ENHANCED PHOTOCATALYTIC PROPERTIES OF AG-LOADED N-DOPED TiO₂ NANOTUBE ARRAYS

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Abstract:

Highly ordered TiO₂ nanotube (TiO₂ NT) arrays were prepared by anodic oxidizing method on the surface of the Ti substrate. Nitrogen-doped TiO₂ nanotube (N-TiO₂ NT) arrays were carried out by ammonia solution immersion, and Ag nanoparticles loaded N-doped TiO₂ nanotube (Ag/N-TiO₂ NT) arrays were obtained by successive ionic layer adsorption and reaction (SILAR) technique. The samples were characterized by the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), photoluminescence (PL) emission spectra, ultraviolet–visible (UV–vis) diffuse reflectance spectroscopy (DRS). The result indicated that the diameter and wall thickness of the TiO₂ NT are 100–120 and 20–30 nm, respectively. Moreover, the morphology and structure of the highly ordered TiO₂ NTs were not affected by N-doping. Furthermore, Ag nanoparticles were evenly deposited on the surface of TiO₂ NTs in the form of elemental silver. Finally, the photocatalytic activity of Ag/N-TiO₂ NTs was evaluated by degradation of methyl orange (MO) under visible-light irradiation. The Ag/N-TiO₂ NTs exhibited enhanced photocatalytic properties, which could reach 95% after 90-min irradiation.

Keywords:

N-doped TiO₂ NTs; Ag nanoparticle; visible light; photocatalysis

1. Introduction

Titanium dioxide (TiO₂) as a semiconductor has extensive application in the field of photocatalytic degradation of organic pollutants from dyeing and finishing because of its low cost, pollution-free, low toxicity, outstanding chemical stability, and unique photochemical properties [1-3]. TiO₂ nanotubes (TiO₂ NTs) have attracted considerable attention in recent years because of their highly ordered structure, large surface area, strong pollutant adsorption, high photocatalytic activity, and convenient recycling when compared with conventional TiO₂ powder [4-6].

However, the wide band gap of TiO₂ is approximately 3.2 eV, leading to its photocatalytic activity only under UV light irradiation (about 5% of the solar light) and low catalytic efficiency in the visible light (about 42% of the solar light) [7]. In addition, the surface of TiO₂ is lack of effective electron capture agent, and the photogenerated electron and hole are easy to compound in a short time, which leads to lower quantum efficiency and greatly limits its practical application [8, 9]. Various doping or modification attempts have been tried to improve its response to visible light, reduce photogenerated electron–hole pair recombination time, and improve the photocatalytic efficiency [10, 11].

Among the non-metal-doped TiO₂ photocatalysts, nitrogen-doped TiO₂ is becoming more feasible and attractive to enhance the photocatalytic activity of TiO₂ in the visible light

region because of its comparable atomic size with oxygen and metastable center [12]. Besides, nitrogen-doping can narrow the band gap and shift the absorption edge of TiO₂ to the visible region [13]. However, it is difficult to obtain TiO₂ photocatalysts with high concentration of N dopants. Moreover, photogenerated carriers may try to recombine during the photocatalytic process for this N monodoping. Some researches showed that further modification of N-doped TiO₂ with transition or noble metal (e.g., Pt, Au, and Ag) could improve the stability of the desired defects, reduce the recombination of an electron and hole, and improve the charge transfer efficiency [14, 15].

To our knowledge, there are few studies on the facile preparation of Ag-loaded N-doped TiO₂ nanotube (Ag/N-TiO₂ NT) arrays and their photocatalytic activity [16-18]. In this study, anodic oxidizing method, ammonia solution immersion, and successive ionic layer adsorption and reaction (SILAR) method were used to prepare Ag/N-TiO₂ NT arrays. The morphologies, structures, and the photocatalytic properties of as-prepared materials were studied.

2. Experimental

2.1 Synthesis of N-doped TiO₂ nanotube arrays

TiO₂ NTs were prepared by anodization of Ti foils (99.8% purity) at 50 V for 3 h in ethylene glycol solution containing 0.5 wt.% NH₄F and 3 vol.% H₂O. After anodic oxidation, the as-prepared

samples were immersed in 1M $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution for 12 h and annealed under ambient atmosphere at 450 °C for 1 h to obtain the TiO_2 NTs [14].

2.2 Preparation of Ag/N- TiO_2 NTs

Ag nanoparticles were deposited on the N- TiO_2 NTs by using SILAR process [16]. The N- TiO_2 NTs were dipped into a 0.1 M AgNO_3 solution for 5 min and then dipped for another 5 min into a 0.1 M NaBH_4 solution. This SILAR process was repeated for three cycles, which were denoted as Ag/N- TiO_2 NTs.

2.3 Characterizations

The morphologies of the samples were observed by field-emission scanning electron microscopy (FESEM, JOEL, JSM-6700F) and transmission electron microscopy (TEM, Philips, and CM120). The crystal structure of samples was characterized by X-ray diffraction (XRD) technique (MAC Science Co. Ltd. MXP 18 AHF, $\text{CuK}\alpha$). The surface chemical composition of samples was analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantum 2000). The photoluminescence (PL) emission spectra of the samples were measured at room temperature by Fluoromax-4 spectrofluorometer (USA).

2.4 Photocatalytic activity test

The photocatalytic activity of the as-prepared samples was evaluated by photocatalytic decomposition of 30 mL of methyl orange (MO, 10mg/L) aqueous solution under 250W xenon lamp. The cut-off filters were used for obtaining visible light ($\lambda > 400$ nm). The change in the concentration of MO was monitored by determining the UV–visible adsorption every 15 min at 464 nm.

3. Results and Discussion

Figure 1a–d shows the typical scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images of both the as-prepared samples. From Figure 1a and 1b, it can be seen that the samples had a clear vertical tubular structure with diameter of 110–130 nm, wall thickness of 15 nm, and length of 17 μm . From Figure 1b, the ordered TiO_2 NT arrays structure was well preserved after N-doping. Figure 1c shows that the Ag nanoparticles have been successfully deposited on the surface of TiO_2 NTs with diameter of 10–60 nm. Because the defects or active sites are not evenly distributed on the nanotubes, there will be preferential deposition and growth of Ag on the surface of the nanotubes. Two different lattices with d spaces of 0.189 and 0.235 nm can be found from HRTEM images shown in Figure 1d, corresponding to the (200) plane of TiO_2 and the (111) plane of Ag, respectively [19].

Figure 2. XRD patterns of (a) TiO_2 NTs, (b) N- TiO_2 NTs, and (c) Ag/N- TiO_2 NTs.

Figure 1. SEM and HRTEM image of (a) TiO_2 NTs, (b) N- TiO_2 NTs, (c & d) Ag/N- TiO_2 NTs.

The XRD patterns of TiO₂ NTs, N-TiO₂NTs, and Ag/N-TiO₂ NTs are shown in Figure 2. The diffraction peaks in the 40.5° and 53.2° are the characteristic peaks of the Ti substrate, corresponding to the (101) and (102) crystal faces of Ti substrate, respectively. The peaks with 2θ of 25.5°, 37.1°, 37.8°, 48.2°, 54.1°, 55.2°, 62.9°, 68.8°, and 70.6° are assigned to the crystal structure of anatase TiO₂ (JCPDS, card no: 21-1272), corresponding to planes (101), (004), (112), (200), (105), (211), (204), (116), and (220), respectively. The direction peaks at 38.3°, 44.3°, and 64.7° are in good agreement with the standard spectrum of elemental silver (JCPDS, card no: 04-0783), which can be indexed to Ag (111), (200), and (220), respectively. The average particle size was calculated by applying the Scherrer equation to the (101) diffraction plane of TiO₂: $d = 0.89 \lambda / (\beta \cos \theta)$, where d is the crystal size, k is the constant (0.89), λ is the X-ray wavelength (1.54Å), β is the full width at half maximum (FWHM) of the Ag peaks, and θ is the diffraction angle. The calculated crystallite sizes of TiO₂ NTs, N-TiO₂ NTs, and Ag/N-TiO₂ NTs are 31.22, 27.92, and 28.06 nm, respectively. It reveals that N-doping inhibits the growth of the titania crystallite during thermal process, while the effect of Ag loading on the crystallite sizes of TiO₂ is not obvious.

The chemical composition and chemical states of Ag/N-TiO₂ NTs were examined by XPS, as shown in Figure 3a–e. Figure 3b shows the full-scale XPS survey spectrum of the hybrid samples, which indicates the existence of C, Ti, O, Ag, and N. The presence of C1s is mainly due to the pollution caused during the sample preparation process and by the XPS instrument itself [20]. Figure 3b demonstrates the N1s XPS spectrum of the Ag/N-TiO₂ NTs. The N1s XPS peak with a core level binding energy of 399.8 eV can be assigned to the interstitial nitrogen atoms in crystal lattice of TiO₂ as O–Ti–N structural feature instead of molecularly chemisorbed N species on the surface of TiO₂ NTs [21, 22]. It reveals that N dopants may be

stable because of the tendency of electron transfer from the oxygen vacancies to the partially occupied and lower energy N 2p states [23]. As shown in Figure 3c, binding energies of 458.2 and 464.4 eV are ascribed to the peaks of Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. They are assigned to the lattice of titanium in TiO₂ corresponding to a 2p3 binding energy of Ti (IV) ion. The deconvolution of O1s XPS spectrum in Figure 3d gives two peaks centered at 531.1 and 530.0 eV. In addition to the substitutional N, it further confirms the formation of the O–Ti–N structure. Figure 3e shows the XPS spectrum of Ag3d regions. The two peaks located at 373.6 and 367.7 eV are originated from Ag3d_{5/2} and Ag3d_{3/2}, respectively. The splitting of the 3d doublet is 6.0 eV, which indicates that the Ag loading on the TiO₂ surface mainly exists as the Ag⁰ state [24]. Moreover, the Ag loading could further stabilize the N dopants in the oxide because of the electron transfer from the Ag 5s orbitals to the 2p orbitals of the implanted N [25].

Figure 4. Photoluminescence emission spectra of the samples

Figure 3. XPS survey spectra of (a) Ag/N-TiO₂ NTs and XPS high-resolution spectra of (b) N1s, (c) Ti2p, (d) O1s, and (e) Ag3d.

The fluorescence emission spectra of TiO_2 NTs, N- TiO_2 NTs, and Ag/N- TiO_2 NTs excited by 300-nm laser are shown in Figure 4. Each sample showed a strong and broad emission signal within the scope of 350–550 nm, and two excitation peaks at 400 and 470 nm were clearly exhibited, which may be caused by the free exciton luminescence of band edge and the bound exciton luminescence originating from oxygen vacancies and defects on the surface of nanocrystalline [26, 27]. Compared with TiO_2 NTs, the peak intensity of N- TiO_2 NTs was reduced to a certain extent. This is due to the impurity energy level introduced to the top of TiO_2 valence band, and the separation of photogenerated electrons and holes from vacancies can be effectively promoted. The peak intensity of Ag/N- TiO_2 NTs decreased significantly compared with N- TiO_2 NTs, which indicates that the separation efficiency of photogenerated carriers was further improved because of the synergetic effect of Ag and N. It is showed that the fluorescence intensity is positively correlated with the recombination rate of electron–hole pairs, and Ag/N- TiO_2 NTs has the highest photocatalytic efficiency, which can be proved from photocatalytic degradation test of MO solution.

Figure 5. UV-vis absorption spectra of the samples

Figure 5 shows the UV-vis absorption spectra of TiO_2 NTs, N- TiO_2 NTs, and Ag/N- TiO_2 NTs. It can be observed from Figure 5 that the strong absorption below 400 nm for the TiO_2 NTs is due to the intrinsic interband transition absorption of TiO_2 . The absorption of TiO_2 NTs in the visible region can be attributed to the scattering of light caused by pores or cracks in the nanotube arrays [28]. Compared with TiO_2 NTs, N- TiO_2 NTs show stronger visible-light absorbance and a slight red-shift owing to the stable oxygen vacancies on the surface and interaction between N 2p and O 2p orbit [29]. Moreover, the optical absorption edge of the Ag/N- TiO_2 NTs also extends to the visible region with an obvious visible-light absorption peak at 425 nm indicating Ag nanoparticles, which could be ascribed to the synergistic effect of Ag, N, and TiO_2 [30].

Figure 6a shows the photocatalytic activity of photocatalysts under visible light. The result showed that the degradation rate from high to low in sequence was Ag/N- TiO_2 NTs, N- TiO_2 NTs, and TiO_2 NTs. It is obvious that the Ag/N- TiO_2 NTs has the best photocatalytic ability. TiO_2 NTs had almost no photocatalytic activity of visible light, which can only be activated under UV light. The degradation rates after 90 min were increased to 66% and 95%, respectively. The increasing photocatalytic activity indicates that N-doping may enhance the separation and transferring efficient of the photogenerated carriers [31]. Ag nanoparticles were applied to act as electron reservoirs to suppress the electron–hole recombination, and more holes were available for the oxidation reactions. The enhanced photocatalytic properties for the Ag/N- TiO_2 NTs in visible region were attributed to the localized surface plasmon resonance effect and synergistic effect between Ag nanoparticles and N- TiO_2 NTs. Thus, the Ag/N- TiO_2 NTs demonstrated the highest photocatalytic activity toward the degradation of MO, which was consistent with the fluorescence quenching effect revealed by PL spectra in Figure 4.

Figure 6b demonstrates the kinetic behaviors of the MO photodegradation by these photocatalysts. The degradation reactions for the samples are in accord with the first-order

Figure 6. (a) The degradation rate of MO against irradiation time under visible light; (b) plots of $-\ln(C/C_0)$ versus irradiation time for MO representing the fit using a pseudo-first-order reaction rate.

kinetic equation ($\ln(C/C_0) = -kt$), where the slope k , C , and C_0 are the photocatalytic reaction constant, the actual concentration of the MO, and initial concentration of the MO, respectively. In comparison, the apparent rate constant for Ag/N-TiO₂ NTs (0.02397 min⁻¹) is much greater than the N-TiO₂ NTs and TiO₂ NTs (0.01072 and 0.00037 min⁻¹, respectively), which means the higher.

4. Conclusions

In summary, the N-TiO₂ NTs have been successfully fabricated directly by anodic oxidation of Ti foils, followed by ambient heat treatment of the TiO₂ NTs pre-soaked in ammonia solution. Then, Ag nanoparticles were successfully introduced into the N-TiO₂ NTs by the ionic layer adsorption and reaction route. TiO₂ NTs are in good tubular structure after N-doping, and nitrogen atoms were successfully incorporated into the interstitial sites of the TiO₂ crystal lattice, while Ag mainly existed in the form of zero valence and makes the N dopants stable during the photocatalytic process. The photocatalytic degradation rate of Ag/N-TiO₂ NTs was increased by 95% compared with that of unmodified TiO₂. It is considered that the Ag and N co-doped TiO₂ NTs significantly exhibited a synergistic effect on the improvement of the photocatalytic capability in degrading MO dye under visible light irradiation.

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