, c) Magnified images of the regions enclosed by the white and yellow squares in (a), respectively. (d) Bright-field STEM image and EELS elemental mapping of W (blue), O (green) and Ag (red) of $\text{Ag}/\text{WO}_{3-x}$ heterostructure.

successfully constructed with local crystalline and amorphous interface. The crystalline structure with the lattice fringes of 0.35 nm corresponds to WO_{3-x} (Fig. 1b)²⁸. The well-resolved lattice fringes with d -spacing of 0.23 nm correspond to the (111) lattice plane of Ag (Fig. 1c)²⁹. Elemental mappings (Fig. 1d) clearly reveal the homogeneous distribution of W, O and Ag atoms over the entire nanosheets.

The XRD patterns shown in Fig. 2a demonstrate the crystallinity of the amorphous substrate enhanced obviously. As can be seen the XRD pattern of a-WO_{3-x} nanosheets, only a bread-shape peak can be found, suggesting the as-obtained product is amorphous. After annealing at 400 °C, the intensity of the diffraction peaks increases. The peaks at $2\theta = 22.9^\circ$, 31.7° and 45.5° both in Ag/WO_{3-x} heterostructure can be indexed to $\text{WO}_{2.9}$ (JCPD card No. 05-0386) and $\text{WO}_{2.72}$ (JCPD card No. 05-0392), respectively. Moreover, another two relatively weak peaks appearing at $2\theta = 28.6^\circ$ and 33.5° correspond to WO_3 (JCPD card No. 43-1035). Beyond the diffraction peaks of WO_{3-x} , the other new diffraction peaks are indexed to face centered cubic structure Ag (JCPD card No. 65-2871)³⁰.

X-ray photoelectron spectroscopy (XPS) characterization was always employed to investigate the surface composition and chemical states of the elements. Fig. 2b, c show that the binding energies of O 1s and W 4f in Ag/WO_{3-x} are negatively shifted, as compared to the ones for a-WO_{3-x} . Moreover, the binding energy of Ag 3d in Ag/WO_{3-x} is positively shifted compared to that of

Ag nanoparticles (Fig. 2d). All of these results confirm that the electrons transfer from Ag and WO_{3-x} ^{28,31}. The binding energies of W 4f and O 1s more negative shift and Ag 3d more positive shift in Ag/WO_{3-x} than that of Ag nanoparticles demonstrate better contact may be formed between the metals and the matrix during the process of calcination, facilitating the transformation of more electrons from metals to the substrate. In the O 1s region of the spectra, the peak locating at 532.4 eV is attributed to nonstoichiometric tungsten oxides, while the binding energy at ca. 532 and 533.4 eV are related to adsorbed H_2O molecules inside and on the surface of the tungsten oxide³²⁻³⁴. And the increase in peak area at 532.4 eV and the decrease in peak area at 532 and 533.4 eV indicate an increase in crystallinity of the as-prepared sample. From the XPS spectra analysis, we also verify that the doped Ag nanoparticles are both in metallic state. The peaks observed at around 368 and 374 eV are ascribed to metallic Ag³⁵.

The effect of metal nanoparticles on the optical properties of as-prepared substrate materials was studied by optical absorption spectroscopy. The UV-Vis absorption spectra of a-WO_{3-x} , Ag/WO_{3-x} and Ag nanoparticles are compared in Fig. 3. For a-WO_{3-x} nanosheets, they exhibit strong peaks below 400 nm assigned to the inter-band absorbance^{36,37}. It can be seen that Ag/WO_{3-x} shows a broad peak centered on 480 nm, corresponding to the LSPR of Ag nanoparticles³⁶. The broaden LSPR peaks of the metal nanoparticles in these nanocomposites

Fig. 2 (a) XRD patterns of a-WO_{3-x} nanosheets and Ag/WO_{3-x} heterostructure. Deconvoluted high-resolution XPS of selected core level peak region: (b) O 1s and (c) W 4f XPS spectra of a-WO_{3-x} and Ag/WO_{3-x} . (d) Deconvoluted high-resolution XPS of selected core level peak regions: Ag 3d for Ag nanoparticles and Ag/WO_{3-x} .

Fig. 3 Absorption spectra of Ag/WO_{3-x}, a-WO_{3-x} and Ag nanoparticles.

obviously mainly attribute to the electronic interaction between the embedded metal nanoparticles and the a-WO_{3-x} nanosheets³¹.

The photocurrent responses of the PEC devices based on a-WO_{3-x} and Ag/WO_{3-x} along with Ag nanoparticles and blank FTO are recorded to compare their PEC behavior for several ON-OFF cycles under simulated solar light illumination (AM 1.5, 100 mW·cm⁻²) (Fig. 4a). It can be obviously observed that Ag/WO_{3-x} exhibits enhanced photocurrent density as compared with a-WO_{3-x} and Ag nanoparticles. The photoresponse of

Ag/WO_{3-x} heterostructure is about 5 times higher than that of a-WO_{3-x}. Electrochemical impedance spectroscopy (EIS) was commonly used to investigate the electrode kinetics of the catalytic processes on the samples (Fig. 4b)³⁸. The representative Nyquist plots display a remarkably decreased charge transfer resistance (R_{ct}) for Ag/WO_{3-x} compared to a-WO_{3-x}, indicating that the incorporation of metal nanoparticles and the improved conductivity can enhance the electron mobility by suppressing the recombination of photogenerated electrons and holes, thus the photogenerated electrons and holes are effectively separated and the interfacial electron transport is increased³¹.

To better evaluate the PEC efficiency of these as-prepared samples as a function of illumination wavelength, the incident photo-to-current conversion efficiency (IPCE) measurements conducted at a bias potential of 0.8 V vs Ag/AgCl was displayed from 360 to 650 nm (Fig. 4c). The Ag/WO_{3-x} shows much higher IPCE than that of a-WO_{3-x}, which is well-matched with their corresponding LSPR absorption peaks in the visible region. This signifies that excitation of the metal LSPR is responsible for the improved visible-light photoactivity of Ag doped a-WO_{3-x}. And this enhancement is ascribed to more incident photons provided by the plasmonic noble metal nanoparticles *via* multiple

Fig. 4 (a) The photocurrent response (0.8 V bias) of bare FTO glass, Ag nanoparticles, a-WO_{3-x} and Ag/WO_{3-x} coated FTO electrodes in 0.5 mol·L⁻¹ Na₂SO₄ under simulated solar light illumination (AM 1.5, 100 mW·cm⁻²). (b) EIS plots of a-WO_{3-x} and Ag/WO_{3-x} electrode in 0.5 mol·L⁻¹ Na₂SO₄ illuminated by simulated solar light (AM 1.5, 100 mW·cm⁻²). (c) IPCE spectra of a-WO_{3-x} and Ag/WO_{3-x} heterostructure measured at 0.8 V vs Ag/AgCl. (d) The Ag/a-WO_{3-x} photoanode at a constant bias of 0.8 V vs Ag/AgCl in 0.5 mol·L⁻¹ Na₂SO₄ under AM 1.5G simulated sunlight for 200 min.

scattering³⁹. Moreover, the time dependence curve of current density at 0.8 V vs Ag/AgCl shown in Fig. 4d demonstrates that the as-prepared sample has good stability.

Prompted by the unique structural advantages of the as-prepared Ag/WO_{3-x} nanocomposites, a comparative study was carried out on the degradation of methyl orange (MO) measurement as a probe reaction to further confirm the advantages of the as-prepared photoelectrode in the use of sunlight. Fig. 5 show the changes in relative concentration (C/C_0) of MO under UV and Vis light illumination with a-WO_{3-x} and Ag/WO_{3-x} heterostructure as electrode individually and the initial MO concentration of 20 mg·L⁻¹. From Fig. 5, it is found that the Ag/WO_{3-x} has a higher PEC degradation efficiency than that of the a-WO_{3-x} no matter under UV or Vis light illumination. After reaction for 120 minutes under Vis light illumination, the PEC degradation efficiency of Ag/WO_{3-x} can reach 96.7% for MO, while the PEC degradation efficiency of WO_{3-x} is only 63.6% (Fig. 5b). Moreover, under the illumination of UV light, the PEC degradation efficiency of Ag/WO_{3-x} is only 60.3% for MO, which is a little higher than that of WO_{3-x} (47.7%). The significant difference of the PEC degradation efficiency of Ag/WO_{3-x} under UV and Vis light illumination can be attributed to the strong broadened absorption at visible light region arising from the SPR effect of the metallic Ag nanoparticles^{40,41}.

On the basis of above analysis, the possible mechanism for the enhanced photoelectrocatalytic efficiency of the Ag/WO_{3-x}

photoelectrode was proposed and illustrated in Fig. 6. The enhanced crystallinity can effectively improve the conductivity and electrochemical stability as well. Under the irradiation of simulated solar light (AM 1.5, 100 mW·cm⁻²), photogenerated electrons of WO_{3-x} from the valence band are excited to the conduction band, leaving the same amount of holes in the valence band. On the other hand, the incorporation of plasmonic Ag nanoparticles can act as photosensitizers to enhance the optical absorption of the metal/semiconductor heterostructure, the hot plasmonic electrons of Ag can transfer to the conduction band (CB) of WO_{3-x} over the metal/semiconductor Schottky barrier and the small size of metal nanoparticles allows the hot electrons to reach the metal/semiconductor interface before decay². For the plasmonic holes, they can readily accumulate at the interface between Ag and WO_{3-x}. Meanwhile, the LSPR-induced electromagnetic field enhancement effects facilitated photogenerated electrons and holes generation and separation⁴². For PEC water splitting⁴³, the electrons are promptly transferred from the working electrode *via* the FTO substrate toward the Pt counter electrode, where the H⁺ in water is reduced to generate H₂. While the remaining holes on the Ag/WO_{3-x} surface will oxidize OH⁻ to generate O₂. For PEC degradation of MO^{44,45}, the photogenerated electrons (e⁻) could combine with the dissolved O₂ to yield the superoxide anion radicals (·O₂⁻), and further form the hydroxyl radicals (·OH) for the MO degradation into CO₂, H₂O and other products. Meanwhile, the consumption

Fig. 5 (a) PEC degradation of MO with a-WO_{3-x} and Ag/WO_{3-x} at 1.0 V vs Ag/AgCl.
(b) The PEC degradation efficiency of a-WO_{3-x} and Ag/WO_{3-x} heterostructure.

Fig. 6 Schematic of the proposed photoelectrocatalysis mechanism for the Ag/WO_{3-x} system.

of electrons can also inhibit the recombination of the electron/hole pairs to some extent. Moreover, the photogenerated holes (h^+) could easily seize the H_2O molecules to generate high active species of the OH radicals, which also contribute much to the MO degradation. Thus, both the unique substrate and the introduction of metal nanoparticles contribute to the efficient charge transfer and reduced recombination, resulting in enhanced PEC performance.

4 Conclusions

In summary, we have demonstrated that 2D α - WO_{3-x} nanosheets can be used as effective support for metal nanoparticles, and the resultant unique heterostructure exhibit a much superior PEC activity. The enhanced PEC performance can be attributed to the construction of special local crystalline-amorphous interface, which can increase the specific surface area and active sites, and improve the electrical conductivity as well. Moreover, the introduction of Ag nanoparticles can induce LSPR effect, and the excellent contact between the Ag nanoparticles and WO_{3-x} can promote the transfer and separation of charge carriers effectively. Therefore, we believe this designing strategy will lead to more impossibilities for design and fabrication of high-performance catalyst materials in the future.

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