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ARTICLE

Enhanced Visible-Light Photoelectrochemical Behaviour of Heterojunction Composite with Cu₂O Nanoparticles-Decorated TiO₂ Nanotube Arrays

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Heterojunction composites based on n-type TiO₂ nanotubes arrays (TNAs) coupled with p-type Cu₂O nanoparticles were synthesized through a square wave voltammetry deposition method for *in situ* deposition of Cu₂O nanoparticles onto the inner surfaces and interfaces of TNAs. The characterization of the prepared samples were investigated by field-emission scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and UV-vis spectrum. When compared with pure TNAs, the Cu₂O/TNAs heterojunction composites exhibit much higher photocurrent density under visible-light irradiation and enhanced photocatalytic activity for the visible-light-driven photodegradation of methyl orange. Moreover, the photocurrent densities and photocatalytic activity of the Cu₂O/TNAs heterostructures largely depend on the deposition potential which determines the content of the Cu₂O nanoparticles. The Cu₂O/TNAs prepared by the deposition potential of -1.0 V showed the highest photocurrent density (0.91 mA cm⁻²) and the largest photodegradation rate of methyl orange (88.8%) at the applied potential of 0.5 V under visible light irradiation. The enhanced photoelectrocatalytic activity can be attributed to reducing the recombination rate of the photoexcited electron-hole pairs in TNAs when coupled with Cu₂O nanoparticles.

1. Introduction

Highly ordered TiO₂ nanotube arrays have attracted tremendous attention in its wide applications in photocatalysis,¹ sensor,²⁻⁴ solar cell,⁵⁻⁷ biomedical field,^{8,9} and supercapacitor¹⁰ during the past decades due to its excellent physical and chemical properties, such as large surface area, chemical stability, nontoxic, and low cost.^{11,12} However, its wide band gap of 3.0-3.2 eV led to two main drawbacks: the fast recombination rate of electron-hole pairs and low utilization efficiency of solar energy (~5% of the solar photons), which prevent its commercial application.¹³ In recent years, various efforts to overcome these drawbacks have been developed, such as doping with nonmetallic and metallic,¹⁴⁻¹⁷ coupling with narrow bandgap semiconductors,¹⁸⁻²⁰ and dye sensitization.²¹ Among them, modification of TNAs with narrow bandgap semiconductors to construct heterostructure has been considered to be the most effective way to achieve high efficient utilization of solar energy.

As well-known non-toxic and low cost p-type semiconductor with direct bandgap of ~2.17 eV, cuprous oxide (Cu₂O) has been widely studied for use in photocatalysis,²²⁻²⁴ sensor,^{25,26} and energy storage device.²⁷⁻²⁹ As a photocatalyst, Cu₂O has been studied as a useful semiconductor for sensitization of TiO₂ because it could be easily excited by visible light irradiation to produce photoexcited electrons and holes. Since the conduction band of Cu₂O is higher than that of TiO₂, when TiO₂ couples with Cu₂O, excited electrons from the conduction band of Cu₂O can be quickly transferred to that of TiO₂.³⁰ As a result of that, it can not only accelerate the separation of the photoexcited electron-hole pairs but also effectively prolong the lifetime of the photogenerated charge carrier.

To date, various methods have been reported to modify TNAs with Cu₂O, such as chemical bath deposition (CBD)³¹ or ultrasonication-assisted sequential chemical bath deposition (S-CBD),³² photocatalytic reduction,³³ electrochemical or sonoelectrochemical deposition.³⁴⁻³⁷ Among these methods, electroche-

mical deposition is the most straightforward and controllable process to synthesize $\text{Cu}_2\text{O}/\text{TNAs}$, and this method can greatly enhance the photocatalytic activities under visible light. However, either potentiostatic deposition or pulse electrodeposition makes the reaction so rapid that large agglomerates of Cu_2O nanoparticles are formed on the top surface of TNAs, which prevent the precursor solution from penetrating into the inner side of TNAs. As a result, both the inner surfaces and interfaces of TNAs are not fully decorated with Cu_2O nanoparticles, leading to weakening the utilization efficiency of visible light for photocatalysis.

In this work, a novel and facile square wave voltammetry (SWV) method was employed for electrochemical deposition of the uniformly distributed and controlled Cu_2O nanoparticles onto the highly ordered TNAs. To the best of our knowledge, it is the first time to adopt the SWV method to fabricate the $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites. By the mean of the deft SWV method, the Cu_2O nanoparticles can be evenly deposited onto the inner surfaces and the interfaces of TNAs. Moreover, the size and amount of Cu_2O nanoparticles can be controlled by the initial voltage of the SWV electrochemical deposition process. The $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites exhibit much better photoelectrochemical properties and higher photoelectrocatalytic activity toward the degradation of MO under visible light irradiation with great stability.

2. Experimental section

2.1 Materials and chemicals

All chemical reagents used in the present work were analytical grade reagents and used without further purification. Ethanol, acetone, ethylene glycol, ammonium fluoride (NH_4F), copper sulfuric (CuSO_4), sodium sulfuric (Na_2SO_4), sodium hydroxide (NaOH), and lactic acid were all purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Titanium foils (99.6% purity, 0.1 mm thickness) were purchased from Beijing Nonferrous Metals and Rare Earth Research Institute. The deionized (DI) water used in the experiments was produced by Direct-Q3 Water Purification Systems (KTT-111-10, China).

2.2 Preparation of TNAs

The preparation of the highly ordered TNAs was carried out in a two-electrode system using a typical electrochemical anodization process, where the Ti foil and graphite block act as the anode and cathode respectively. Prior to the anodization, the Ti foils were degreased by ultrasonic cleaning in acetone and ethanol, and then rinsed with DI water. The anodization process was performed on DH1722A-3 at 60 V for 6 h in ethylene glycol containing 0.15 M NH_4F and 3 vol% H_2O . The prepared TNAs were cleaned in ethanol glycol solution *via* ultrasonication to remove the barrier layer, and then rinsed with DI water and dried in air. In order to convert the amorphous phase to the crystalline phase, the samples were annealed at 500 °C in air for 2 h with the heating and cooling rate of 2 °C min^{-1} . The annealed TNAs were further used for subsequent deposition of Cu_2O nanoparticles.

2.3 Synthesis of $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites

The $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites were synthesized through SWV method performed on an AUTOLAB electrochemical station (PGSTAT302N, Netherland). A three-electrode

system was employed for SWV in which the annealed TNAs, Ag/AgCl electrode, and platinum wire act as working electrode, reference electrode, and counter electrode respectively. The electrolyte was composed of 0.05 M CuSO_4 aqueous solution (10 ml) and lactic acid solution (3 ml), and was further adjusted to pH 9.0 with 5.0 M NaOH solution. In order to investigate the influence of the deposition potential on morphology and performance of $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites, we present various initial voltages during the deposition process at -0.8, -0.9, -1.0, and -1.2 V respectively. During the deposition, the amplitude potential was employed at 5 mV, the end potential was performed at 0 V, and the frequency was carried out of 2 Hz. The samples obtained, consisting of different content of Cu_2O nanoparticles on TNAs, were denoted as sample I, sample II, sample III, and sample IV respectively.

2.4 Characterizations

The surface morphology and chemical components of the samples were investigated by a SU8020 FESEM (Hitachi, Japan) and an attached EDX spectrum. XRD analysis was performed on D/MAX2500V instrument with $\text{Cu-K}\alpha$ radiation ($\lambda=1.54056\text{\AA}$, Rigaku, Japan). XPS was recorded on the ESCALAB 250 photoelectron spectrometer using a monochromatic Al $\text{K}\alpha$ X-ray beam (1486.60 eV, Thermo, American). The binding energies of elements were calibrated to the C 1s at 284.80 eV. High-resolution transmission electron microscopy (HRTEM) was obtained using a JEM-2100 (JEOL, Japan). The ultraviolet-visible diffusion reflection spectra (DRS) were collected with a Shimadzu UV-3600 spectrophotometer. All the measurements were carried out at room temperature.

2.5 Photoelectrochemical measurements

Photoelectrochemical measurements were performed on an AUTOLAB electrochemical station in a homemade rectangular quartz cell with a three-electrode configuration using Ag/AgCl reference electrode and platinum wire counter electrode. The annealed TNAs and $\text{Cu}_2\text{O}/\text{TNAs}$ with a geometric area of ca 0.5 cm^2 served as working electrodes. The photocurrent response experiments were carried out in 0.1 M Na_2SO_4 solution and the electrochemical impedance spectroscopy (EIS) tests were conducted in 0.1 M KCl aqueous solution containing of 0.05 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ aqueous solution. A 300W Xe lamp (HSC-F300, NBeT Company, China) with an ultraviolet filter ($\lambda > 400\text{ nm}$) was used as the visible light source and positioned 20 cm away from the working electrode.

2.6 Photocatalytic and photoelectrocatalytic measurements

The photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of methyl orange (MO) were tested in self-designed quartz photochemical reactor. In the experiment, the initial concentration of MO was 10 g L^{-1} , with 0.1 M Na_2SO_4 solution as the electrolyte. Before the measurements, the samples were immersed in the electrolyte (20 ml) for 60 min in the dark to achieve the adsorption/desorption equilibrium. During the measurements, the MO solution was continuously stirred at room temperature and the applied potential was kept at 0.5 V for PEC process. A 300 W Xe lamp (HSC-F300, NBeT Company, China) with a 400 nm ultraviolet cutoff filter as the visible light source was positioned 20 cm away from the photochemical reactor. The PEC measurements were performed in the same condition as those of the photoelectrochemical measurements. The applied potential was kept at 0.5 V during the PEC process.

After visible-light irradiation every 20 min, the residual MO concentration was analyzed using a UV-visible spectrophotometer (UV-1800, Shimadzu, Japan) at 464 nm.

3. Results and discussion

3.1 Synthesis and characterization of samples

The Cu₂O nanoparticles were successfully deposited onto the inner surfaces and the interfaces of TNAs by the means of SWV method to form Cu₂O/TNAs heterojunction composites. The steps of synthesis can be illustrated as follows: (a) copper sulfuric and lactic acid solution were firstly mixed to form copper lactate sapphire solution; (b) sodium hydroxide solution was added in drop wise to the above solution to adjust its pH to 9.0 (mazarine); (c) TNAs were immersed in the solution for 10 min and then employed the SWV method for electrochemical deposition of Cu₂O depicted in following equation (1) :

Figure 1 shows the dependence of current density of the SWV process on the different deposition potential ranging from -0.8 to -1.2 V. The current densities for all the electrodes decrease with decreasing deposition potential and drop down to nearly 0 mA cm⁻² when the deposition potential decreases to -0.4 V, which indicate that the mean activity of ions in the solution is very low. Moreover, the deposition potential influences the morphology and content of Cu₂O nanoparticles deposited on the TNAs, which can be identified by the following characterization analysis results.

Figure 1. The dynamic process of SWV electrochemical deposition.

The morphologies of the TNAs and Cu₂O/TNAs heterojunction composites are characterized by FESEM images as shown in Figure 2. As can be clearly observed from Figure 2a and Figure 2b, after anodization of Ti foils and subsequent annealed at 500 °C, highly ordered TNAs were obtained with an average inner diameter around 140 nm and a tube length of 15 μm. It is clear to observe that the pore opening is almost circular in shape, and the bottom surface of TNAs has a regular hexahedron shape. The top views of the Cu₂O/TNAs heterojunction composites prepared by the different deposition potential are shown in Figure 2(c-f). The uniformly dispersed Cu₂O nanoparticles were successfully deposited onto the inner surfaces and interfaces of TNAs by the means of SWV method.

As the deposition potential increases from -0.8 to -1.2 V, the loading contents of Cu₂O nanoparticles also increase accordingly.

Figure 2. FESEM images of (a) top view of pure TNAs, insert showing the typical image of the cross-section of pure TNAs; (b) bottom view of pure TNAs, insert showing the magnified cross-section of pure TNAs; and top views of the Cu₂O/TNAs heterojunction composites prepared by the different deposition potential: (c) -0.8 V; (d) -0.9 V; (e) -1.0 V; (f) -1.2 V.

Figure 3 shows the typical cross-section FESEM images with the EDX spectrometry results of the corresponding area of Cu₂O/TNAs heterojunction composites prepared by -0.8 V (sample I), -0.9 V (sample II), -1.0 V (sample III), and -1.2 V (sample IV).

Figure 3. Typical cross-section FESEM images of Cu₂O/TNAs heterojunction composites prepared by the different deposition potential: (a) -0.8 V; (b) -0.9 V; (c) -1.0 V; (d) -1.2 V; (a'-d') corresponding EDX spectrum of Cu₂O/TNAs heterojunction composites (sample I - IV).

(sample IV) respectively. It can be seen that the Cu_2O nanoparticles are homogeneously dispersed on the inner surfaces of TNAs and the content of Cu_2O increases upon the increasing of deposition potential (Figure 3a-d). These results suggest that SWV is an excellent method for depositing Cu_2O nanoparticles onto TNAs. The corresponding EDX spectra of the samples shown in Figure 3a'-d' reveal that the samples are composed of Ti, O, and Cu elements, where the atomic ratio of O to Ti is more than 2:1, meaning a part of O come from Cu_2O . Moreover, the atomic ratio of Cu increase from 1.5% to 5.1% with the potential increasing from -0.8 to -1.2 V, which are consistent with the results of FESEM images.

The internal structure of the Cu_2O /TNAs heterojunction composites was further investigated by TEM. Figure 4a-d show the TEM images of the Cu_2O /TNAs prepared by -0.8, -0.9, -1.0, and -1.2 V respectively. The Cu_2O nanoparticles with diameter ranging from ca. 5 to 20 nm are evenly dispersed on the wall of the TNAs, with the formation of the heterojunctions between Cu_2O and TNAs. It can also be noticed that the size and density of the Cu_2O nanoparticles increase with increasing deposition potential, and this is in agreement with the FESEM and EDX results. Figure 4e depicts a HRTEM image taken from the corresponding selected area of Cu_2O /TNAs prepared by -1.0 V (sample III), showing the Cu_2O nanoparticles are embedded inside the TNAs, where the lattice fringes of 0.352 nm and 0.237 nm which correspond to the (101) and (004) planes of anatase TiO_2 , while the lattice planes with spacing of 0.246 nm and 0.213 nm correspond well with (111) and (200) planes of Cu_2O respectively. Moreover, a typical electron diffraction pattern from Sample III is shown in Figure 4f, where the diffraction rings corresponding to the (111), (200), and (220) planes of Cu_2O revealing that the Cu_2O nanoparticles are polycrystalline.

Figure 4. TEM images of the Cu_2O /TNAs prepared by (a) -0.8 V; (b) -0.9 V; (c) -1.0 V; and (d) -1.2 V; (e) HRTEM image of the corresponding selected area of sample III; (f) typical electron diffraction pattern of sample III.

The XRD patterns of pure TNAs annealed at 500 °C and Cu_2O /TNAs heterojunction composites are shown in Figure 5. It can be observed that the TNAs synthesized in our work are

pure anatase phase with the peaks at $2\theta = 25.3$, 37.8 , and 48.0° , corresponding to the (101), (004), and (200) crystal planes of anatase TiO_2 (JCPDS no. 21-1272). There is no obvious difference between sample I and pure TNAs, indicating that no Cu_2O diffraction peak appears, which is attributed to the low content of the Cu_2O phase that cannot be detected through XRD techniques. With increasing deposition potential, two additional diffraction peaks at $2\theta = 36.42$ and 42.29° appear in sample II, sample III, and sample IV, which can be ascribed to the (111) and (200) crystal planes of Cu_2O (JCPDS no. 05-0667). In addition, the sample IV also exhibits other peak at $2\theta = 61.34^\circ$, which corresponds to the (220) reflection of Cu_2O . It is worth mentioning that no characteristic peaks of Cu and CuO are observed in the samples, indicating that the heterojunction composites prepared by SWV method are composed of Cu_2O and TiO_2 crystalline structures. This is also further demonstrated by the XPS results.

Figure 5. XRD patterns of pure TNAs and Cu_2O /TNAs heterojunction composites.

To further determine the chemical compositions and oxidation states of Cu_2O /TNAs heterojunction composites, XPS tests were employed, and the spectra are shown in Figure 6. It can be clearly seen from the XPS survey spectrum that all the Cu_2O /TNAs heterojunction composites also contain Cu element besides Ti, O and C element compared with pure TNAs

Figure 6. (a) XPS spectra of pure TNAs and Cu_2O /TNAs heterojunction composites; (b) high-resolution XPS spectrum of Cu 2p region; (c) high-resolution XPS spectrum of O 1s region; and (d) Auger electron spectrum of Cu LMM.

(Figure 6a). The C 1s peak can be attributed to adventitious carbon from the XPS instrument itself. A high-resolution XPS spectrum of Cu 2p is shown in Figure 6b. Two peaks at 932.5 and 952.3 eV are assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, which are in good agreement with the characteristic peaks of Cu⁺ in Cu₂O. Figure 6c presents a typical high-resolution XPS spectrum of O 1s region. The main peak at 529.9 eV can be assigned to the Ti-O bonds of TiO₂, and the shoulder peak at higher binding energy of 531.8 eV is attributed to -OH adsorbed in the surface of TiO₂.³⁸ In order to further distinguish between Cu₂O and Cu or CuO, the Cu LMM Auger transitions was employed, as displayed in Figure 6d. We can clearly see that one main peak appeared at 917.0 eV, which is in agreement with the kinetic energy of Cu₂O,³⁹ which further demonstrate the coexistence of Cu₂O and TiO₂ in Cu₂O/TNAs heterojunction composites and no existence of Cu or CuO, is in good agreement with the XRD analysis.

Figure 7 shows the UV-vis diffusion reflection spectra (DRS) of the pure TNAs and Cu₂O/TNAs heterojunction composites. For the pure TNAs, a primary absorption of the ultraviolet light with a wavelength below 400 nm is observed due to the intrinsic band gap absorption of TiO₂. The weak absorption of pure TNAs in the visible light region is assigned to the scattering of light caused by pores or cracks in the nanotube arrays. By contrast, the DRS of all the Cu₂O/TNAs heterojunction composites are much different from that of pure TNAs, where the absorption edges shift to the visible light region ranging from 380 to 500 nm. The extended absorption edges and the enhanced absorption in the visible light region can be attributed to Cu₂O nanoparticles, indicating that deposition Cu₂O nanoparticles can significantly improve the visible light absorption of TNAs. The results indicate that deposition Cu₂O nanoparticles onto the inner surfaces of TNAs can effectively prevent the recombination of photo-generated charge carriers and make it a promising application in visible light-driven photocatalyst.

Figure 7. DRS spectra of pure TNAs and Cu₂O/TNAs heterojunction composites.

3.2 Photoelectrochemical performance

The photoelectrochemical performances of pure TNAs and Cu₂O/TNAs heterojunction composites were examined by the photocurrent response experiments and EIS tests using a three-electrode cell. Figure 8a presents the photocurrent response of pure TNAs and Cu₂O/TNAs heterojunction composites at a 0 V bias vs Ag/AgCl electrode with a pulse of 50 s under intermit-

ent Xe lamp ($\lambda > 400$ nm) irradiation. All the samples have no significant photocurrent response in the dark. It can be clearly seen that all the Cu₂O/TNAs heterojunction composites exhibit evidently enhanced visible light response while pure TNAs show very low photocurrent density under Xe lamp irradiation. The average photocurrent densities are 0.055, 0.29, 0.32, 0.52, and 0.43 mA cm⁻² for pure TNAs, sample I, sample II, sample

Figure 8. a) Photocurrent response of pure TNAs (a) and sample I - IV (corresponding to b-e) at the bias potential of 0 V (vs Ag/AgCl); b) the dependence of photocurrent response for pure TNAs (a,a') and sample I - IV (corresponding to b-e) on the applied potential at the scan rate of 100mV s⁻¹, pattern a' and d' is the dark current; c) photocurrent response of pure TNAs (a) and sample I - IV (corresponding to b-e) at the bias potential of 0.5 V (vs Ag/AgCl).

III, and sample IV respectively. It should be noted that the photocurrent densities of Cu₂O/TNAs heterojunction composites depend on the deposition potential of Cu₂O nanoparticles. The photocurrent densities increase first and then decrease with increasing Cu₂O loading. The decrease of photo-current density can be attributed to formation of charge recombination sites as the result of excess Cu₂O nanoparticles.⁴⁰ When the TNAs are filled up with Cu₂O nanoparticles, although more photo-generated charge carrier are created, the charge carriers cannot be efficiently separated and will be recombined unavoidably, resulting in a low photocurrent density. Figure 8b shows the

dependence of the photocurrent response of pure TNAs and $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites on the applied potential at a scan rate of 100 mV s^{-1} under visible light irradiation. The photocurrent densities for all the samples increase with increasing of bias potential in the range of -0.4 to 0.6 V vs Ag/AgCl electrode. Pattern a' and d' in Figure 8a show the current densities of pure TNAs and sample III without visible light irradiation as the function of applied potential. The photocurrent densities of these two samples increase tremendously when irradiated under visible light, especially for sample III, the photocurrent density is approximately 9.74 times that of itself without visible light irradiation, and is 6.11 times higher than that of pure TNAs under visible light irradiation.

Meanwhile, the photocurrent response of pure TNAs and $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites at a 0.5 V bias potential (vs Ag/AgCl electrode) under Xe lamp ($\lambda > 400 \text{ nm}$) irradiation with the pulse of 50s are shown in Figure 8c. Similarly, no photocurrent response is observed in the dark. However, the current densities at above zero can be attributed to the bias potential of 0.5 V . Under visible light irradiation, the photocurrent densities of the $\text{Cu}_2\text{O}/\text{TNAs}$ electrodes are higher than that of pure TNAs. For the $\text{Cu}_2\text{O}/\text{TNAs}$ electrode, the photocurrent densities also increase first and then decrease with an increasing amount of Cu_2O nanoparticles as the same as those at 0 V bias potential. The highest photocurrent density of 0.91 mA cm^{-2} obtained from sample III is 5.05 times as high as pure TNAs (0.18 mA cm^{-2}) and much higher in comparison with sample I, sample II, and sample IV. These results suggest that the bias potential has enhanced the photocurrent densities of the samples owe to it can greatly accelerate the separation of the photoexcited electron-hole pairs and effectively prolong the lifetime of the photogenerated charge carrier.

It is noteworthy that the EIS is a powerful measurement that gives lots of information regarding photogenerated charge carrier separation and transport properties on the interface of the electrodes. A semicircle in the Nyquist plot at high frequency represents the charge-transfer process, and the diameter of the semicircle reflects the charge-transfer resistance.^{17,41} Figure 9 shows a Nyquist impedance spectra of the pure TNAs and $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites recorded in a three electrode cell under visible light irradiation. For each set of date

Fig. 9 Electrochemical impedance spectra Nyquist plot of pure TNAs and sample I - IV with the insert showing the enlargement of the high frequency region under visible light irradiation.

points, the analysis was carried out at open circuit potential with an amplitude of 10 mV in the frequency range from 0.1 Hz to 100 kHz . Obviously, the semicircle on the EIS Nyquist plot of $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites are smaller than that of pure TNAs, which indicate that a more effective separation of photoexcited electron-hole pairs and faster interfacial charge transfer occurred on the $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites.^{42,43} Similarly to results of photocurrent response, sample III possesses the smallest semicircle of the Nyquist plot (inset in Figure 9), suggesting that sample III exhibits the lowest recombination rate of photoexcited electron-hole pairs. The EIS results demonstrate that deposition Cu_2O nanoparticles onto TNAs enables fast separation of photogenerated charge carrier and easier electron transfer, and thus improve its photoelectrocatalytic capability.

3.3 Photocatalytic and photoelectrocatalytic activities

The photocatalytic (PC) activities of the pure TNAs and $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites were evaluated by degradation of MO under visible light irradiation as depicted in Figure 10a. After adsorption in the dark for 60 min, the absorption rates of MO are 3.0%, 3.5%, 3.7%, 5%, and 4.4% for pure TNAs, sample I, sample II, sample III, and sample IV, respectively. The initial concentration (C_0) is considered as the concentration of MO after adsorption-desorption equilibrium. In general, pure TNAs shows a low decomposition rate of the organic pollutant under visible light irradiation due to its wide bandgap. However, the concentration of MO can be degraded to 81.6% by pure TNAs, which owing to the adsorption of a small amount of UV light and self-sensitization of MO molecules on pure TNAs surface under visible light irradiation. As reported by Wu *et al.*,⁴⁴ the dye can be excited under visible light and lead to electron injection from the dye into the conduction band of TiO_2 , which results in the degrada-

Fig. 10 a) Photocatalytic activities of pure TNAs and sample I - IV toward the degradation of MO under visible light irradiation; b) the corresponding linear relationship of $\ln(C/C_0)$ as a function of time.

tion of MO molecules by pure TNAs. It can also be observed that the PC activities of Cu₂O/TNAs heterojunction composites are higher than that of pure TNAs. After 180 min irradiation, the degradation rates are 51.5, 54.3, 71.7, and 60.6% for sample I, sample II, sample III, and sample IV, respectively. Figure 10b shows the linear relationship of $\ln(C/C_0)$ as a function of time, demonstrating that the PC process clearly followed first-order kinetics, which can be expressed as follows: $\ln(C/C_0) = kt$, where $|k|$ is the apparent rate constant, while C and C_0 are the reaction and initial concentration of MO, respectively. Clearly, the apparent rate constants of all the Cu₂O/TNAs heterojunction composites are higher than that of pure TNAs. Among the Cu₂O/TNAs heterojunction composites prepared at different deposition potential, sample III possesses the optimal PC performance and a highest apparent rate constant. Upon increasing amount of Cu₂O nanoparticles via increasing the deposition potential to -1.2 V, the degradation rate goes down, which is in accordance with the result of photocurrent response.

The enhanced photocatalytic activity of TiO₂ nanotube arrays decorated with Cu₂O nanoparticles can be attributed to the synergetic effects of strong visible-light absorption and p-n heterojunction structures which promote the separation of photoexcited electron-hole pairs. The degradation process can be expressed as follows:^{19,32}

When the Cu₂O/TNAs heterojunction composites are illuminated under visible light, Cu₂O nanoparticles can be easily excited and the electron-hole pairs are generated (eq. 2). As the conduction band of Cu₂O lies more negative than that of TiO₂, the photoexcited electrons from Cu₂O can quickly be transferred to the conduction band of TiO₂ (eq. 3), whereas holes can accumulate in the valence band of Cu₂O to form hole center. Thus, the electron transfer from Cu₂O to TiO₂ can effectively accelerate the separation of photogenerated charge carrier and prevent the recombination of the electrons and holes, which can facilitate the photocatalytic degradation of MO. On one hand, accumulated electrons in the conduction band of TiO₂ will react with oxygen adsorbed on the surface of TiO₂ to form superoxide radicals ($\bullet\text{O}^-$), and then combine with H^+ to form H_2O_2 , which could react with $\bullet\text{O}^-$ and be further reduced to hydroxyl radicals ($\bullet\text{OH}$) (eq. 4-6). On the other hand, the holes accumulated in the valence band of Cu₂O will react with H_2O or OH^- to generate $\bullet\text{OH}$ (eq. 7 and 8). Ultimately, the formed $\bullet\text{OH}$ will degrade MO to final the products (eq. 9).

Likewise, Figure 11a shows the photoelectrocatalytic (PEC) activities of pure TNAs and Cu₂O/TNAs heterojunction composites measured under visible light irradiation with a bias potential of 0.5 V. Compared to the PC process, PEC process can

Fig. 11 a) Photoelectrocatalytic activities of pure TNAs and sample I - IV toward the degradation of MO at an applied potential of 0.5 V (vs Ag/AgCl) under visible light irradiation; b) the corresponding linear relationship of $\ln(C/C_0)$ as a function of time; c) comparison of the photoelectrocatalytic activities of pure TNAs and sample I - IV with photocatalytic process.

speed up the degradation rate of MO for both pure TNAs and Cu₂O/TNAs heterojunction composites. In the case of sample III, the degradation rate can reach to 88.8% after 180 min in PEC process, which is much faster than that of PC process. Additionally, the fitting result of kinetic behaviours of PEC process is shown in Figure 11b. The same as PC process, the PEC process also obeys the first-order kinetics. Evidently, the apparent rate constants of both pure TNAs and all the Cu₂O/TNAs heterojunction composites in the PEC process are significantly higher than those in PC process. Such as sample III, the apparent rate constant is 0.01168 min^{-1} in PEC process, which is almost 1.71 times as compared to PC process (0.00684 min^{-1}). Figure 11c compares the PEC degradation rates of MO with PC process. It is obvious that the degradation rates of MO can be enhanced by PEC process for both the pure TNAs and Cu₂O/TNAs heterojunction composites. The results indicate that the synergistic effect between the visible light irradiation and the electricity can provide an effective way to degrade MO solution.

According to the above results, the enhanced PEC activity of $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites can be attributed to the synergistic effect between the visible light irradiation and the applied external electrostatic field. It is well-known that the Cu_2O can accelerate the separation of the photoexcited electron-hole pairs in PC degradation process. The photoexcited electrons and holes can migrate to the surface to react with the adsorbed reactants. However, when Cu_2O nanoparticles are deposited onto TNAs, the charge of the depletion layer could form at the heterojunction interface, which hamper the photoexcited electrons and holes pass through it and recombine easily in the volume or the surface of the heterojunction composites.^{19,32,45} Therefore, the applied positive bias added on the $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites can greatly accele-

Fig. 12 The schematic diagram of the photoelectrocatalytic mechanism of $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composite.

rate the movement of the photoexcited electron-hole pairs by making the depletion layer thinner or even disappear. Moreover, the internal electric field can promote the separation of the photoexcited electrons and holes in $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites. As a result of this, the recombination of the photoexcited electron-hole pairs can be reduced, thus the separated electrons and holes are then free to react with the adsorbed reactants with enhanced PC activity. Based on this, the schematic diagram of photoelectrocatalytic mechanism is shown in Figure 12. When $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites are irradiated with visible light, the photoexcited electrons on the conduction band of Cu_2O will transfer to the conduction band of TNAs. With the external electrostatic field, the photoexcited electrons travel vectorially along the TNAs and pass through the interface between TiO_2 and Ti to the external circuit, leaving the photoexcited holes in the valence band of Cu_2O . Consequently, the photoexcited electron-hole pairs are separated effectively and subsequently enhance the photoelectrocatalytic activity.

The electrochemical (EC), PC, and PEC process based on sample III are illustrated in Figure 13a. The results shows that 88.8% of the MO is degraded by PCE process after 180 min, while only 4.8% and 71.7% of MO can be removed in EC and PC process during the same irradiation time. It demonstrates that photoelectrocatalysis is a promising process to degrade MO solution. The stability of the prepared $\text{Cu}_2\text{O}/\text{TNAs}$ hetero-

junction composites is performed by a recycling MO photoelectrocatalytic degradation test on sample III under visible light irradiation 5 times. After the 5th degradation of MO, as shown in Figure 13b, the degradation rate remained at 86.9%, which is almost the same as that of the first cycle. This result indicates that the $\text{Cu}_2\text{O}/\text{TNAs}$ heterojunction composites have an excellent photoelectrocatalytic stability.

Fig. 13 a) Comparison of the electrochemical, photocatalytic, and photoelectrocatalytic activities toward the degradation of MO for sample III; b) Cycling photoelectrocatalytic degradation test on sample III for 5 times.

Conclusions

We have successfully decorated uniformly distributed Cu_2O nanoparticles into the inner surfaces and interfaces of TiO_2 nanotube arrays through a novel and facile square wave voltammetry electrochemical deposition technique. The $\text{Cu}_2\text{O}/\text{TiO}_2$ nanotube arrays heterojunction composites exhibited much enhanced photocurrent response and higher photocatalytic or photoelectrocatalytic degradation rate of methyl orange under visible light irradiation than that of pure TiO_2 nanotube arrays. In particular, with loading appropriate amount of Cu_2O nanoparticles (i.e., prepared at the deposition potential of -1.0 V), the $\text{Cu}_2\text{O}/\text{TiO}_2$ nanotube arrays heterojunction composite achieve the highest photocurrent density of 0.91 mA cm^{-2} at a 0.5 V bias potential and photoelectrocatalytic activity can reach as high as 88.8%. This study opens a new technique to improve the photoelectrochemical and photocatalytic activity of TiO_2 coupling with narrow bandgap semiconductors, making it a promising material for various potential applications.

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