

Highly enhanced photoelectric catalysis of WO₃ nanoblocks loaded with Ag nanoparticles*

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WO₃/Ag composite film photoanodes were synthesized by hydrothermal combined electrodeposition method. Characterization of samples was conducted by scanning electron microscope (SEM) and X-ray diffraction (XRD), which showed that WO₃/Ag composite films had been synthesized. Diffuse reflectance spectra show WO₃/Ag composite film has more strong absorption than WO₃ film under simulated visible light irradiation. Electrochemical impedance spectroscopy shows WO₃/Ag composite film photoanode enhances charge transfer efficiency compared with WO₃ film. WO₃/Ag composite film photoanodes show higher photocurrent and photoelectric catalytic activity than WO₃ film, and the WO₃/Ag composite film obtained by depositing Ag nanoparticles at 50 s (WO₃/Ag-50) shows the highest photocurrent and photoelectric catalytic activity. Meanwhile, the photoelectric catalytic activity of the composite film is higher than their direct photocatalytic and electric catalytic activity. The higher photocurrent and photoelectric catalytic activity of the WO₃/Ag composite film photoanodes are attributed to the surface plasmon resonance effect of Ag nanoparticles and Schottky junction effect at the WO₃/Ag interface.

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With the quick development of industrial technology, huge amounts of organic pollutants were discharged into water bodies, which caused serious environmental pollution problem^[1,2]. Thus, the high effective wastewater treatment technology has become a focus of researchers. In recent years, photoelectric catalysis (PEC) has been proved to be a promising technology for degrading organic pollutants^[3]. WO₃ is one of the most studied semiconductor PEC materials because of its low cost, harmlessness, and chemical stability^[4]. WO₃ exhibits strong PEC activity in the visible light range due to the narrow band gap (about 2.7 eV) of WO₃^[5]. However, the electrons and holes produced by WO₃ PEC were easy to recombine with each other, which will be harmful to PEC activity^[6,7]. In order to solve this problem, numerous studies have shown that loading noble metals nanoparticles can act as electron traps on the surface of a catalyst matrix to achieve better electrons and holes separation efficiency^[8]. Among various noble metals^[9], Ag nanoparticles (Ag NPs) have received extensive attention because of its relatively low price^[10]. And, surface plasmon resonance (SPR) effect of Ag NPs can expand the absorption range of visible light^[8,11]. In addition, Ag NPs can capture electrons and the separation of electrons and holes is improved, which increases PEC efficiency^[8,12].

So far, the electrochromic performance, photocatalytic performance, and hydrogen production performance by water splitting of tungsten oxide of WO₃/Ag composites have been explored by some researchers. SUN et al^[13] studied the WO₃-Ag composite thin films synthesized by magnetron sputtering and electron beam evaporation. The results show that the introduction of the Ag layer can significantly shorten the response time of the device. NASERI et al^[14] studied that the WO₃ thin film photoanodes containing different concentrations of Ag nanoparticles were synthesized by sol-gel method and were measured by the amount of hydrogen produced during water splitting. The results showed that the highest efficiency for H₂ production was obtained for the Ag/WO₃ composite photoanodes with 2 mol% Ag nanoparticles. CHEN et al^[15] studied the photocatalytic activity of the Ag/WO₃₋₃₅₀ hybrids synthesized by the bovine serum albumin (BSA) based optical bio-sensing system and solid phase reduction method. The results showed that the photocatalytic activity of the Ag/WO₃₋₃₅₀ hybrids was about 2.3 times higher than that of pure WO₃₋₃₅₀. However, as far as we know, there are few studies on photoelectric catalytic performance of WO₃/Ag composite film photoanodes. On the other hand, among some Ag nanoparticles deposition methods^[16], the

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deposition of Ag nanoparticles by electrodeposition method has the advantages of good particle uniformity, easy operating^[17] and low cost^[18]. At the same time, the preparation of WO₃ by the hydrothermal method has the advantages of low cost, high stability, and large specific surface area.

Therefore, in the present paper, WO₃ nanoblocks were synthesized on the fluorine-doped tin oxide (FTO) substrate by hydrothermal method. Different amounts of Ag NPs (20 s, 50 s and 80 s) were loaded onto WO₃ nanoblocks by the electrodeposition method to prepare WO₃/Ag composite film photoanodes (WO₃/Ag-20, WO₃/Ag-50 and WO₃/Ag-80). A systematic characterization was carried out for WO₃ nanoblocks and WO₃/Ag composite film photoanodes. The performances of WO₃ nanoblocks and WO₃/Ag composite film photoanodes were evaluated by photocurrent and PEC measurements under visible light illumination. To prove the benefits of PEC process, WO₃/Ag photoanode was tested by direct photocatalysis (DP), electrocatalysis (EC) and PEC. Then, theoretical analysis is performed.

Materials contained acetone, isopropanol, methanol, 97 wt% H₂SO₄, and 37 wt% HCl (Beijing Chemical Works, China), Na₂WO₄·2H₂O (Tianjin Guangfu Fine Chemical Research Institute, China), (NH₄)₂C₂O₄·H₂O (Tianjin Guangfu Technology Development Co., Ltd., China), Na₂SO₄ (Xilong Chemical Co., Ltd., China), AgNO₃ (Sinopharm Chemical Reagent Co., Ltd., China) and methylene blue (MB, Tianjin Guangfu Fine Chemical Research Institute, China). FTO substrates (F: SnO₂, 8·sq⁻¹, transparency 80%; Pilkington, United States).

Scanning electron microscope (SEM, JSM-6480LV, FEI, United States) was used to analyze the surface morphology of the samples. The crystallographic structures were characterized by X-ray diffraction (XRD, Rigaku D/MAX 2550 V/PC, Rigaku Corporation, Japan). Photoelectrochemical measurements were carried out on a workstation (LK98C, Lanlike Instrument Corp, Tianjin, China). A 300 W Xe lamp with a 420 nm cut-off filter was used as the light (50 W, PLS-SXE300, Perfectlight Instrument Corp, Beijing, China). UV-vis diffuse reflectance spectrum (DRS) of the sample was measured by using a UV-visible-near-infrared spectrophotometer (Cary 5000, Agilent Technologies Inc.). Use the UV-vis spectrophotometer to analyze the dye concentration (TU-1810, Beijing Purkinje General Instrument Co., Ltd., China).

The FTO substrate was firstly cleaned by ultrasonication for 10 min each in acetone, isopropanol, methanol, and distilled water, consecutively, and then dried in an N₂ stream at room temperature. 2.31 g of Na₂WO₄·2H₂O was dissolved in 70 mL of distilled water. Then, 50 mL of 3.0 M HCl was added into the aqueous solution drop by drop under vigorous stirring, and a yellowish precipitate was formed. 2.0 g of (NH₄)₂C₂O₄ was added into the

suspension, and after stirring for 20 min, the suspension appeared transparent, the as-prepared solution was transferred into a 25 mL Teflon-lined stainless autoclave. Finally, the FTO substrate was placed into the stainless autoclave at an angle against the wall, and the conducting side faced down. The hydrothermal process reacted at 120 °C for 4 h. After hydrothermal reaction, the obtained samples were taken out, washed with distilled water and dried in an N₂ stream at room temperature. At last, the WO₃ samples was dried at 60 °C for 30 min and annealed at 450 °C for 1 h in air.

Ag NPs were electrodeposited onto WO₃ nanoblocks by potentiostatic method from 1 mM AgNO₃ solution containing 0.5 M H₂SO₄. The WO₃ samples acted as the photoanode, the platinum foil was used as the counter electrode, and mercury sulfate electrode (MSE) was used as the reference electrode. The deposition potential was -0.6 V (vs. MSE) for Ag NPs, and deposition time for 20 s, 50 s and 80 s. The WO₃/Ag composite film samples (WO₃/Ag-20, WO₃/Ag-50 and WO₃/Ag-80) were washed with distilled water and annealed at 300 °C for 1 h in air.

Photoelectrochemical measurements were carried out on an LK98C workstation. A 300 W Xe lamp with a 420 nm cut-off filter was used as the light source to simulate visible light irradiation. The electrode was illuminated from the front side and the exposed area was 2.25 cm², and the incident light intensity on electrode surface was 50 mW·cm⁻². The WO₃/Ag composite films and WO₃ film were used as the photoanodes, respectively. The platinum foil acted as the counter electrode, and Ag/AgCl electrode was used as the reference electrode, respectively. The photocurrent measurement was performed in 0.01 M Na₂SO₄ solution. Prior to catalytic experiment, the three-electrode was immersed in the dye for 20 min to obtain a good dispersion and establish absorption/desorption equilibrium between the organic molecules and the photoanode surface. The PEC activities of the WO₃/Ag composite film photoanodes were evaluated by monitoring the degradation of MB solution (90 mL, MB=6 mg/L, Na₂SO₄=0.01 M) under the illumination of simulated visible light and bias voltage at 1.5 V. The electrocatalytic (EC) performance of WO₃/Ag composite film photoanodes at a bias voltage of 1.5 V were evaluated. The DP performance of WO₃/Ag composite film photoanodes under simulated visible light irradiation was evaluated. At given time intervals for 20 min, the concentration of MB dye was measured by UV/vis spectrophotometer (TU-1810) with detection wavelength of 665 nm. Electrochemical impedance spectra (EIS) were carried out in 0.01 M Na₂SO₄ solution, with frequency scanning range of 1—10 Hz, bias voltage of 0.01 V (vs. Ag/AgCl), and alternating voltage amplitude of 5 mV.

The crystal structure of samples was well-characterized using XRD technique. Fig.1 demonstrates the XRD

patterns of WO_3 and WO_3/Ag -50 samples. The XRD patterns of films show significant diffraction peak at 2θ (Bragg's angle) of 23.9° , 34.1° , 42.1° , 49.1° , 55.2° and 61.1° , and all peaks can be indexed to cubic phase WO_3 crystal structure (JCPDS card No.41-0905). In addition, the diffraction peaks of FTO were also observed (JCPDS card No.46-1088). However, the diffraction peaks of Ag NPs in the XRD patterns of WO_3/Ag -50 sample were not observed. We believe that this can be attributed to the Ag NPs are lower than the detection limit of the XRD technique.

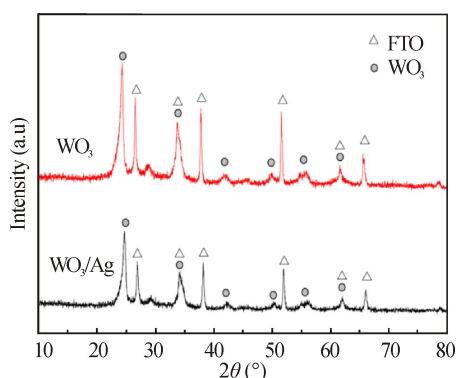


Fig.1 XRD patterns of WO_3 nanoblocks and WO_3/Ag -50 composite film

The microstructures of the prepared WO_3 nanoblocks, WO_3/Ag -20, WO_3/Ag -50 and WO_3/Ag -80 composite films were observed by SEM in Fig.2. Fig.2(a) shows that the pure WO_3 nanoblocks are interconnected to each other at various angles, and the average length and width of WO_3 nanoblocks are about 963.5 nm and 124.8 nm, respectively. Inset of Fig.2(a) shows the cross-sectional SEM image of WO_3 nanoblocks, which shows the film thickness of 1.711 μm . Fig.2(b), (c) and (d) show that the morphology of WO_3/Ag -20, WO_3/Ag -50 and WO_3/Ag -80 composite films have no obvious changed compared with pure WO_3 nanoblocks. However, Fig.2(b), (c) and (d) can indicate that Ag NPs are loaded on the surface of WO_3 nanoblocks, and the content of Ag NPs on the surface of WO_3 nanoblocks increases with the increasing of the deposition time.

Energy dispersive spectrometer (EDS) and X-map graph of WO_3/Ag -50 composite film are shown in Fig.3. The elemental composition of WO_3/Ag -50 composite film was analyzed by EDS. The presence of Ag, W and O elements in the WO_3/Ag -50 composite film was indicated. There are no other impurity elements in the samples, which is consistent with the results of XRD. The X-map graph shows that Ag, W and O elements are evenly distributed on the surface of WO_3/Ag -50 composite film. The percent mass of Ag element is 1.02%, the percent mass of W element is 78.24%, and the percent mass of O element is 20.74%. It strongly confirmed the successful preparation of WO_3/Ag composite film.

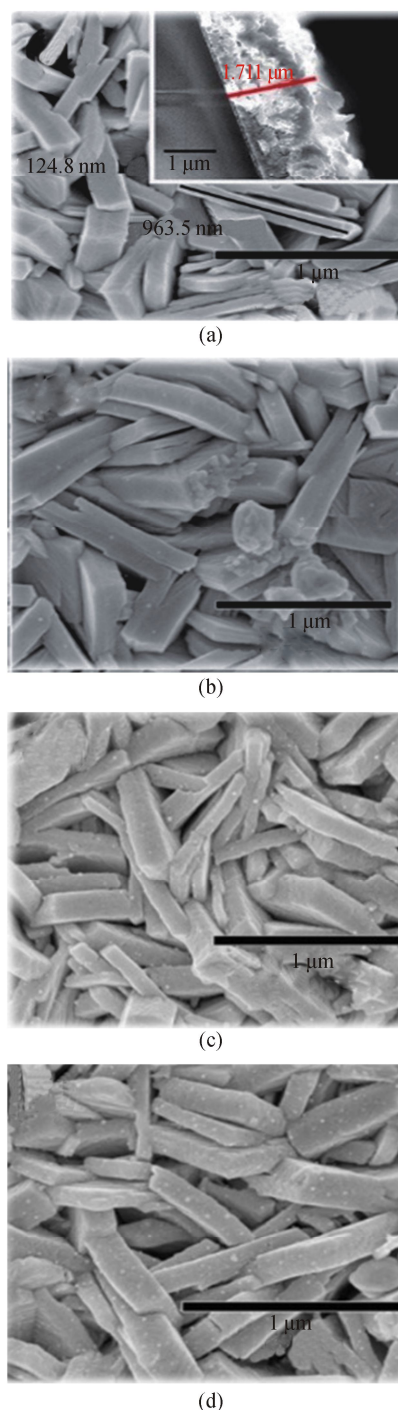


Fig.2 SEM images at different deposition time: (a) WO_3 nanoblocks; (b) WO_3/Ag -20 composite film; (c) WO_3/Ag -50 composite film; (d) WO_3/Ag -80 composite film

The light absorption property of a plasmonic metal/semiconductor electrode is very important for its photoelectric properties research. Fig.4(a) shows the UV-vis absorption spectra of the WO_3 nanoblocks and WO_3/Ag -50 composite film. We can find that the WO_3/Ag composite films exhibit similar absorption spectra as the WO_3 nanoblocks. However, the visible light absorption of

WO₃/Ag composite films is obviously enhanced compared with that of pure WO₃ nanoblocks, and the absorption curve shows an obviously red shift. The results can be attributed to the SPR effect of Ag NPs^[15,19]. The SPR peaks of Ag NPs are reported in numerous literatures^[20]. However, the SPR peaks of Ag NPs are not observed in the WO₃/Ag-50 composite film. We speculate that this may be attributed to the low content of Ag NPs in the WO₃/Ag-50 composite film^[10].

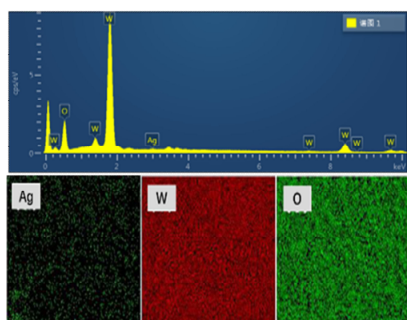


Fig.3 EDS and X-Map graph of WO₃/Ag-50 composite film

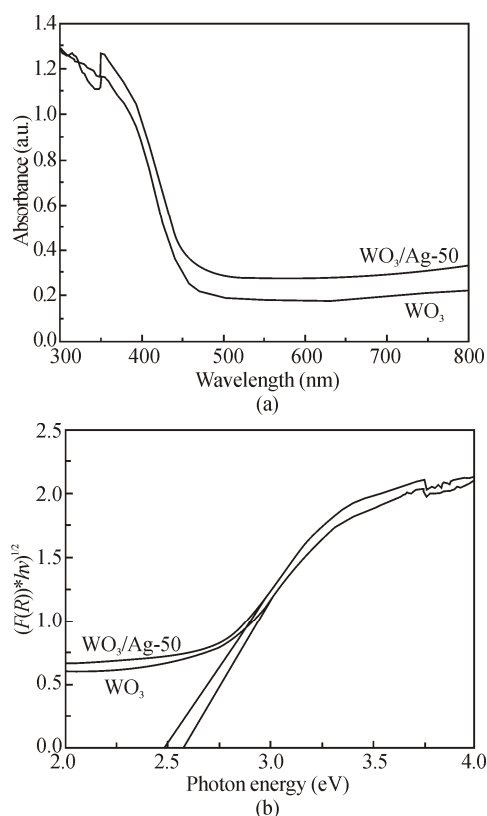


Fig.4 (a) UV-vis absorption spectra and (b) band gaps of WO₃ nanoblocks and WO₃/Ag-50 composite films

The optical band gap energies (E_g) of these samples were calculated from the absorption data by using the following equation

$$\alpha h\nu = a(h\nu - E_g)^n, \quad (1)$$

where α is the absorption coefficient which is estimated using Kubelka-Munk theory, $h\nu$ is the energy of photons,

a is the constant, and n is dependent on the type of band transition. Because WO₃ has an indirect band gap, the value of n is 1/2. The E_g values of all samples are estimated from the intercept of the tangent in the Tauc plots, and the band gap spectra of WO₃ nanoblocks and WO₃/Ag-50 composite film were also shown in Fig.4(b), which are about 2.60 eV and 2.50 eV for WO₃ nanoblocks and WO₃/Ag-50 composite film, respectively. The change of the optical band gap can be attributed to charge transfer from Ag NPs to WO₃ interface, which leads to the downward shift of conduction band and the upward shift of valence band^[21].

In order to understand the photoelectrochemical performance of WO₃/Ag composite film photoanodes, photo-current and photoelectric catalytic activity of different loadings samples (WO₃/Ag- X) were measured, and compared with the pure WO₃ sample. Fig.5(a) shows the I - V curves of WO₃ nanoblocks, WO₃/Ag-20, WO₃/Ag-50 and WO₃/Ag-80 composite film photoanodes under the visible light illumination. The photocurrents of all samples increase with the increasing of bias potential under the visible light illumination. In addition, we also observed that the sequence of photocurrent is WO₃/Ag-50 sample > WO₃/Ag-20 sample > WO₃/Ag-80 sample > WO₃ sample. The photocurrent of the WO₃/Ag-50 sample reached 1.23 mA·cm⁻² at a bias voltage of 1.5 V (vs. Ag/AgCl), which is twice as high as WO₃ sample (0.52 mA·cm⁻²). Due to the obvious difference of the photocurrent at a bias voltage of 1.5 V (vs. Ag/AgCl), we perform the PEC activity measurements at a bias voltage of 1.5 V. The photoelectric catalytic degradation efficiency (C/C_0) of WO₃ nanoblocks, WO₃/Ag-20, WO₃/Ag-50 and WO₃/Ag-80 composite film photoanodes for degradation of MB was shown in Fig.5(b), where C is the concentration of organic pollutants with different catalytic degradation time, and C_0 is the initial concentration of organic pollutant. We observed that the sequence of PEC is WO₃/Ag-50 sample > WO₃/Ag-20 sample > WO₃/Ag-80 sample > WO₃ sample. The degradation rate of WO₃/Ag-50 sample is 67.28% at 140 min, which is 15.61% higher than that of the WO₃ sample. This is basically consistent with the measurement results of photocurrent. The photoelectrocatalytic cycle tests of WO₃/Ag-50 composite film photoanode were repeated for five times, and the cycle stability of the samples was further investigated. As shown in Fig.5(c), this result clearly indicates that the WO₃/Ag composite film photoanodes have excellent photoelectrocatalytic stability for MB degradation.

To further verify the benefits of PEC activity, we also measured DP and EC of the WO₃/Ag-50 composite film photoanode as shown in Fig.5(d). The measurement of DP was carried out under visible light irradiation, while the measurement of EC was carried out in the dark at a bias voltage of 1.5 V (vs. Ag/AgCl). From Fig.5(d), obviously, the result of activities is PEC > DP > EC. In the DP process, the WO₃/Ag composite film photoanodes

create electron-hole pairs under simulated visible light irradiation. The electrons are transferred from WO_3 interface to the Ag NPs, and then more holes were generated on the surface of WO_3 and lead to the redox reaction process^[14]. Unfortunately, the recombination of some electrons and holes will occur on the surface of photocatalyst, which is very unfavorable to the catalysis efficiency. In the EC process, the WO_3/Ag composite film photoanode generates electron-hole pairs under a bias voltage of 1.5 V (vs. Ag/AgCl). And then the electrons were separated from the holes. However, the efficiency of electron-hole pairs generation is still low, which leads to low catalytic efficiency. In the PEC process as shown in Fig.6, under the simulated visible light irradiation, electron-hole pairs are produced. At the same time, under the applied bias voltage of 1.5 V (vs. Ag/AgCl), the electron-hole pairs are further formed, and the electrons and holes are separated. The results show that PEC process can effectively promote the generation and separation of electrons and holes. In a word, we believe that the combination of light irradiation and bias voltage leads to the highest PEC activity.

EIS analysis is a powerful way for studying the charge-transfer processes. The EIS Nyquist plots of the WO_3 nanoblocks, $\text{WO}_3/\text{Ag-20}$, $\text{WO}_3/\text{Ag-50}$ and $\text{WO}_3/\text{Ag-80}$ composite film photoanodes are shown in Fig.7. It was clear that the sequence of arc radius in the plots is $\text{WO}_3/\text{Ag-50}$ sample < $\text{WO}_3/\text{Ag-20}$ sample < $\text{WO}_3/\text{Ag-80}$ sample < WO_3 sample. The result show that the introduction of Ag NPs greatly enhances charge

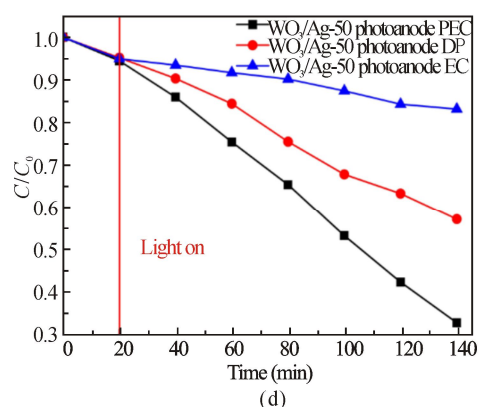
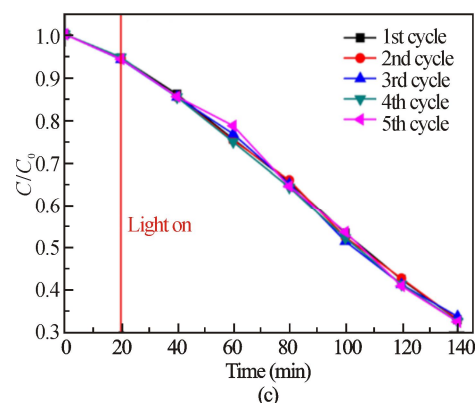
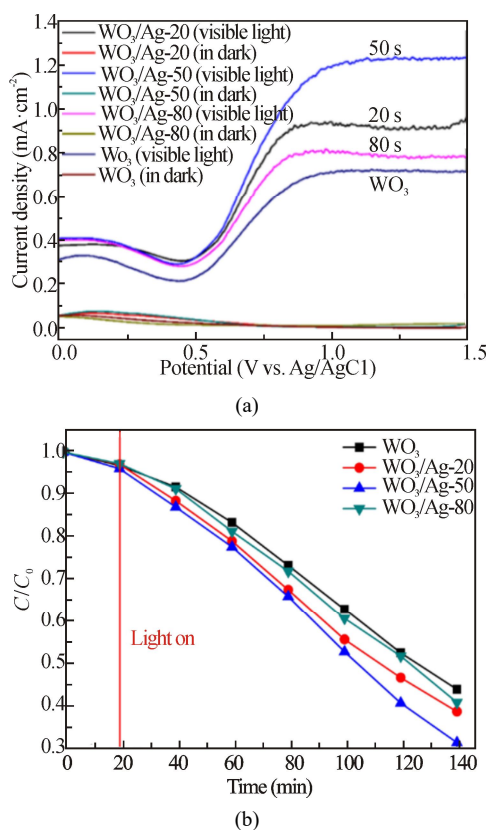


Fig.5 (a) I - V curves; (b) PEC activity of WO_3 nanoblocks, $\text{WO}_3/\text{Ag-20}$, $\text{WO}_3/\text{Ag-50}$ and $\text{WO}_3/\text{Ag-80}$ composite film photoanodes; (c) Photoelectrocatalytic cycle tests; (d) PEC, DP and EC degradation curves of $\text{WO}_3/\text{Ag-50}$ composite film photoanode

transfer from WO_3 to Ag NPs, which is attributed to effective trapping of electrons by Ag NPs^[22,23]. These results further confirm that the WO_3/Ag composite film photoanodes have higher photocurrent and PEC activity than the pure WO_3 ^[24].

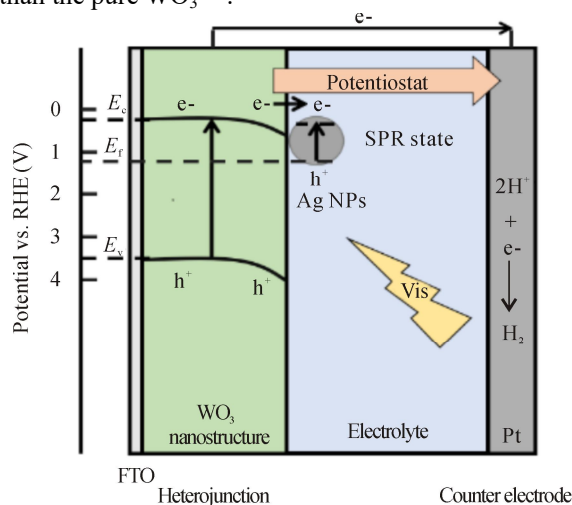


Fig.6 Schematic illustration of the PEC mechanism of the WO_3/Ag composite film photoanodes

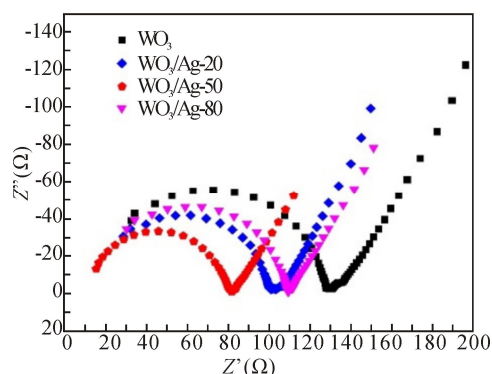


Fig.7 Nyquist plots of the WO_3 nanoblocks, $\text{WO}_3/\text{Ag-20}$, $\text{WO}_3/\text{Ag-50}$ and $\text{WO}_3/\text{Ag-80}$ composite film photoanodes

In order to analysis the performance of the WO_3/Ag composite film photoanodes, the above experiments had been performed. And all results show that the $\text{WO}_3/\text{Ag-50}$ composite film photoanode has the best photocurrent and PEC activity. This may be recognized for the following two reasons. Firstly, the SPR effect of Ag NPs improved the absorption range of visible light as indicated by the results of DRS in Fig.4(a)^[11], which promoted the generation of electrons and holes. Thus, this leads to higher photocurrent and PEC activity for WO_3/Ag composite film photoanodes than the pure WO_3 . Secondly, the Schottky junction at the WO_3/Ag interface could be used as an electron trap to trap electrons as shown in Fig.6, which improved electrons and holes separation efficiency in WO_3 as shown in Fig.7. The electrons were transferred from WO_3 interface to the Ag NPs, and then more holes were generated on the WO_3 surface^[11,12,14]. Thus, WO_3/Ag composite film photoanodes show higher photocurrent and PEC activity than the pure WO_3 . However, excessive loading of Ag NPs on WO_3 will occupy the surface-active site of WO_3 ^[25], which will be harmful to photocurrent and PEC activity as indicated by the results of $\text{WO}_3/\text{Ag-80}$ in Fig.5(a) and (b). The photocurrent and PEC activity of $\text{WO}_3/\text{Ag-50}$ composite film photoanode are obviously better than other samples, which indicates that there should be an optimal loading value for increasing photocurrent and PEC activity by loading Ag NPs.

The WO_3/Ag composite film photoanodes were synthesized by the hydrothermal combined electrodeposition methods. The DRS shows that WO_3/Ag composite film photoanodes expand the absorption range of visible light compared with WO_3 film. The EIS shows that the load of Ag NPs enhanced the charge transfer rate from the surface of WO_3 to Ag NPs. Due to the SPR effect of Ag NPs and Schottky junction effect of WO_3/Ag interface, we found that the photocurrent and PEC activity of $\text{WO}_3/\text{Ag-50}$ composite film photoanode were the highest. This work shows that WO_3/Ag composite film photoanodes have a broad development prospect in treating organic pollutant, which also lay the foundation

for metal/semiconductor PEC systems.

Statements and Declarations

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

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