

FABRICATION OF TITANIUM DIOXIDE (TiO₂) NANOTUBE ARRAYS DOPED WITH PLATIN (Pt) AND THEIR PHOTOELECTROCHEMICAL CHARACTERISTICS

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Abstract. In this work, titanium dioxide nanotube arrays (TiO₂ NTAs) doped with Platin (Pt/TiO₂ NTAs) was successfully synthesized at low temperature by anodic and chemical reduction methods. The synthesized nanomaterials are characterized by X-ray energy dispersion (EDX), and scanning electron microscope (SEM). The photochemical properties of the catalyst were characterized by cyclic voltammetry method (CV), photocurrent responses (I-t) and UV-Vis diffuse reflectance spectra. Results showed that Pt/TiO₂ NTAs with 0.57 (wt.%) Pt exhibited the highest photoelectrochemical properties. Furthermore, high surface area, small particle size, and enhanced visible-light absorption, as well as improved charge transfer and separation, are believed to be important for the improvement of photocatalytic activity of the doped materials.

Keywords: nanotube array, Platin, Titanium dioxide, photoelectrode.

Classification numbers: 2.4, 2.4.1.

1. INTRODUCTION

TiO₂ has long been an important photocatalytic material, it was discovered by Fujishima and Honda (1972) through its ability to split water into oxygen and hydrogen on TiO₂ electrodes [1]. TiO₂ semiconductor photocatalyst has been one of the most promising advanced oxidation processes in the decomposition of environmental pollutants, the detoxification of water and air, etc. TiO₂ has the advantage over other semiconductors with photocatalytic activity because TiO₂ is a low cost, chemically inert, photoactive as well as self-recovery, easy to reuse [2, 3]. However, the applications of TiO₂ in the photocatalytic field have not yet brought about high efficiency due to certain limitations: (i) - TiO₂ has a large Eg (3.0 - 3.2 eV bandgap energy) corresponds to light energy of short wavelength ($\lambda \leq 400$ nm). Therefore, it can only absorb ultraviolet (UV) radiation, while UV radiation accounts for a minimal proportion (~ 5 %) in the solar radiation spectrum; (ii)-The rapid recombination of photogenerated electron-hole pairs also significantly reduces its photocatalytic efficiency [4, 5]. To improve the catalytic activity, various metal nanoparticles like Pt, Au, and Ag, etc [6 - 8] have been doped onto TiO₂ nanotubes

through deposition precipitation or ion exchange. This strategy is considered a Schottky junction formed by contact of semiconductor with metal. Precious metal particles have the property of concentrating free charges at the Schottky junction when the particles are excited by light, known as surface Plasmon resonance. In recent years, there have been many methods for improving the photocatalytic performance of TiO₂, including noble metal doping [9 - 12], surface modification [13, 14], coupling with other semiconductor compounds [15 - 17], etc. For noble metal nanoparticles (NPs), the Pt NPs decorate onto the TiO₂ NTAs exhibits convenient electrochemical performance and excellent durability. The photo-excited electrons in the TiO₂ nanotube array transfers from conduction band to Pt NPs due to the Schottky barriers formed at the interface between TiO₂ nanotube array and Pt NPs, which depresses the recombination of photogenerated electron/hole pairs and good enhances the photocatalytic performance [7, 18].

In this study, the fabrications of TiO₂ nanotube arrays doped with Pt photoelectrode (Pt/TiO₂ NTAs) by anodic and chemical reduction methods at low temperature were investigated. Their structure and photoelectrochemical properties were also studied by SEM, EDX, cyclic voltammetry (CV) method, photocurrent responses (I-t) and UV-Vis diffuse reflectance spectra.

2. MATERIALS AND METHODS

2.1. Materials

Titanium foil (99.8 % purity, 0.127 mm thick), NaF, NaHSO₄, Cd(NO₃)₂ (98 %), 3CdSO₄·8H₂O (99 %), Na₂S·9H₂O (99.9 %), Na₂SO₃ (99 %), HF, H₂PtCl₆ (99.99 %, Merk), NaBH₄ (92 %, Merk), ethanol, iso-propanol. Twice distilled water was used throughout the experiments.

2.2. Methods

Fabrication of TiO₂/Pt NTAs photoelectrodes: First, Piece of titanium (1 × 3 × 0.127 mm) were cleaned in 3 % hydro fluoridic acid (20 s) and twice distilled water, then ultrasonic cleaned for 20 min in acetone and ethanol solution. TiO₂ NTAs were fabricated by anodizing cleaned Ti foil using a two-electrode configuration with a platinum cathode in an aqueous electrolyte containing 0.1 M NaF and 0.5 M NaHSO₄ at room temperature for 2.0 h [19, 20]. The as-anodized were ultrasonic cleaned for 10 min in iso-propanol solution to remove the debris on the surface of NTAs and dried in air, then annealed at 500 °C for 3 h in air with heating and cooling rate of 2 °C min⁻¹. Pt NPs were deposited into pores and onto surface of the TiO₂ NTAs by successive ionic layer adsorption and reaction (SILAR) technique [7], in which the TiO₂ NTAs photoelectrode was immersed into a 10 g L⁻¹ H₂PtCl₆ solution for 5 min, and then moved into 0.0022 g L⁻¹ NaBH₄ solution for 5 min, achieving a uniform deposition of Pt NPs within the TiO₂ NTAs internal surface. The two-step dipping procedure is termed as one SILAR cycle and the procedure was repeated until a desired deposition of Pt NPs was achieved. The achievement photoelectrode denoted Pt (x)/TiO₂ NTAs (x: deposition cycles).

2.3. Characterization methods

The morphologies of the as-prepared materials were studied using scanning electron microscope (SEM, Model Jeol 6510LV). Energy dispersive X-ray spectrometers (EDX) fitted to the electron microscope was used for elemental analysis.

All electrochemical measurements were performed with a CHI electrochemical analyzer (CHI660B, Shanghai Chenhua Instrument Co. Ltd.), using a conventional three-electrode system including a Ag/AgCl reference electrode, a Pt sheet counter electrode, and the Pt/TiO₂ NTAs sample as the working electrode. A 500 W Xe lamp (CHF-XQ-500 W, Beijing Changtuo Co., Ltd.) was used as the light source, filtered to 100 mW cm⁻² AM1.5G as determined by a radiometer (NOVA Oriel 70260). Photoelectrochemical properties were measured in a 0.24 M Na₂S and 0.35 M Na₂SO₃ aqueous solution. The method of cyclic potential scanning (CV) was measured by the device IM6 electrochemical equipment firm Zahner Elektrik – Germany. UV–vis absorption spectra were recorded using a UV–Visible Cary 300 spectrophotometer equipped with an integrating sphere 150 mm in diameter.

3. RESULTS AND DISCUSSION

3.1. Morphology of Pt/TiO₂ photoelectrode

Figure 1 shows the SEM images of Pt/TiO₂ NTAs with different Pt deposition cycles.

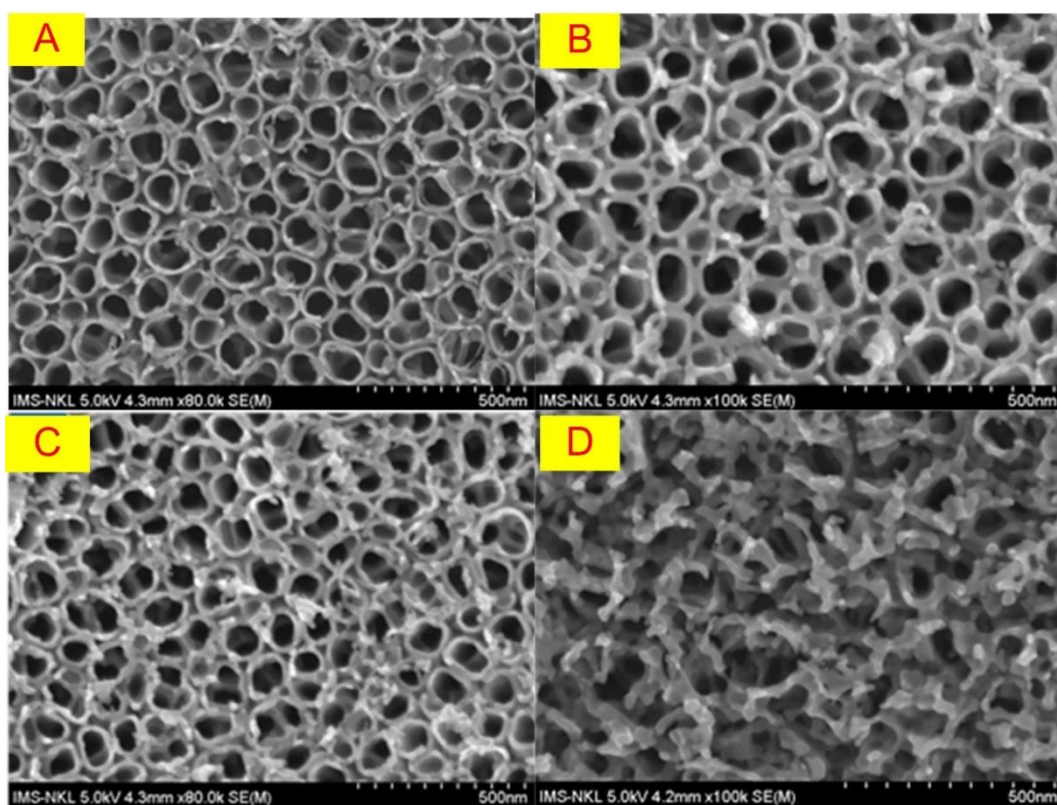


Figure 1. SEM images of the Pt/TiO₂ NTAs: (A) 1, (B) 3, (C) 5, (D) 7 Pt deposition cycles, respectively.

TiO₂ NTAs was fabricated by anodizing Ti foil have an average size of about 90 - 110 nm diameter and a length of about 400 nm and wall thickness of about 15 nm [7, 20]. The Pt NPs have an average size of around 25 nm are deposited successfully onto the surface of the TiO₂ NTAs as shown in the SEM top view of the photoelectrodes (Figs. 1(A-D)). The loaded Pt NPs

onto the TiO₂NTAs surface increased with increasing the cycle deposition (Figs 1. A-D). While with too much loading, the Pt NPs block the nanotube array pores (Fig. 1D). The deposition of the sensitizers significantly increased the surface area, benefitting the photoelectrochemical properties due to the enhanced adsorption of targets.

3.2. Photoelectrochemical properties of the as-prepared materials

Figure 2 shows the cyclic voltammetry (CV) curves of the TiO₂ NTAs and Pt(5)/TiO₂ NTAs under light and black conditions. Figure 2A shows a comparative cyclic voltammetry (CV) study of the TiO₂ NTAs light on and TiO₂ light off at a scan rate of 10 mV/s. It clearly reflects the significant increase in the area under the CV curve that was achieved for the active TiO₂ NTAs electrode material under fixed light intensity. Photocurrent density increased with an increase in the applied potential under fixed light intensity. Notably, the Pt NPs link with the TiO₂ NTAs can act as electron sinks, store and shuttle photo-generated electrons, thereby it can facilitate the charge carrier separation and reduce the charge carrier recombination rate [21]. Compared with the TiO₂ electrodes, Pt/TiO₂ NTAs electrodes (Fig. 2B) show larger voltammetric currents; therefore, supporting superior charge storage property. The difference in potential of anodic (E_A) and cathodic peaks (E_C) is a measure of reversibility and internal resistance of the material [22]. The smaller value of ($E_C - E_A$) of Pt/TiO₂NTAs electrode indicates that the electrode material is highly reversible; the origin of which is described as lower internal resistance due to improved electrical conductivity upon Pt NPs doping. This could be attributed the increased carrier mobility and thus higher electron diffusion coefficient.

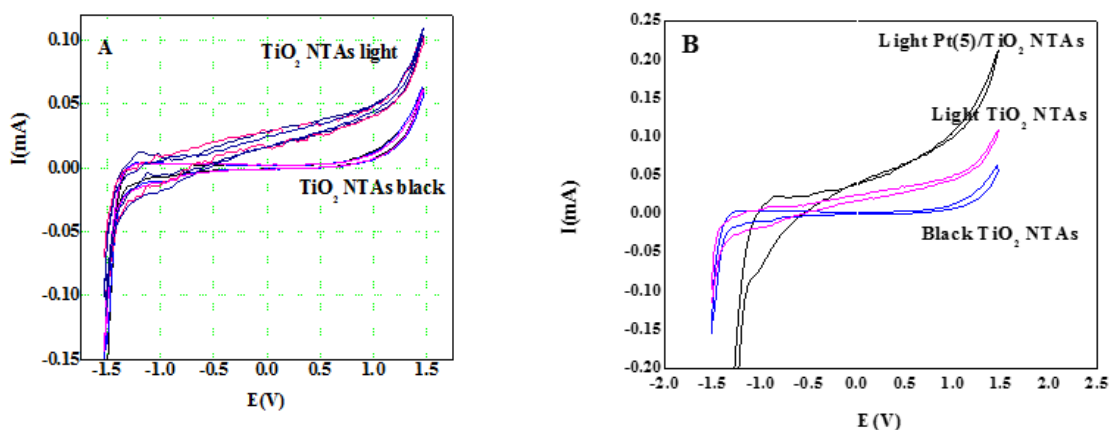


Figure 2. (A, B). CV curves of (a) TiO₂ and (b) TiO₂NTAs and Pt (5)/TiO₂NTAs at a 3 cycles in purified 0.24 M Na₂S and in 0.35 M Na₂SO₃ electrolyte, scan rate of 10 mV/s.

Figure 3 shows the photocurrent response diagram of TiO₂ and TiO₂/Pt NTAs with different Pt content under AM1.5G illumination. The photocurrent density of the modified TiO₂ NTAs photoelectrodes is higher than the unmodified TiO₂ NTAs. This result implies that the formation of the Schottky barrier at the interface of Pt and TiO₂ suppresses the recombination of photogenerated charge carriers [7, 23]. The photocurrent density increased with the deposition cycles as shown in Fig. 3(b–e). The highest photocurrent was achieved with the 5 cycles deposition, i.e. the Pt(5)/TiO₂ NTAs (curve d) on which as high as 0.538 mA·cm⁻² is obtained. Compared with pure TiO₂ NTAs, Pt/TiO₂ NTAs with 5 deposition cycles of Pt (Pt(5)/TiO₂) are higher photocurrent response of about 3 times. It recognized that there is an optimum number of

cycles deposition: low Pt NPs loading results in minimal sensitization, while the deposition of too many Pt NPs block the nanotube array pores which in turn decreases overall photoactivity.

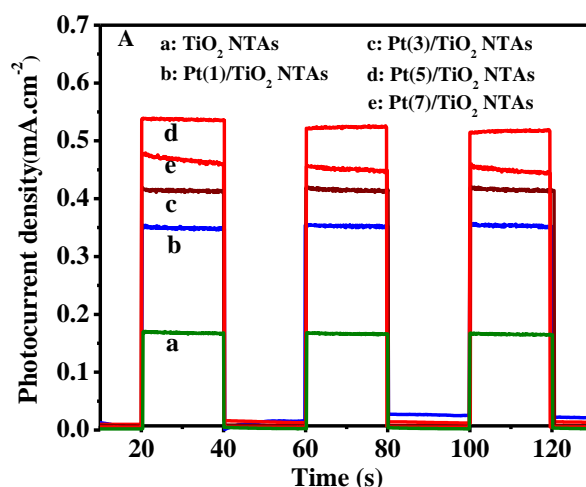


Figure 3. Photocurrent response diagram of: (a) TiO₂ NTAs annealed at 500 °C, (b) Pt(1)/TiO₂ NTAs, (c) Pt(3)/TiO₂ NTAs, (d) Pt(5)/TiO₂ NTAs, and (e) Pt(7)/TiO₂ NTAs photoelectrodes.

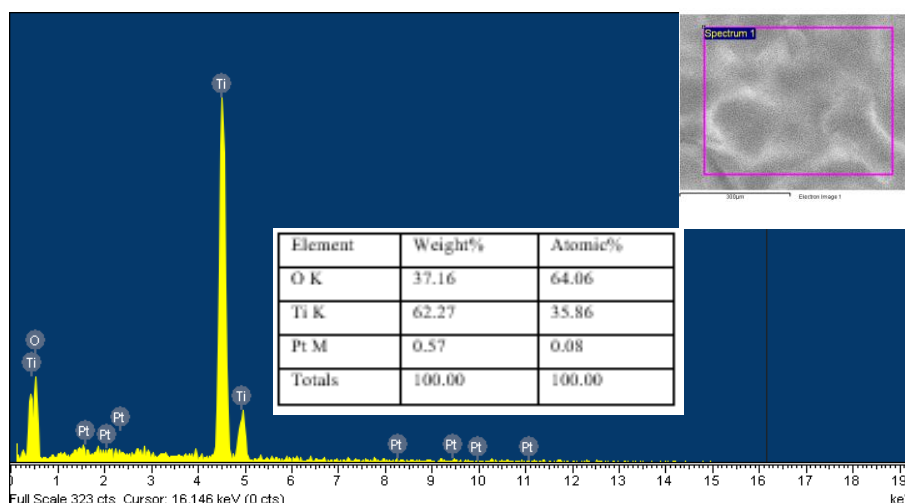


Figure 4. EDX spectrum of Pt(5)/TiO₂ NTA.

The EDX analysis shown in Fig. 4 reveals that the Pt(5)/TiO₂ NTAs are composed of Ti, O, Pt, with Pt content of 0.57 wt.%. Figure 5 shows the UV-Vis diffuse reflectance spectra of a pure TiO₂ NTAs sample (curve a) and Pt(5)/TiO₂ NTA sample (curve b). As can be seen, the absorption band for pure TiO₂ is observed in the UV region (at ~ 400 nm), whereas it was shifted to the visible region for Pt/TiO₂ NTAs due to the contribution of the Pt NPs localized surface Plasmon resonance (LSPR) absorption at 416 nm. The deposition of Pt NPs (curve b) has extended and enhanced the absorption spectrum into the visible light region, with a red shift of the absorption peaks from 571 nm for TiO₂ NTAs to 704 nm for Pt(5)/TiO₂ NTAs.

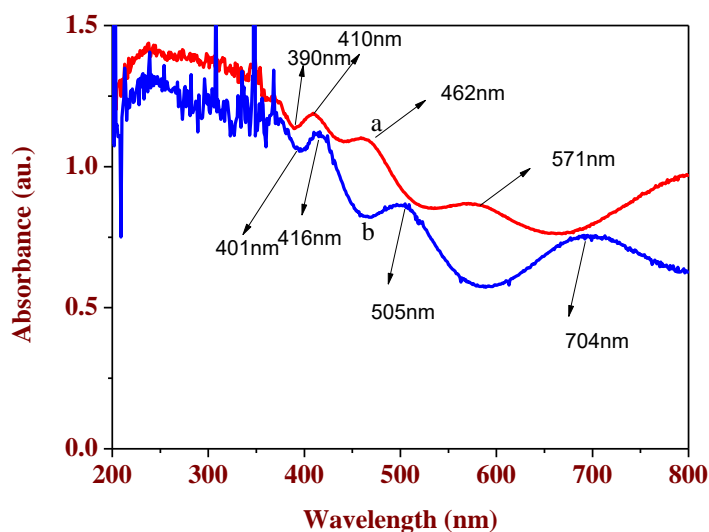


Figure 5. UV-Vis absorption spectra of (a) TiO₂ NTAs, and (b) Pt(5)/TiO₂ NTAs.

4. CONCLUSIONS

A Pt/TiO₂ nanotube array photoelectrode was successfully prepared and characterized. The TiO₂ nanotube arrays were achieved by anodization of Ti foil. After that Pt NPs with an average size of approximately 25 nm were deposited onto the TiO₂ nanotube arrays using the SILAR technique. With five cycles deposition of Pt onto TiO₂ NTAs surface, the highest obtained photoelectric current density is 0.538 mA.cm⁻². The UV-Vis measurement results of the material showed that the light absorption spectrum was widened and shifted to the visible region. As expected, the material promises good results in photoelectric sensing applications, decomposition of organic pollutants and other photocatalytic applications, etc.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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