TiO₂/Au 纳米棒阵列的制备及其光催化性能

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摘要: 采用电沉积和旋转涂膜相结合的方法成功制备了高度有序的 TiO₂/Au 纳米棒阵列催化剂。扫描电镜和透射电镜结果表明, TiO₂ 薄膜均匀地包覆在 Au 纳米棒的表面, 形成核壳型的一维阵列结构。X 射线衍射分析表明所获得 TiO₂ 为 (101) 晶面优先生长的锐钛矿晶相。紫外-可见漫反射光谱显示, 由于 Au 和 TiO₂ 间肖特基结的存在造成吸收红移, Au 纳米棒表面的等离子共振效应导致 400~800 nm 间出现吸收峰。在紫外光催化降解罗丹明 B 反应中, TiO₂/Au 纳米棒阵列催化剂表现出优异的催化活性, 其动力学常数分别为 TiO₂ 和 TiO₂/Au 膜的 2.0 和 1.3 倍。这主要归结于 Au 与 TiO₂ 间的肖特基结和一维阵列结构所带来的大的比表面积、宽的光响应范围和有效的光生载流子分离与传递。

关键词: 二氧化钛; 金纳米棒阵列; 肖特基结; 光生载流子分离; 光生载流子迁移; 光催化活性

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Fabrication of a TiO₂/Au Nanorod Array for Enhanced Photocatalysis

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Abstract: A highly ordered TiO₂/Au nanorod array was successfully fabricated by direct current electrodeposition and subsequent spin-coating. Scanning electron microscopy and transmission electron microscopy images revealed that the TiO₂ film completely covered the surface of the Au nanorods, which resulted in TiO₂ shell Au core nanorods. X-ray diffraction patterns revealed that the TiO₂ film was anatase with preferential orientation in the (101) plane. UV-Vis diffuse reflectance spectra showed a shift in the absorption edge toward the visible region because of the formation of a Schottky junction between Au and TiO₂. A new absorption peak that ranged from 400 to 800 nm appeared because of the localized surface plasmon resonance of the Au nanorod arrays. For the photocatalytic degradation of rhodamine B under UV light irradiation, the TiO₂/Au nanorod array exhibited excellent photocatalytic activity and its kinetic constant was 2.0 times that of pristine TiO₂ and 1.3 times that of a TiO₂/Au film. The enhanced photocatalysis was attributed to the high surface volume ratio, an improved UV light response, efficient separation, and the convenient migration of photogenerated charge carriers because of the one-dimensional nanorod structure and the Schottky junction between Au and TiO₂. This work could provide new insights into the fabrication of a high performance photocatalyst and thus facilitate practical environmental applications.

Key words: titania; gold nanorod array; Schottky junction; photogenerated charge carrier separation; photogenerated charge carrier migration; photocatalytic activity

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Because of its high photocatalytic activity, non-toxicity, and good stability, TiO_2 has attracted considerable interest in many fields such as environmental purification [1–3], water splitting [4–6], photovoltaic cells [7–9], etc. However, the practical application of TiO_2 is somewhat limited by its low quantum efficiency as a result of the fast recombination of photogenerated charge carriers. Much effort has been put into doping with metal ions [10], nonmetal atoms [11–12], and semiconductor coupling [13–14] to improve photocatalytic activity. Although these modifications can partly improve the quantum efficiency of TiO_2 , some key problems remain unresolved, for example, the lattice distortion and limited thermal and chemical stability.

One of the promising strategies to overcome the above drawbacks is the incorporation of noble metals such as Pt [15–16], Pd [17–18], Au [19–20], and Ag [21–22] with TiO_2 . This semiconductor-metal system can realize an efficient separation of photogenerated charge carriers by forming a Schottky junction, which improves the quantum efficiency of the photocatalyst. Sonawane and Donaare [23] prepared a Au/TiO_2 thin film and found its phenol decomposition rate in sunlight improved 2–2.3 times compared with pristine TiO_2 . Sangpour et al. [24] fabricated a Au/TiO_2 film, which exhibited enhanced methylene blue degradation in the presence of UV and visible light irradiation when using the radio frequency reactive magnetron co-sputtering method. Pradhan et al. [25] investigated enhanced methanol degradation with Au/TiO_2 snowman-like heterodimer nanoparticles, which was attributed to the efficient separation of photogenerated electrons and holes at the Au/TiO_2 interface.

The morphology of the catalyst is also a critical element that affects the quantum efficiency of the photocatalyst. Highly ordered one-dimensional (1D) nanostructures such as nanotubes or nanorods, which align vertically to the substrate, have attracted considerable attention because of their high surface to volume ratios and the convenient migration of photogenerated charge carriers. Until now, research into the structural forms of this metal-semiconductor material has mainly focused on nanoparticles [26], core-shell structures [27], nanoclusters [28], etc. Few studies of this composite material have reported a 1D nanostructure.

In this work, a highly ordered TiO_2/Au nanorod array

photocatalyst was successfully fabricated by direct current (DC) electrodeposition and subsequent spin-coating. The novel photocatalyst combined the advantages of a Schottky junction between Au and TiO_2 , which accelerated the separation of photogenerated charge carriers and the 1D nanostructure. This favored the vectorial transfer of photogenerated electrons giving efficient photogenerated charge carrier utilization and consequently improved the photocatalytic activity. Moreover, this kind of system can prevent handling problems during the pollutant degradation process compared with suspended particles. Rhodamine B (RhB) was used as a model substance for the photocatalytic degradation reaction to evaluate the photocatalytic activity of the prepared TiO_2/Au nanorod array photocatalysts.

1 Experimental

1.1 Preparation of the TiO_2/Au nanorod array

The fabrication process for the well-aligned TiO_2/Au nanorod array is outlined in Scheme 1. The Au nanorod array was prepared using anodic aluminum oxide (AAO, Anodisc 47, 0.2 μm , Whatman) as a template. Before electrodeposition, a thin Ag film was evaporated onto one side of the templates and served as a conductive contact, and then the templates were dipped into a 25 mmol/L HAuCl_4 solution containing 0.21 mol/L Na_2SO_3 and 0.21 mol/L $\text{Na}_2\text{S}_2\text{O}_3$ for 20 min to ensure that the inner wall of the pore channel was wetted. A three-electrode system with the Ag-coated AAO templates, Pt foil, and a saturated calomel electrode (SCE) as the working electrode, counter electrode, and reference electrode, respectively, was used to fabricate the Au nanorod array, and the potential of the DC electrodeposition was maintained at -0.35 V for 3 min. After the electrodeposition process the AAO templates containing Au nanorods were washed with Milli-Q water and fixed on a pretreated Ti foil using high-purity silver paint. To expose the Au nanorod the AAO templates were dissolved in a 3.0 mol/L NaOH solution for 5 min.

The deposition of the TiO_2 film was carried out by spin-coating. Tetrabutyl titanate (TBOT, 99%, Tianjin Kermel Chemical Reagents Co., Ltd., 17.02 ml) and diethanol amine (AR, 4.80 ml) were added to ethanol (67.28

Scheme 1. Fabrication process for the TiO_2/Au nanorod array. (a) AAO templates with an evaporated Ag film; (b) Deposition of the Au nanorod array by DC electrodeposition; (c) Dissolved AAO templates; (d) Deposition of TiO_2 by spin-coating.

ml) and the resulting solution was stirred for 2 h at room temperature. A mixed solution of 0.9 ml Milli-Q water and 10 ml ethanol was added slowly to the mixed solution of TBOT, diethanol amine, and ethanol. The resulting mixture was stirred for a further 30 min, generating a transparent and straw sol. The TiO_2 sol was spin-coated onto the Au nanorod array at a rotation speed of 1000 r/min for 3 min. To convert the amorphous phase of TiO_2 to a crystalline phase the sample was calcined at 350 °C for 60 min at a heating rate of 2 °C/min. The TiO_2/Au film was prepared under the same conditions, only without the AAO templates, and was employed in the control experiments to compare with the 1D nanostructure.

1.2 Characterization of the TiO_2/Au nanorod array

The morphology of the TiO_2/Au nanorod array was characterized using a scanning electron microscope (SEM, Hitachi S-4800) with an accelerating voltage of 3.0 kV and a transmission electron microscope (TEM, Tecnai G² 20) operating at 200 kV. The crystallinity of the prepared sample was determined by X-ray diffractometry (XRD) using a diffractometer (Shimadzu LabX XRD-6000) with $\text{Cu } K_\alpha$ radiation. Light absorption properties were measured using UV-Vis diffuse reflectance spectroscopy (DRS, Shimadzu UV-2450) in a wavelength range of 200–800 nm.

1.3 Photocatalytic experiment

The photocatalytic activity of the prepared catalysts was evaluated using RhB (Tianjin Bodi Chemical Reagents Co., Ltd) as a test substance. A 300 W high-pressure mercury lamp (Beijing Huiyixin Lighting Co.) was used as the UV light source ($I_0 = 0.8 \text{ mW/cm}^2$). The initial concentration of

RhB was 10 mg/L. During the photodegradation process the RhB solution was collected at 10 min intervals for analysis. The concentration of RhB in the solution was determined by measuring the absorbance intensity at 553 nm with a UV-Vis spectrometer (XinMao, UV-7504). To investigate the application potential of the TiO_2/Au nanorod array in the photoelectrocatalytic process, a photoelectrocatalytic reaction was implemented. The prepared catalyst, Pt foil, and SCE served as a photoanode, a cathode, and a reference electrode, respectively. A constant potential of 0.6 V vs SCE was applied during the photoelectrocatalytic process.

2 Results and discussion

2.1 Determination of morphology

SEM images of the Au nanorod array were taken before and after modification with TiO_2 , as shown in Fig. 1. From the top-view (Fig. 1(a) and (b)) and a cross-sectional examination (Fig. 1(c)) of the Au nanorod array, Au nanorods with an average diameter of around 200–250 nm and an average rod length of approximately 900–1000 nm were found to be separate and vertical to the substrate. After the spin-coating process, TiO_2 particles of about 150 nm in size were deposited onto the Au nanorod array.

Figure 2 shows typical TEM images of the TiO_2/Au nanorod array. From the TEM images, we observed a thin TiO_2 film that covered the surface of a Au nanorod and this could be clearly distinguished from the inner Au nanorod wall while it formed a TiO_2 shell Au core nanorod. This completely coated nanostructure could efficiently avoid the corrosion or dissolution of noble metals during the photocatalytic reaction, which improved the chemical stability of the photocatalyst [29].

Fig. 1. SEM images of the Au nanorod array (a–c) and TiO_2/Au nanorod array (d–f). (a, b, d, e) Top-view; (c) Cross-section.

Fig. 2. TEM images of the TiO_2/Au nanorod (a) and the high magnification of the marked region corresponding to the TiO_2 layer and the Au nanorod (b).

2.2 XRD analysis

Figure 3 shows the XRD patterns of the TiO_2/Au nanorod array. The diffraction peaks at $2\theta = 38.1^\circ$, 44.4° , 64.5° , and 77.5° corresponded to the (111), (200), (220), and (311) facets of Au (JCPDS 893697), respectively. The peak of the (101) crystal face at $2\theta = 25.2^\circ$ indicated a fine preferential growth of the TiO_2 film that covered the surface of the Au nanorod. Usually, the phase transformation temperature from amorphous to anatase is higher than 400°C . For the TiO_2/Au nanorod array the phase transformation occurred at 350°C , which may be attributed to the presence of Au nanorods.

Fig. 3. XRD pattern of the TiO_2/Au nanorod array.

2.3 UV-Vis DRS characterization

Figure 4 gives the absorption spectra of TiO_2 , the TiO_2/Au film, and the TiO_2/Au nanorod array. Compared with pristine TiO_2 , a red shift of the optical absorption was observed for the TiO_2/Au film and the TiO_2/Au nanorod array, which is due to the Schottky junction between Au and TiO_2 . Furthermore, a new light absorption peak that ranged from 400 to 800 nm was obtained for the TiO_2/Au nanorod array. This is attributed to the localized surface plasmon resonance (LSPR) of the Au nanorod array, which is pro-

Fig. 4. UV-Vis DRS spectra of TiO_2 , the TiO_2/Au film, and the TiO_2/Au nanorod array.

duced by the collective oscillations of the surface electrons [30–31]. The photocatalyst TiO_2/Au nanorod array gave the most efficient light harvesting by combining the advantages of the 1D nanostructure and the Schottky junction.

2.4 Photocatalytic performance

Dyestuffs from textile industries are usually difficult to degrade because of their high stability against chemical and bacterial attack. Semiconductor photocatalysis may induce the effective decomposition or even mineralization of dye pollutants because of strong oxidative species such as holes and hydroxyl radicals, which are generated during the photocatalytic process [32–34]. RhB degradation was investigated as a model reaction to evaluate the photocatalytic activity of the prepared photocatalyst under UV light irradiation. The degradation of RhB followed pseudo-first-order kinetics as shown in Fig. 5. The corresponding kinetic constant (k) and the regression coefficient (R^2) were calculated and are given in Table 1. The direct photolysis of RhB was

Fig. 5. The kinetics of RhB degradation under UV light irradiation using direct photolysis (1), TiO_2 (2), a TiO_2/Au film (3), a TiO_2/Au nanorod array (4), and a TiO_2/Au nanorod array with a 0.6 V vs SCE constant potential (5).

Table 1 Kinetic constants (k) and regression coefficients (R^2) of RhB degradation under UV light irradiation

Process	k/h^{-1}	R^2
Direct photolysis	0.0630	0.995
TiO ₂	0.1212	0.991
TiO ₂ /Au film	0.1902	0.995
TiO ₂ /Au nanorod array	0.2436	0.997
TiO ₂ /Au nanorod array, 0.6 V vs SCE	0.3156	0.995

investigated for comparison. During the 120 min irradiation pristine TiO₂ exhibited the lowest photocatalytic activity. This result is due to the rapid recombination of photogenerated charge carriers resulting in a low quantum efficiency [35]. After Au film deposition, a 28% increase in RhB degradation was achieved because of the efficient separation of the photogenerated charge carriers by the Schottky junction between Au and TiO₂. This is similar to the photocatalytic performance of the Au/TiO₂ film prepared by Subramanian et al. [36]. Among these photocatalysts, the TiO₂/Au nanorod array gave the highest photocatalytic activity and its kinetic constant was 2.0 times higher than that of TiO₂ and 1.3 times higher than that of a TiO₂/Au film. The enhanced photocatalysis benefited from the combined effects of a high surface to volume ratio, an improved UV light response, efficient separation and the convenient migration of photogenerated charge carriers because of the 1D nanostructure and the Schottky junction between Au and TiO₂ [36–37]. Additionally, the photoelectrocatalytic activity of the TiO₂/Au nanorod array was also investigated. By applying a low potential between the anode and the cathode, the pollutant degradation efficiency using the TiO₂/Au nanorod array increased by about 29%, which is attributed to suppressed photogenerated charge carriers recombination upon driving the electrons to the counter electrode via an external circuit [11]. This shows great potential for application in the photoelectrocatalytic process.

2.5 Discussion on the photocatalytic mechanism

Generally, the photocatalytic reaction can be considered to be a generation, transfer, and consumption process of photogenerated charge carriers [38]. Any approach that could enhance each step in the process would improve the photochemical reactions. Here, the enhanced photocatalysis of the TiO₂/Au nanorod array resulted from the efficient separation and transfer of photogenerated charge carriers. The mechanism can be explained as follows. The TiO₂ that covers the Au nanorod surface is excited by UV light and induces the generation of excess electrons and holes. Because of the high work function of Au [39] the photogenerated electrons can transfer from the conduction band of TiO₂ to the Au nanorods until an equilibrium is reached, which

hinders charge recombination. The well-aligned Au nanorod array, which is vertical to the substrate, benefits the vectorial transfer of the photogenerated charge carriers. This efficient separation and convenient migration gives the photogenerated charge carriers more opportunity to participate in follow-up photochemical reactions. The holes at the valence band may migrate to the surface and combine with the water adsorbed onto the TiO₂ surface resulting in the formation of hydroxyl radicals ($\bullet$ OH) and the electrons can react with O₂ to generate superoxide anions ($\bullet$ O₂[−]). Both these radicals are strong oxidants that can completely oxidize organic molecules to water and carbon dioxide [38]. The mechanism responsible for pollutant degradation by the TiO₂/Au nanorod array is illustrated in Scheme 2.

Scheme 2. Schematic illustration of the pollutant degradation mechanism by the TiO₂/Au nanorod array under UV light irradiation.

3 Conclusions

A highly ordered TiO₂/Au nanorod array was successfully fabricated by direct current electrodeposition and subsequent spin-coating. The introduction of the Au nanorod array significantly improved the photocatalytic activity of TiO₂, and this is attributed to the Schottky junction between Au and TiO₂ that suppressed the recombination of photogenerated charge carriers and the well-aligned 1D nanostructure that favored the vectorial transfer of photogenerated charge carriers. We believe that the configuration and fabrication method used for the photocatalyst in this work provides valuable knowledge for the development of highly efficient photocatalysts to meet the requirements of future environmental and energy technologies.

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