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金属氧化物(Fe_2O_3 , CuO , NiO)改性对 TiO_2 纳米管阵列 光电催化活性的增强效应

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摘要: 采用阳极氧化法和阴极电沉积法制备了 Fe_2O_3 , CuO 和 NiO 纳米粒子改性的高度有序的 TiO_2 纳米管($\text{TiO}_2\text{-NT}$)阵列. 运用场发射扫描电子显微镜(FE-SEM), 透射电子显微镜(TEM), X射线衍射(XRD)和紫外-可见漫反射光谱等手段对 $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ 、 $\text{CuO}/\text{TiO}_2\text{-NT}$ 和 $\text{NiO}/\text{TiO}_2\text{-NT}$ 复合电极进行表征. 以苯酚为模拟污染物, 考察复合电极的光电性能. 结果表明, 金属氧化物(Fe_2O_3 , CuO , NiO)纳米粒子成功沉积在 $\text{TiO}_2\text{-NTs}$ 的管口、内壁和管底. 金属氧化物改性复合电极的光电催化活性比未改性的 $\text{TiO}_2\text{-NTs}$ 提高了2倍以上. $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ 在可见光区显示出最高的吸收强度. 以 $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ 为阳极处理苯酚废水, 光照120 min后苯酚去除率达到96%, 而未改性的 $\text{TiO}_2\text{-NTs}$ 的苯酚去除率只有41%. 此外, $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ 在生成低毒中间产物方面表现出良好的性能. 较高的复合电极光电催化活性主要是由于 TiO_2 纳米管和过渡金属氧化物纳米粒子间构筑的高界面面积异质纳米结构, 有效地促进了电子转移, 抑制了光生电子-空穴对的复合.

关键词: TiO_2 纳米管; Fe_2O_3 ; CuO ; NiO ; 光电催化; 可见光

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Enhanced Photoelectrocatalytic Activity of TiO_2 Nanotube Arrays Modified with Simple Transition Metal Oxides (Fe_2O_3 , CuO , NiO)

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Abstract: Composite electrodes consisting of highly ordered, vertically oriented TiO_2 nanotube ($\text{TiO}_2\text{-NT}$) arrays modified with Fe_2O_3 , CuO , and NiO nanoparticles were successfully fabricated by a simple electrochemical anodization and electrodeposition method. Field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and UV-Vis diffuse reflectance spectroscopy were used to characterize the structure and optical properties of the resulting $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$, $\text{CuO}/\text{TiO}_2\text{-NT}$, and $\text{NiO}/\text{TiO}_2\text{-NT}$ composite electrodes. The photoelectrochemical (PEC) activities of the composite electrodes were evaluated using phenol as a model pollutant. Results indicated that transition metal oxide nanoparticles were deposited on the mouth, tube wall, and base of the $\text{TiO}_2\text{-NTs}$. The PEC activity of the composite electrodes was over twice that of an unmodified $\text{TiO}_2\text{-NT}$ electrode. The $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ electrode showed the highest absorption intensity in the visible light region. After treatment for 120 min, the phenol removal efficiency using the $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ anode could reach 96%, while it was only 41% for the unmodified $\text{TiO}_2\text{-NT}$ anode. Moreover, the $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ electrode tended to generate intermediates of low toxicity. The higher PEC activity of the composite electrodes was attributed to the presence of hetero-nanostructures with high interfacial area comprised of $\text{TiO}_2\text{-NTs}$ and transition metal oxide nanoparticles, which efficiently facilitated electron transfer and inhibited the recombination of

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photogenerated electron-hole pairs.

Key Words: TiO₂ nanotube; Fe₂O₃; CuO; NiO; Photoelectrocatalysis; Visible light

1 Introduction

Abatement of environmental pollutants by green technologies is significantly attractive research topic. It is particularly interest in the treatment processes using the solar energy since sunlight is a renewable natural energy. Photoelectrochemical (PEC) process is recognized to be one of the most promising ways to clean our environment.¹ Semiconductor electrodes employed in PEC process can be excited by solar light to generate the electron-hole pairs to remove the pollutants. Assisted electrochemical process promotes the separation of electron-hole pairs and further improves the efficiency of pollutants degradation. An efficient photocatalyst should maximize the utilization of solar energy and minimize the recombination of photoexcited electron-hole pairs. Therefore, the properties of semiconductor materials are crucial for achieving high efficiency in PEC process.²

Various semiconductors have been extensively investigated since Fujishima and Honda³ firstly suggested the water splitting with TiO₂ under UV illumination in 1972. TiO₂ is one of the most studied semiconductors because of its high photocatalytic activity, chemical stability, low cost, and nontoxicity.⁴⁻⁷ However, the widespread usage of TiO₂ is limited by its large band gap energy (3.0–3.2 eV), which can only utilize the ultraviolet region of the solar spectrum. To enhance the photocatalytic activity of TiO₂ under visible light, considerable efforts have been attempted to improve the absorption in the visible spectrum, including dye sensitization,⁸⁻¹⁰ anion or cation doping,¹¹⁻¹³ noble metal deposition,¹⁴⁻¹⁶ and incorporation with transition metal oxides.^{17,18} Another main drawback of TiO₂ is the high recombination rate of photo-generated holes and electrons.¹⁹ Faster recombination largely decreases the quantum efficiency of PEC processes. Therefore, it is essential to suppress the recombination of electron-hole pairs. Among various strategies aimed at improving the absorption in the visible region and separating the electron-hole pairs, the incorporation of transition metal oxides with TiO₂ has been approved to be an effective method.²⁰⁻²³ Zhang and co-workers²³ have synthesized TiO₂/Cu₂O composite film and obtained high degradation efficiency of methylene blue. Although some studies have reported the incorporation of transition metal oxides with TiO₂, there was little information about the molecular-scale architecture control and systematical study on various metal oxides.

In this work, highly ordered vertically oriented TiO₂ nanotube (TiO₂-NT) arrays were fabricated by electrochemical anodization of Ti foil. The self-organized oriented NT structure could provide large surface areas and facilitate vectorial charge transfer from the solution to the substrate, which were expected to accelerate the separation of electron-hole pairs and har-

vest sunlight more efficiently. Simple transition metal oxides (Fe₂O₃, CuO, NiO) nanoparticles were uniformly incorporated with TiO₂-NTs by a novel electrochemical deposition method. The photocatalytic activity of the NT electrodes under visible light irradiation could be enhanced by modifying the surface structure and composition with the special metal oxides. Field emission scanning electron microscopy (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), and UV-visible diffuse reflectance spectroscopy were used to characterize the structure and optical properties of composite electrodes. The PEC activities of composite electrodes were evaluated by phenol removal.

2 Experimental

2.1 Preparation of TiO₂-NT electrodes modified by metal oxides

TiO₂-NT electrodes were prepared by the electrochemical anodization method on a Ti foil (0.25 mm thick, 99.7% purity). Prior to anodization, the Ti foil was polished with sandpaper, and then ultrasonically cleaned with acetone, ethanol, and distilled water. Anodization was performed in a two-electrode system with the pretreated Ti foil as the working electrode and Pt sheet as the counter electrode under constant voltage at room temperature. The anodizing voltage varied from 0 to 20 V with an increasing certain rate and was kept at 20 V for 120 min. The electrolyte was a mixed solution of 0.5% (w) NaF and 0.5 mol · L⁻¹ Na₂SO₄. All reagents were analytical grade. After anodic oxidation, the samples were rinsed with deionized water and dried in air. The as-formed TiO₂-NTs were annealed in a muffle furnace with 2 °C · min⁻¹ heating rate and kept at 773 K for 2 h to convert the amorphous phase to the crystalline one.

Fe₂O₃ nanoparticles were deposited into the crystallized TiO₂-NTs using an electrodeposition method. A two-electrode system was used with TiO₂-NTs as the cathode and a Pt sheet as the anode. First, the TiO₂-NT electrodes were soaked in a 0.1 mol · L⁻¹ Fe(NO₃)₃ aqueous solution for 10 min, always subjected to ultrasound sonication before soaking. Then the TiO₂-NT electrodes were transferred into a new medium that only contained an inert supporting electrolyte (0.1 mol · L⁻¹ Na₂SO₄). The potentiostatic DC electrodeposition was carried out at a constant voltage of 8 V for 20 min and the temperature of the electrolyte was maintained at 85 °C. After the electrodeposition in this medium, Fe nanoparticles were deposited into the interior tubes of TiO₂-NT electrodes (denoted as Fe/TiO₂-NTs). About 1.0% (w) deposition amount of Fe in the NTs was obtained after several repetitions. Then the Fe/TiO₂-NT electrodes were connected as the anode and the Pt sheet as the cathode. The material was electrochemically oxi-

dized in 1 mol · L⁻¹ KOH aqueous solution at a voltage of 8 V for 2 min at room temperature. After this electrochemical oxidation, Fe/TiO₂-NTs were converted into the corresponding oxides Fe₂O₃/TiO₂-NTs. The resulting Fe₂O₃/TiO₂-NT samples were rinsed with distilled water and dried at a low temperature.

The preparation processes of CuO/TiO₂-NTs and NiO/TiO₂-NTs were the same as that of Fe₂O₃/TiO₂-NTs, except that the deposition solution was 0.1 mol · L⁻¹ Cu(NO₃)₂ and 0.1 mol · L⁻¹ Ni(NO₃)₂ aqueous solutions, respectively.

2.2 Characterization

The morphologies and the cross-section views of TiO₂-NT electrodes modified by metal oxides were characterized using a field emission scanning electron microscope (FE-SEM; Hitachi S-4700 II) and a transmission electron microscope (TEM; Philips-FEI Tecnai G2 F30 S-Twin), equipped with energy-dispersive X-ray spectroscopy (EDX; EDAX Analyzer DPP-II). The crystal properties of the prepared samples were determined from X-ray diffraction (XRD) using a diffractometer with Cu K_α radiation (Netherlands PANalytical X'Pert PRO). The accelerating voltage and applied current were 40 kV and 40 mA, respectively. Light absorption properties were measured using UV-Vis diffuse reflectance spectra (Shimadzu, UV-3150) with a wavelength range of 220–600 nm. Electrochemical impedance spectroscopy (EIS) was performed using a CHI 660D instrument (Chenhua, Shanghai) in a three-electrode system, with a saturated Ag/AgCl electrode and a Pt sheet as reference and counter electrodes, respectively.

2.3 Photoelectrochemical activity test

The PEC activity of the composite electrodes was evaluated using phenol as a model pollutant. All the experiments were carried out in a two-electrode glass cell (100 mL) with constant magnetic stirring, using 0.2 mol · L⁻¹ Na₂SO₄ as the electrolyte. The initial concentration of the phenol aqueous solution was 10 mg · L⁻¹. The composite electrode was used as anode and Cu sheet was cathode. Applied voltage was provided by the DC Constant Current Power (WYL603 type, Hangzhou Yuhang Siling Electronic Equipment Co., Ltd.). The anode was irradiated using a tungsten-halogen lamp (500 W), which generates a continuous light distribution across the visible spectrum and relatively weak emission in the ultraviolet portion of the spectrum. A UV cut-off filter (λ > 420 nm) was used for visible light irradiation. The light intensity on the photoanode was ~80 mW · cm⁻². All experiments were carried out under ambi-

ent conditions. The determination of phenol and its degradation intermediates were carried out using high performance liquid chromatography (HPLC, Agilent 1200) by comparing the retention time of the standard compounds. The separation was performed using a Diamonsil C18 reversed phase column (150 mm × 4.6 mm × 5 mm) at the flow rate of 1.0 mL · min⁻¹ and the column temperature of 25 °C. The eluent consisted of methanol/purified water (30:70 (volume ratio)). The analyses were performed with a UV detector at a wavelength of 254 nm.

3 Results and discussion

3.1 Characterization of photocatalysts

Fig.1 shows the SEM morphologies of the as-synthesized TiO₂-NTs, Fe₂O₃/TiO₂-NTs, CuO/TiO₂-NTs, and NiO/TiO₂-NTs. The hollow TiO₂-NTs are almost uniform and have a highly ordered tubular structure. The average inner diameter of TiO₂-NTs is ~80 nm, and their average outer diameter is ~110 nm (Fig.1(a)). Fe₂O₃/TiO₂-NTs, CuO/TiO₂-NTs, and NiO/TiO₂-NTs have the similar tubular structure. The corresponding metal oxide nanoparticles were distinctly deposited on TiO₂ tubular substrates. The surface of TiO₂-NT substrates was not blocked by nanoparticles. To identify the distribution of nanoparticles in TiO₂-NTs, the cross-section views of the composite electrodes were analyzed by TEM images. According to Fig.2, the length of TiO₂-NTs is around 1.2 μm. Fe₂O₃ nanoparticles are deposited on the mouth, the tube wall, and the base of TiO₂-NTs. The average diameter of Fe₂O₃ nanoparticles is about 35 nm. Note that the deposition process has not destroyed the structure of the ordered TiO₂-NT arrays, and Fe₂O₃ nanoparticles can be fabricated into the bottom of TiO₂-NTs. The EDX spectrum in Fig.2 confirms the existence of Fe, Ti, and O, whereas the Cu signal originates from the Cu substrate used in the imaging process. The measured atomic ratio of Fe/Ti was 1.21%. The existence of NiO in NiO/TiO₂-NTs was also confirmed (figure not shown). The measured atomic ratio of Ni/Ti was 1.35%. The atomic ratio of Cu/Ti could not be determined due to the interference of Cu substrate used in EDX measurement. Fig.3 shows the XRD patterns of different composite electrodes annealed at 773 K. TiO₂ is converted from amorphous state to anatase state with a fine preferential growth of the self-organized highly oriented TiO₂-NT arrays in the (101) direction. The peak of the (101) crystal (2θ = 26.2°) can be seen from all the patterns. The characteristic peaks cor-

Fig.1 SEM images of TiO₂-NTs and the metal oxide modified TiO₂-NTs

(a) TiO₂-NTs, (b) CuO/TiO₂-NTs, (c) NiO/TiO₂-NTs, (d) Fe₂O₃/TiO₂-NTs

Fig.2 TEM images with different magnifications (a, b) and energy-dispersive X-ray (EDX) spectroscopy (c) of $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ electrode

responding to CuO , NiO , and Fe_2O_3 are also identified in Fig.3. It indicates that $\text{TiO}_2\text{-NTs}$, $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$, $\text{CuO}/\text{TiO}_2\text{-NTs}$, and $\text{NiO}/\text{TiO}_2\text{-NTs}$ have been successfully synthesized.

UV-Vis diffuse reflectance spectra of the composite $\text{TiO}_2\text{-NT}$ electrodes modified by different metal oxides are shown in Fig.4. In the wavelength range from 220 to 325 nm, $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$, $\text{CuO}/\text{TiO}_2\text{-NTs}$, and $\text{NiO}/\text{TiO}_2\text{-NTs}$ have lower absorbance intensity than the unmodified $\text{TiO}_2\text{-NTs}$. When the

wavelength is longer than 325 nm, however, the absorbance intensities of $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$, $\text{CuO}/\text{TiO}_2\text{-NTs}$, and $\text{NiO}/\text{TiO}_2\text{-NTs}$ are higher than that of $\text{TiO}_2\text{-NTs}$. Especially for $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$, its absorbance intensity is significantly higher than other electrodes in the visible light region. Considering the large proportion (47%) of visible light in solar spectrum, the composite $\text{TiO}_2\text{-NT}$ electrodes modified by Fe_2O_3 , CuO , and NiO are superior to the unmodified $\text{TiO}_2\text{-NTs}$.

3.2 Photoelectrocatalytic degradation of phenol

To investigate the PEC activity of composite electrodes, phenol degradation experiments were carried out using the composite electrodes as the photoanodes. Fig.5 shows the comparison of phenol removal efficiency under irradiation. The removal rates of phenol using the three composite electrodes have been significantly improved relative to the unmodified $\text{TiO}_2\text{-NT}$ electrodes. After 120 min treatment, phenol removal efficiencies of $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$, $\text{NiO}/\text{TiO}_2\text{-NT}$, and $\text{CuO}/\text{TiO}_2\text{-NT}$ anodes were 96%, 93%, and 90%, respectively, while it was only 41% for the unmodified $\text{TiO}_2\text{-NT}$ anode. The PEC activity of the composite NT electrodes was over twice that of the unmodified $\text{TiO}_2\text{-NT}$ electrode. The improved PEC performance was apparently attributed to the modification of metal oxides.

3.3 Comparison of different processes

The electrocatalytic, photocatalytic, and photoelectrocatalytic processes were performed to investigate the role of different

Fig.3 XRD patterns of (a) $\text{TiO}_2\text{-NTs}$, (b) $\text{NiO}/\text{TiO}_2\text{-NTs}$, (c) $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$, and (d) $\text{CuO}/\text{TiO}_2\text{-NTs}$

Fig.4 UV-Vis diffuse reflectance spectra of the composite $\text{TiO}_2\text{-NT}$ electrodes modified by different metal oxides

Fig.5 Comparison of phenol removal efficiency under irradiation using different electrodes

processes on phenol degradation using Fe₂O₃/TiO₂-NTs as the anode since it has the best PEC activity. In electrocatalytic process, applied potential was performed and the experiments were carried out in the dark. In photocatalytic process, light irradiation was performed at open circuit (without applied potential). In photoelectrocatalytic process, applied potential and light irradiation were simultaneously used. All other operating conditions were the same. Fig.6 shows the comparison of different processes on phenol degradation. After 120 min treatment, phenol removal efficiency could reach 96% in the photoelectrocatalytic process, while it was only 15% for photocatalytic process and 4% for electrocatalytic process. It was evident that the photoelectrocatalytic process has synergetic effects in enhancing the removal efficiency of phenol in comparison with the individual photocatalytic or electrocatalytic process.

Comparison of Fe₂O₃/TiO₂-NTs and TiO₂-NTs on phenol degradation under UV-Vis light and visible light irradiation is shown in Fig.7. Phenol removal efficiency of Fe₂O₃/TiO₂-NTs is ca 2.3 times higher under UV-visible light irradiation and 8 times higher under visible light irradiation than that of TiO₂-NTs. It is obvious that the modification of Fe₂O₃ on TiO₂-NTs significantly improves the PEC activity under visible light irradiation.

Fig.6 Comparison of different processes on phenol degradation using Fe₂O₃/TiO₂-NTs as the anode

Fig.7 Comparison of Fe₂O₃/TiO₂-NTs and TiO₂-NTs on phenol degradation under UV-Vis light and visible light irradiation

3.4 Determination of phenol degradation intermediates

Fig.8 shows the HPLC chromatograms of phenol degradation at different treatment time. The main intermediates were identified to be benzoquinone, hydroquinone, and maleic acid by comparing the retention time of the standard compounds (Table 1). It can be seen that phenol was continuously degraded with time. Benzoquinone is an important intermediate of phenol degradation. Fig.9 shows that the yields of benzoquinone under irradiation using TiO₂-NT, Fe₂O₃/TiO₂-NT, CuO/TiO₂-NT, and NiO/TiO₂-NT electrodes. Benzoquinone yields on the composite NT anodes first increased and then decreased with time. This was quite beneficial to the detoxification of wastewater because benzoquinone was regarded as one of the most toxic intermediates.²⁴ Benzoquinone yields of Fe₂O₃/TiO₂-NT, NiO/TiO₂-NT, CuO/TiO₂-NT, and TiO₂-NT anodes were 1%, 4%, 7%, and 9% at 120 min, respectively. Fe₂O₃/TiO₂-NTs showed good performance to generate the low toxic intermediates. A possible reason was that some benzoquinone intermediate was simultaneously degraded when phenol was

Fig.8 HPLC chromatograms of phenol degradation at different treatment time under UV-Vis light irradiation

Table 1 HPLC retention time of phenol and its intermediates

Identification	Retention time/min	Chemical structure
maleic acid	2.145	
hydroquinone	3.295	
benzoquinone	4.638	
phenol	12.127

Fig.9 Yields of benzoquinone under irradiation using different electrodes

converted to benzoquinone. $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ had the highest PEC activity among these composite electrodes and could generate the most oxidizing reagents to degrade the pollutants (see Fig.5). Therefore, sufficient oxidants could further degrade the benzoquinone to achieve the lower yields of benzoquinone.

3.5 EIS analysis

$\text{TiO}_2\text{-NT}$ electrodes modified by simple transition metal oxides were analyzed by electrochemical impedance spectroscopy (EIS). Experiments were carried out in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution under dark condition. Fig.10 shows the Nyquist plots of $\text{TiO}_2\text{-NT}$ electrodes and $\text{TiO}_2\text{-NTs}$ modified by various metal oxides. For each electrode, only one arc could be observed in the complex plane, which was related to the porous nature of the electrodes. The radius of the arc reflects the charge transfer resistance at the surface of the electrode.²⁵ It is obvious that the arc radius on $\text{TiO}_2\text{-NTs}$ modified by various metal oxides is smaller than that on unmodified $\text{TiO}_2\text{-NTs}$. This indicates that the modification of transition metal oxides improves the interfacial charge transfer of $\text{TiO}_2\text{-NTs}$.

3.6 Possible mechanism

Current density–potential curves of various electrodes were tested in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution using a three-electrode system (Fig.11). The photocurrent density of various electrodes increased as the applied voltage rose. Composite electrodes showed a better photoresponse under visible light irradiation

Fig.10 EIS Nyquist plots of $\text{TiO}_2\text{-NT}$ electrode and $\text{TiO}_2\text{-NT}$ electrodes modified by various metal oxides under dark condition

Fig.11 Current density–potential curves of different electrodes under chopped visible light irradiation

(a) $\text{TiO}_2\text{-NTs}$, (b) $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$, (c) $\text{CuO}/\text{TiO}_2\text{-NTs}$, (d) $\text{NiO}/\text{TiO}_2\text{-NTs}$

than $\text{TiO}_2\text{-NT}$ electrode. The photocurrent of $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ (or $\text{NiO}/\text{TiO}_2\text{-NTs}$) was ca 3 times higher than that of $\text{TiO}_2\text{-NTs}$ at 0.4 V (vs Ag/AgCl). $\text{CuO}/\text{TiO}_2\text{-NTs}$ had a lower photocurrent relative to $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ (or $\text{NiO}/\text{TiO}_2\text{-NTs}$), but its photocurrent was still over 2 times higher than that of $\text{TiO}_2\text{-NTs}$. The recombination peaks of photogenerated electron-hole pairs were found at lower applied voltage, however, they could decrease as the applied voltage bias increased. In addition, $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ and $\text{CuO}/\text{TiO}_2\text{-NT}$ electrodes showed higher dark current density than $\text{TiO}_2\text{-NTs}$ and $\text{NiO}/\text{TiO}_2\text{-NTs}$, which indicated that Fe_2O_3 and CuO nanoparticles had higher conductivity and reduced the charge transfer resistance of the $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NT}$ and $\text{CuO}/\text{TiO}_2\text{-NT}$ electrodes. These results were consistent with EIS analysis in Fig.10. We tentatively put forward that Fe_2O_3 and CuO nanoparticles may perform as the channel for electron migration and improve the separation of photogenerated electron-hole pairs since they have higher conductivity than TiO_2 .

The differences in PEC activity among these composite electrodes were probably associated with their band structure and surface chemical nature. Table 2 lists the valence band (VB) and conduction band (CB) positions of TiO_2 , Fe_2O_3 , NiO , and CuO .²⁶ Fe_2O_3 and CuO have the low band gap, which would favor the absorption of the solar energy in visible light region. Since the CB position of Fe_2O_3 (or CuO) is more positive than that of TiO_2 , some photogenerated electrons in $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ (or $\text{CuO}/\text{TiO}_2\text{-NTs}$) may transfer from TiO_2 to Fe_2O_3 (or CuO), leaving more holes to carry out the oxidation reaction. However, it might also serve as a recombination center since the photogenerated holes may move from TiO_2 to Fe_2O_3 (or CuO).

Table 2 Valence band (VB) and conduction band (CB) positions of TiO_2 , Fe_2O_3 , NiO , and CuO

Sample	E_{CB}/V (vs NHE)	E_{VB}/V (vs NHE)	Band gap/eV
TiO_2	−0.29	2.91	3.20
Fe_2O_3	0.28	2.48	2.20
NiO	−0.50	3.00	3.50
CuO	0.46	2.16	1.70

NHE: normal hydrogen electrode

Fig.12 Schematic diagrams of pollutants degradation on MO/TiO₂-NT electrodes under irradiation

(a) possible pathway of the photogenerated charge separation and electron transport on Fe₂O₃/TiO₂-NT or CuO/TiO₂-NT electrode;

(b) *p-n* junction formation model on NiO/TiO₂-NT electrode

Therefore, the deposition amount of Fe₂O₃ (or CuO) should be appropriately controlled. A schematic diagram of the photogenerated charge separation and electron transport on Fe₂O₃/TiO₂-NT or CuO/TiO₂-NT electrode is shown in Fig.12(a). The low band gap of Fe₂O₃ (or CuO) played an important role in the enhanced PEC activity of Fe₂O₃/TiO₂-NTs (or CuO/TiO₂-NTs). NiO/TiO₂-NTs also showed a higher PEC activity compared to the TiO₂-NTs, but the band gap of NiO was larger than that of TiO₂. Therefore, the possible mechanism of enhanced PEC performance on NiO/TiO₂-NTs was different from Fe₂O₃/TiO₂-NTs (or CuO/TiO₂-NTs). Since NiO is a *p*-type semiconductor and TiO₂ is an *n*-type semiconductor, a number of *p-n* junctions would be formed when NiO was deposited on TiO₂. As shown in Fig.12(b), the inner electric field was formed at the equilibrium, which made *p*-type NiO region had the negative charge and *n*-type TiO₂ region had the positive charge. Thus, the photogenerated holes moved to the negative field, while the electrons transferred to the positive field under the inner electric field. As a result, electron-hole pairs were effectively separated and the PEC activity of NiO/TiO₂-NTs was significantly improved compared with the unmodified TiO₂-NTs.

When the phenol molecules were adsorbed on the surface of electrodes, some photogenerated holes directly reacted with phenol molecules to produce phenol^{•+} radicals. Further, the reactive phenol^{•+} radicals were transformed into degradation intermediates. And other holes reacted with H₂O to produce hydroxyl radicals (HO[•]), which further oxidized organic compounds into H₂O and CO₂.¹⁸ The possible reactions on the heteronanostructures comprised of TiO₂-NTs and transition metal oxide (MO) nanoparticles could be expressed as follows:

Note that Fig.12 shows just a tentative mechanism and the differences in PEC activity among various composite electrodes have not been completely clarified. The PEC activity is also sensitive to the interface, which is more complicated. The crystal-face exposed to the electrolyte at the interface may cause a different structure of the electric double layer. Thus this study illustrates the enhanced PEC activity of TiO₂-NTs modified by simple transition metal oxides, and more work will be done to further clarify the mechanism.

4 Conclusions

The present study has demonstrated that TiO₂-NTs, Fe₂O₃/TiO₂-NTs, CuO/TiO₂-NTs, and NiO/TiO₂-NTs could be successfully synthesized by a simple electrochemical anodization and electrodeposition method. The obtained TiO₂ and composite NT electrodes had a uniform and highly oriented tubular structure. The characteristic peaks corresponding to Fe₂O₃, CuO, and NiO were identified by XRD and the main phase of TiO₂-NTs was anatase. Nanostructured composite electrodes showed a PEC activity more than 2 times higher than the pure TiO₂-NTs. After 120 min treatment, phenol removal efficiency using Fe₂O₃/TiO₂-NT, NiO/TiO₂-NT, and CuO/TiO₂-NT electrodes could reach 96%, 93%, and 90%, respectively, while it was only 41% for the unmodified TiO₂-NT anode. Moreover, Fe₂O₃/TiO₂-NTs showed good performance to generate the low toxic intermediates. The low band gap of Fe₂O₃ (or CuO) played an important role in the enhanced PEC activity of Fe₂O₃/TiO₂-NTs (or CuO/TiO₂-NTs). The enhanced performance of NiO/TiO₂-NTs was attributed to the formation of *p-n* junctions. The results indicate that TiO₂-NTs modified by simple transition metal oxides (Fe₂O₃, CuO, NiO) are promising candidates for environmental applications.

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