One-Step Preparation of N-Doped Nanowhisker TiO_2 by Micro Arc Oxidation *

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Flowers, trees and coral like TiO_2 films are first produced by the micro-arc-oxidation method in electrolyte of phosphate. Nanowhiskers with high surface area grow at the tail ends of the coralloid film when the positive current density is set to be 17.14 A/dm^2. With acetamide in electrolyte, N element is doped. The analysis results indicate that the ratio of anatase phase to rutile phases is about 2 : 1 in the micro-arc-oxidation produced N-TiO_2 film. The optical absorption edge red shifts in the presence of N doping.

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Since 1972, titania (TiO_2) has been viewed as one of the effective materials for photocatalytic degradation and dye-sensitized solar cells.[1] In order to improve its light absorption efficiency ability, efforts have been taken for the fabrication of TiO_2 nanostructures.[2,3] To increase its surface area, micro-hollow-ball, porous microstructure and nanofibres were prepared to increase the number of surface reactive sites.[4–8] In the process of degradation, it is difficult to separate and recover TiO_2 nanoparticles, which are easily aggregated in the reactive solution. Therefore, great attention has been paid to how to immobilize TiO_2, which is feasible for practical applications. However, TiO_2 films supply a finite interface between photocatalyst and solution.

At the same time, applications of TiO_2 have also been limited by its band gap energy, around 3.2 eV, which only allows the absorption within the ultraviolet (UV) light spectrum. Since UV light makes up of less than 5% of the whole solar spectrum that reaches the Earth's surface, applications of these processes have been retarded.[9] Impurity doping was proved to be effective for narrowing the band gap, which enlarges the absorption width to visible light spectrum. Many researchers focused on nonmetal ions, such as N, C, F and Si doping, among which N-doped TiO_2 (N-TiO_2) was studied mostly for its diversion of the absorption edge to the visible-light region.[10–13]

There are several ways to prepare N-doped TiO_2 films, such as plasma enhanced chemical vapor deposition (PECVD),[14] hydrothermal method,[15] sol-gel,[16] etc. However, how to enlarge the limited effective surface area of TiO_2 films is still a difficult problem. Micro-arc-oxidation (MAO), which was developed from anodic oxidation, is a new oxidation method for the growth of oxide on the surface of valuable metals such as aluminum, titanium, magnesium and zirconium.[17] Because of the *in situ* growth process, the MAO produced film, with uniformly porous geometry, has a high adhension with substrates.

In this work, the phosphate-electrolyte containing amine salt is used to prepare N-doped TiO_2 films via the MAO method. The surface topography, microstructure, and optical absorption properties are investigated.

The analytically pure sodium phosphate (Na_3PO_4), sodium hydroxide (NaOH) and acetamide (CH_3CONH_2) were used for the preparation of anodizing electrolyte. The industrially pure titanium (98%) sheet was selected as anode. There are 10 g Na_3PO_4, 1 g NaOH and 4 g acetamide that were dissolved with distilled water in a beaker, which was finally filled to 1 L with distilled water. The rectangular Ti sample with dimensions 15 mm × 10 mm × 1 mm was polished with waterproof abrasive papers (#1500) and ultrasonically cleaned in alcohol, acetone and distilled water in sequence before the MAO processing.

Table 1. Detailed parameters for MAO process.

Frequency	Duty cycle (%)		Current density (A/dm^2)		Voltage (V)		Treatment time
	Positive	Negative					
500 Hz	30%	5%	+17.14	−1.7 ∼ −4.2	+250 ∼ 400	−100	60 min

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The MAO power source is working at a bipolar pulse mode, and the solution in a beaker was put in cooling water (10–20°C during the whole discharge process. The micro spark was ignited when the positive voltage was increased to 250 V. In this experiment, the positive current density was stabilized while the anodic voltage was risen slowly with the processing time. Negative voltage and negative duty cycle were −100 V and 5%, respectively, during the process. The detailed parameters are listed in Table 1. The MAO produced N-TiO_2 film was rinsed, dried and enclosed in a drying chamber after the process.

The microstructures of the MAO produced N-TiO_2 film were characterized by using an x-ray diffractometer (XRD/XD-III) with Cu ($K\alpha$, $\lambda = 1.54$ Å) and a transmission electron microscope (TEM, JEM-2010). The bonding situation was analyzed by x-ray photoelectron spectroscopy (XPS/ESCALAB5). The surface topography was investigated by using a scanning electron microscope (SEM/HITACH S-4200). The optical absorption properties were investigated by using a UV-vis spectrophotometer (Lambda 950).

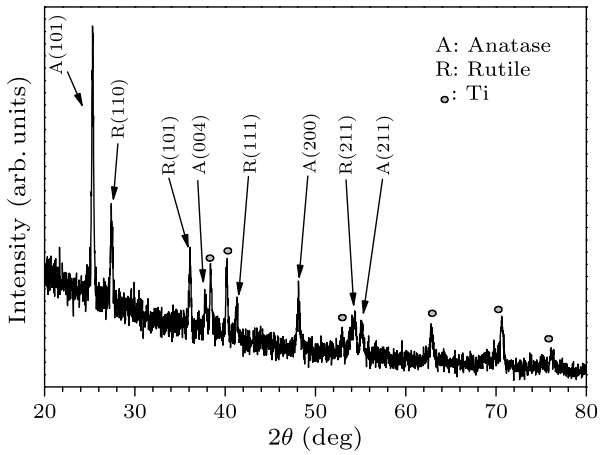

Fig. 1. XRD pattern of the MAO prepared N-TiO_2 sample (Ti peaks are substrated).

Figure 1 shows the XRD pattern of the MAO prepared N-TiO_2 sample (2θ from 20° to 80°). It can be seen that the film exhibits orientations of anatase phase (101), (004), (200), (211) peaks (2θ = 25.3°, 37.74°, 48.12°, 55.2°, respectively) and rutile phase (110), (101), (111), (211) peaks (2θ = 27.4°, 36.1°, 41.32°, 54.36°, respectively), among which the anatase (101) peak has the strongest intensity. The other peaks marked with circles are denoted as Ti substrate (PDF number of JCPDS database: 44-1294) of the substrate. It can be deduced from Fig. 1 that there are more anatase than ritule phases in the MAO processed N-TiO_2 film. It can also be estimated from the equation[18]

$$W_A = 1/(1 + 1.265 I_R/I_A), \quad (1)$$

where W_A is the weight percentage of anatase phase in the film, I_R is the intensity of rutile (110) peak (2θ = 27.4°) and I_A is the intensity of anatase (101) peak (2θ = 25.4°), respectively. From the formula and Fig. 1, it can be calculated that the weight percentage of anatase is 68%, which means that the content ratio of anatase phase to rutile phase is about 2.1 : 1. From Fig. 1, the peaks of rutile and anatase are most evident, although there are some peaks of Ti substrate. Thus it is reasonable to neglect brookite and amorphous phases which change to rutile phase at a high temperature easily.

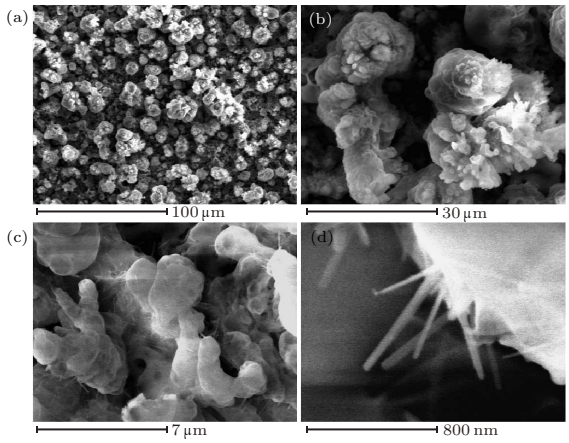

Fig. 2. SEM top-view images of the titania film with nanowishkers on the coralloid surface: (a) ×300, (b) ×1000, (c) ×5000, (d) ×40000.

Top-view SEM images of the MAO produced TiO_2 film on the Ti substrate at different ratio scales are shown in Fig. 2. Low-magnification SEM image (see Fig. 2(a)) shows that the film is composed of numerous, loose and random arranged grains whose size varies from several to tens of micrometer. Flowers and trees like coralloid grains are shown in Fig. 2(b), in which small holes can be found at the roots of the coralline. Diameters of tail ends of the trees like coralline grains, whose height is within 10–30 μm, are about 0.5–5 μm, as shown in Fig. 2(c). Moreover, nanowhiskers with hundreds of nanometer in length and one hundred nanometers in diameter are noticed in Fig. 2(d). Then, a novel porous surface topography of the MAO produced N-TiO_2 film, which certainly has large specific surfacce area, is obviously depicted. It is known that MAO processed surface always grows with densely packed grains and various holes. In our experiment, the anodic current density was 17.14 A/dm^2, which is larger than those of other conditions (1–10 A/dm^2).[17] TiO_2 grains can be quickly synthesized from molten titanium. There was no enough time for TiO_2 grains to reform a regular and compact arrangement before they were solidified by the super-cooled electrolyte. Many holes, which

were produced by discharge channels, can be seen at the roots of the coralloid TiO_2 film. The hollow coralloid column in Fig. 2(b) was concreted by the huge temperature difference between the internal and external as the molten titanium ejected.

As we know, the irregular topography is easily formed in MAO process due to fact that the growth rate of TiO_2 grains can be decreased by duty ratio, negative current, and temperature of electrolyte, but MAO processed nanowhiskers have not been reported before. A typical TEM image of the MAO produced TiO_2 nanowhiskers is shown in Fig. 3(a), which presents clear nanorods (segments of nanowhiskers, broken by ultrasonic) well separated on the grid, with uniform lengths of about 400 nm, diameters of about 100 nm. Figure 3(b) gives a high-resolution TEM image. It shows that the nanowhiskers are polycrystalline, which can also be attributed to the drastically reaction and the huge temperature difference.

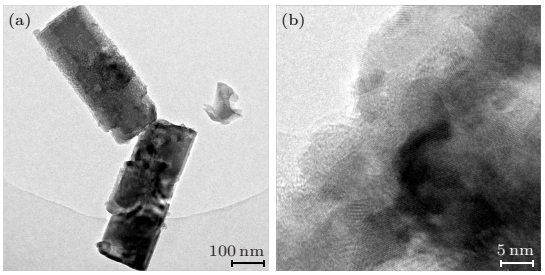

Fig. 3. High-resolution TEM images of nanowhiskers in (a) low magnification and (b) high resolution.

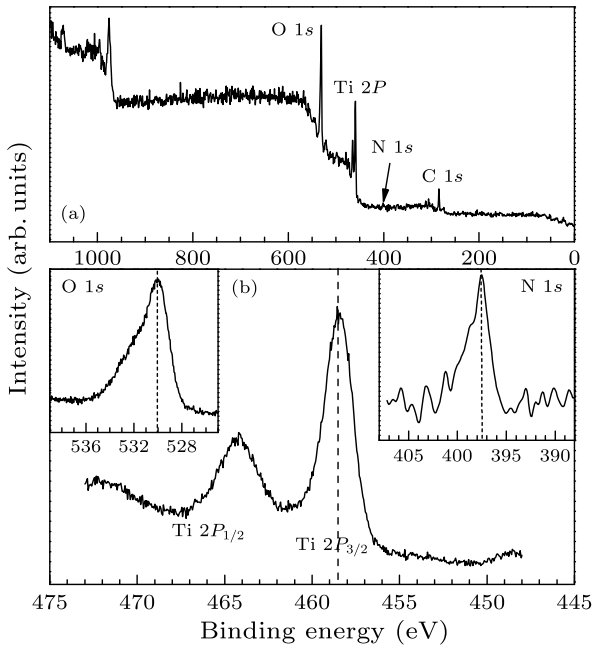

Fig. 4. XPS spectra of the MAO processed sample surface: (a) wide scan (1100–0 eV), (b) detailed scan for Ti 2*p*, O 1*s* and N 1*s*.

Figure 4 presents the XPS spectra for the MAO processed sample surface. Peaks of O, C and Ti can be found in the 0–1100 eV scanning energy spectrum (see Fig. 4(a)). Although the signal of N element is very weak, we do find the XPS peak of N (Fig. 4(b)) in detailed scanning around 397 eV. Figure 4(b) shows cores of Ti 2*p*, O 1*s* and N 1*s*. The binding energies of Ti $2p_{3/2}$ and O 1*s* in the TiO_2 film are 458.5 and 530.1 eV, respectively, which agrees well with the values reported in the standard references. The peak of N 1*s* is at 397.5 eV, which corresponds to the combination valence bond. The bonded N in the TiO_2 film may be helpful for visible light absorption. Asahi *et al.* reported the photocatalytic ability (visible light) with samples that have a larger peak at 396.7 eV.[19]

The UV-vis diffusion reflectance spectra (DRS) of the MAO processed sample and AEROXIDE TiO_2 P25 by Evonik Degussa Corporation (Degussa P-25, P25) were measured (see Fig. 5). It is found that the absorption edge for the MAO processed TiO_2 film in the DRS spectrum red shifts to the red-side about 31 nm (380 nm for P25-TiO_2 and 411 nm for N-TiO_2). The absorption edge is due to the band gap transition.[20] The band gap E_g can be calculated by the[21]

$$E_g = \frac{hc}{\lambda} = \frac{1239.8}{\lambda}, \tag{2}$$

where E_g is the band gap (eV) of the specimen; λ is the cut-off wavelength of the spectrum (nm); h is Plank's constant; c is the velocity of light in vacuum. In this work, λ is chosen as the wavelength corresponding to the intersection point of the reverse extended lines of vertical and horizontal parts in the spectra (dashed line). The optical band gaps were estimated to be about 3.0 eV for the N-TiO_2 film and 3.26 eV for P25-TiO_2 from the absorption edge around 411 nm and 380 nm, respectively. It could be a promising visible light photocatalyst, because N-TiO_2 absorbs a larger amount of visible light than P25-TiO_2.

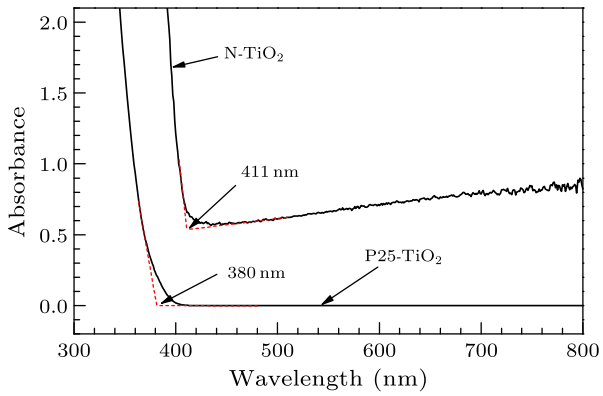

Fig. 5. The UV-vis diffuse reflectance spectra (DRS) of the MAO processed sample and the P25 TiO_2 (Degussa P-25) powder.

In conclusion, a novel porous N-TiO_2 film with

nanowhiskers was prepared by a simple method, and the surface characteristics of the N-TiO_2 film were measured. Flowers, trees and coral like TiO_2 films were formed because of the huge temperature difference between the internal and external of micro arc discharge channels. Nanowhiskers with high surface area grew in the super-cooled electrolyte as molten titanium flashed out. The UV-vis diffusion reflectance spectra show a red shift of absorption edge owing to the N doping.

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