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Photoelectrochemical properties of N doped black TiO_2 nanotube arrays

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ABSTRACT

TiO_2 nanotube arrays (TNT) were grown by anodization on Ti foils in ethylene glycol electrolyte. After electrochemical reduction and calcination under nitrogen process, Ti^{3+} and interstitial N in the lattice were found by XPS and Raman test. The co-doped black TNT sample yielded a high photocurrent density of 2.54 mA·cm^{-2} without bias voltage, while pure TNT has photocurrent density of 0.38 mA·cm^{-2}, it is much higher than ever reported black TiO_2. The electron transport resistances decreased from 594.8 ohm·cm^{-2} to 274.3 ohm·cm^{-2} and the carrier density increased from 1.35×10^{22} cm^{-3} to 6.68×10^{22} cm^{-3} after N, Ti^{3+} co-doped. Valence-band XPS spectra and Mott-Schottky plot indicated that presence of interstitial N, Ti^{3+} state in the lattices can reduce the energy gap from 3.2 eV to about 2.0 eV. In addition, TNT cathodic polarization in 0.1 M NaH_2PO_4 has better photoelectrochemical properties than that in 0.5 M Na_2SO_4 solution.

1. Introduction

TiO_2 material has been extensively studied as a novel material in various applications including dye-sensitized solar cells, photocatalysis and sensors [1–5]. Recently, black TiO_2 was impressively reported to boost solar light harvesting for enhanced photocatalytic performances [6]. TiO_2 achieves wide solar spectrum absorption after reduction by molten Al or hydrogen plasma [7]. This change of electronic state in TiO_2 accompanied by electrochromism is well explained by the proton intercalation ($Ti^{4+} + e^- + H^+ \rightarrow Ti^{3+}H^+$) possibly leading to the Ti^{3+} sites [8]. The reduction annealing condition creates oxygen vacancy sites that can yield donor states below the conduction band [7,9], which results in improved light absorption and charge transport behavior similar to a kind of n-type semiconductor [10].

In this paper, one dimensional TiO_2 nanotube arrays (TNT) was fabricated by anodization method, followed by electrochemical reduction and doped N by annealing method to extend light absorption range. The electrochemical reduction process was used to form self-doped black TNT. The TNT exhibits enhanced charge collection and transport properties, and improved the photoelectrochemical properties.

2. Experiments and methods

One dimensional TNT (1 cm^2) was fabricated by anodization method, which was thermally pretreated at 200 °C for 1 h under atmospheric conditions leading to red TNT formation. Pretreatment at 200 °C is a necessary step to achieve high performance of photocurrent (Supporting information, Figs. S10 and S13). A conventional three-electrode system was made by employing the TNT, Pt mesh and Ag/AgCl as cathode, anode and reference electrode, respectively. Initially, the TNT was subjected to an electrolysis running at cathodic potentials of −0.4 V (vs. RHE) for 60 s in 0.1 M NaH_2PO_4 aqueous solution. Its color turned from red to black, which is due to the presence of interstitial Ti^{3+} state in the lattices [21]. After deionized water cleaning, the sample was calcined at 450 °C under nitrogen or argon conditions for 1 h, labelled as P-TNT-N_2 in Fig. 1. The diameter and length of the self-organized pure TNT prepared by anodizing method is about 80 nm and 400 nm, respectively (Fig. S2).

3. Results and discussion

3.1. Photoelectrochemical properties of TNT

3.1.1. XPS, linear sweep voltammetry and I-t curve

The XPS was employed on reduced TNT to identify chemical composition and oxidation state. Fig. 2a shows the Ti 2p XPS spectra of pure TNT sample, in which two broad peaks centered at about 458.5 eV and 464.3 eV corresponding to the characteristic

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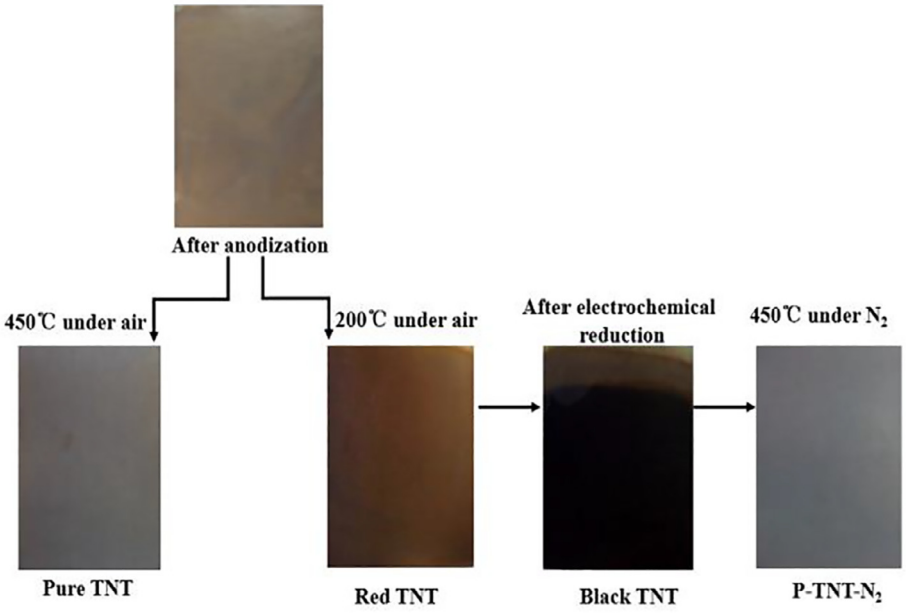

Fig. 1. TNT samples colour change during reduction and calcination.

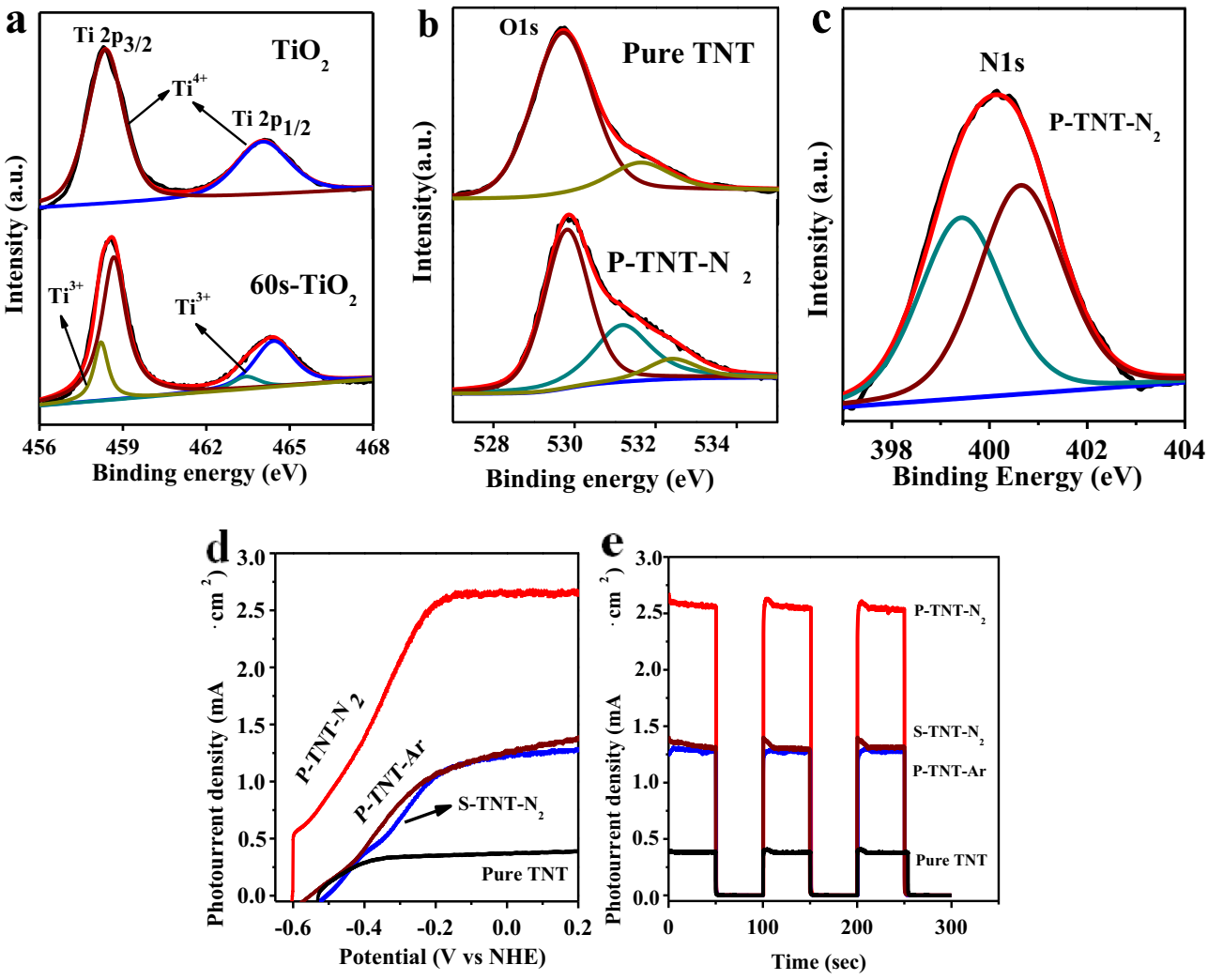

Fig. 2. XPS spectra of TNT for (a) Ti 2p, (b) O 1s, (c) N 1s. Linear sweep voltammograms (d) and I-t curves (e) of TNT.