Fabrication and photo-catalytic properties of pure and cation doped TiO$_2$ nanotube arrays*

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The highly ordered and vertically oriented pure TiO$_2$ nanotube arrays (TONTAs) are synthesized by anodic oxidation of titanium foils in fluoride-based electrolytes under different temperatures and voltages. Then TONTAs are treated at different temperatures. X-ray diffraction (XRD) patterns show that its structure is anatase at 500 ℃ with the temperature increasing to 700 ℃, the most of anatase will transform to rutile, the nanotube arrays form granular titanium oxide, while at 900 ℃, anatase will transform to rutile completely. The experimental results of photocatalytic degradation of methylene blue solution show that the cobalt-manganese co-doped TONTAs have good photocatalytic degradation efficiency.

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Recently, lots of research efforts dedicated to TiO$_2$ have been made since the discovery of the phenomenon of photocatalytic splitting of water on TiO$_2$ electrode under ultraviolet light[1]. TiO$_2$ nanotube arrays have been found to possess outstanding charge transport and carrier lifetime properties enabling a variety of advanced applications, including sensors, dye sensitized solar cells, hydrogen generation by water photoelectrolysis, photocatalytic reduction of CO$_2$ under outdoor sunlight, and super-capacitors. Furthermore, the nanotube arrays have demonstrated great utility in biomedical related applications, including biosensors, molecular filtration, drug delivery, and tissue engineering[2-9]. The doping of metal cations on a semiconductor surface can change the photocatalytic process by modifying the semiconductor surface properties. The metal cations can enhance the yield of a particular product or the rate of photocatalytic reaction. Mn^{3+} and Co^{2+} are often applied to modify TiO$_2$, because they can act as electron trapper to slow the rate of electron-hole recombination.

This study is focused on the fabrication, modification (doping of Mn^{3+} and Co^{2+}), and thermal treatment of highly ordered and vertically oriented TONTAs and their photocatalytic properties. In order to analyze the degradation ability of methylene blue solution by TONTAs, the definition of degradability is given.

Ethylene glycol, ammonium fluoride, ammonium tungstate, hydrogen peroxide, methylthionine chloride, cobalt acetate, manganese acetate and titanium foil are obtained from the Tianjin Chemical Co., Ltd. and used without

further purification. The experimental water is redistilled water.

The titanium foils (0.03 mm thickness, 99.9% purity) were polished and chemically cleaned in volume ratio (1:1) of HF and H$_2$O$_2$ following sonication in acetone before anodization. The pure TONTAs were fabricated by using the electrochemical anodic oxidation titanium foils and graphite as counter electrode in 100 mL fluoride-based electrolytes solution, including ethylene glycol (98 mL), distilled water (2 mL), ammonium tungstate (0.05 g) and ammonium fluoride (0.05 g), using a high-voltage potentiostat (Maynuo DC Source Meter, M8812) for 24 h. The prepared sample was taken out, cleaned with distilled water many times, and dried. The pure TONTAs were heat treated in the vacuum tube furnace (Hefei Kejing Materials Technology Co., Ltd., OTF-1200X-4-RTP) at heating rate of 5 °C/min from room temperature to 500 °C, 700 °C and 900 °C for 5 h, and then taken out after natural cooling to room temperature.

The pure TONTAs were differently immersed into the saturation ethylene glycol solution of cobalt acetate, manganese acetate and mixed cobalt, manganese acetate, and then TONTAs were pulled out from the solutions until they became transparent. The excess liquid on the surface of treated TONTAs was wiped using filter paper. The treated TONTAs were heat treated in the vacuum tube furnace (Hefei Kejing Materials Technology Co., Ltd., OTF-1200X-4-RTP) at heating rate of 5 °C/min from room temperature to 500 °C, 700 °C and 900 °C for 5 h, and then taken out after natural cooling to room temperature.

The size and the morphology of the prepared samples were examined by scanning electron microscopy (SEM) (HITACHI, S-4800) (Fig.1). The crystalline phases of the TONTAs were analyzed by X-ray powder diffraction (LabX XRD-6000, Shimadzu) and identified according to the JCPDS powder-diffraction files. The diffraction peaks on the X-ray diffraction (XRD) patterns were coded as follows: R-rutile, A-anatase (Fig.2).

(a)

(b)

(c)

(d)
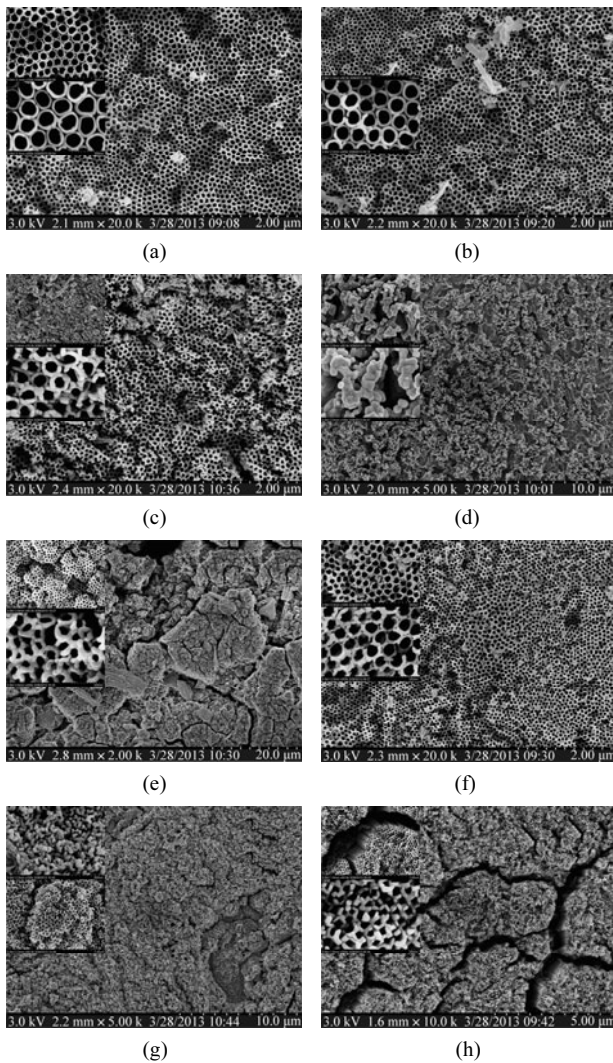

(e)

(f)

(g)

(h)

Fig.1 SEM images of TONTAs obtained form different experimental conditions (anodic oxidation voltage, temperature and heat-treatment temperature): (a) 40 V, 50 ℃, 500 ℃; (b) 40 V, 30 ℃, 500 ℃; (c) 40 V, 50 ℃, 700 ℃; (d) 30 V, 30 ℃, 900 ℃; (e) 50 V, 30 ℃, 500 ℃ Co-doped arrays; (f) 50 V, 30 ℃, 500 ℃ Co-Mn co-doped arrays; (g) 30 V, 30 ℃, 700 ℃ Mn doped arrays; (h) 30 V, 30 ℃, 700 ℃ Co-Mn co-doped arrays

100 mL methylene blue solution (10 mg/L) was placed in a beaker, and the TONTAs were immersed into the methylene blue solution under the sunlight. The UV visible spectrophotometer (Shanghai Heli Co., Ltd., UNIC-2100) was used to determine the solution absorbance changes at 664 nm every 20 min (Fig.3).
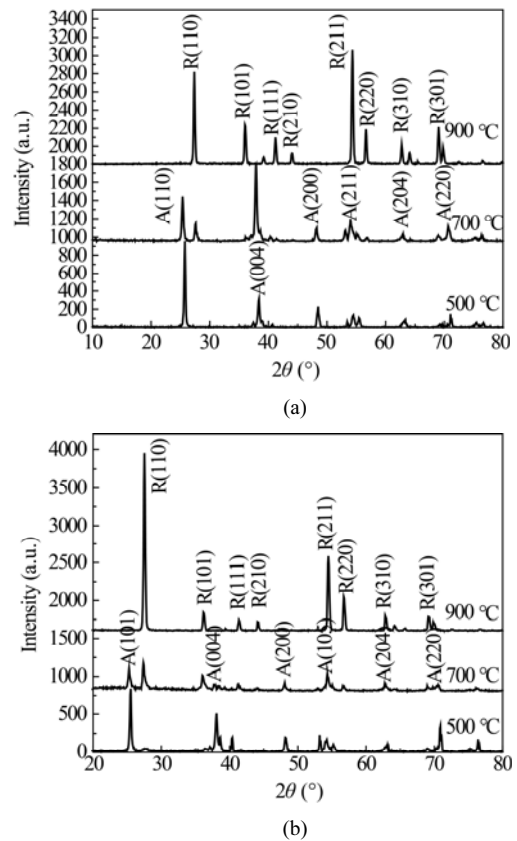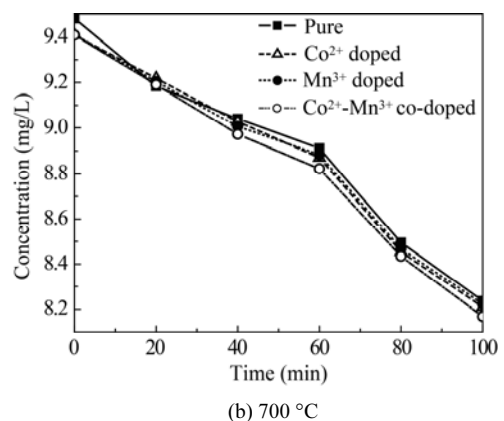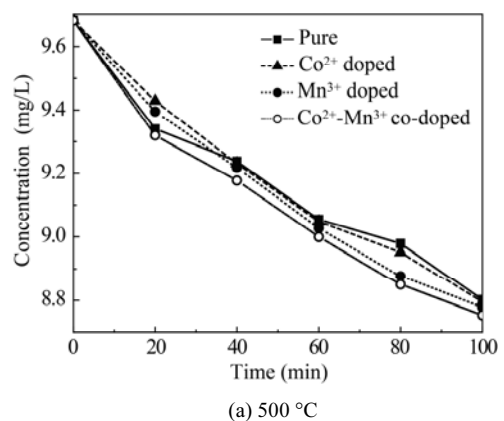

(a)

(b)

Fig.2 The typical XRD patterns: (a) the pure TiO_2 nanotube arrays heat-treated at different temperatures; (b) the Mn^{3+} doped TiO_2 nanotube arrays heat-treated at different temperatures
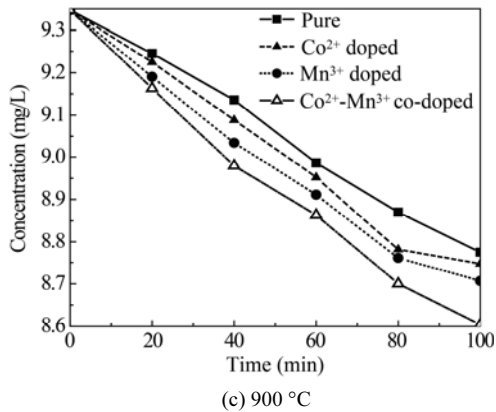

(a) 500 ℃

(b) 700 ℃

(c) 900 °C

Fig.3 Relationship between concentration and irradiation time for pure and doped TiO$_2$ nanotube arrays after heat-treatment at different temperatures

The results of SEM show that temperature has great effect on the pore size and wall thickness (Fig.1). The lower temperature results in the smaller pore size and wall thickness. The pore size of the TONTAs prepared at 50 °C is about 89−102 nm, and the wall thickness is about 23−28 nm, while the pore size of the TiO$_2$ nanotube arrays prepared at 30 °C is about 88−94 nm, and the wall thickness is about 18−20 nm. The samples were heat treated at heating rate of 5 °C /min at the temperature of 500 °C, 700 °C and 900 °C. XRD patterns show that its structure is anatase at 500 °C and 700 °C. With the temperature increasing to 900 °C, the part of anatase transforms to rutile (Fig.2). SEM results show that the nanotube arrays form granular titanium oxide (Fig.1(d)).

The cobalt-doped, manganese doped and cobalt/manganese co-doped TONTAs were successfully prepared by heat treatment. The results from the SEM indicate that there are many particles on the surface of the nanotube arrays (Fig.1(h)). The results of XRD suggest that the excessive doped cations form metal oxides.

In order to compare the abilities of photocatalytic degradation of organic pollutants for different samples, the definition of degradability (η) is given: under the condition of a certain temperature and light irradiation, the concentration of organic pollutants in aqueous solution degraded per unit time and unit photo-catalyst mass.

The experimental results of photocatalytic degradation of organic pollutants show that the degradation efficiency depends on the experimental conditions, such as the temperature of the electrolyte, the electrolytic voltage, the doped cations and the thermal treatment temperature. Under the same thermal treatment temperature, the electrolyte temperature has a significant effect on degradation efficiency. The curves in Fig.3(a) show that the photocatalytic efficiency of the samples prepared at 30 °C is better than that at 50 °C. The electrolytic voltage and thermal treatment temperature also have a significant effect on degradation efficiency. The photocatalytic efficiency of the samples prepared at 40 V is better than that at 50 V and 30 V. The degradabilities of the samples calcined at different temperatures are η_{700}=1.41205 > η_{500}=1.02209 > η_{900}=0.68952. It indicates that the degradability decreases with increasing temperature. Cations doping also has great effect on degradation efficiency. The sequence of degradability is η_{d}=1.45906 > η_{c}=1.44585 > η_{b}=1.42774 > η_{a}=1.41205, where η_{a} is the degradability of pure TONTAs, η_{b} is the degradability of Co-doped TONTAs, η_{c} is the degradability of Mn-doped TONTAs, and η_{d} is the degradability of cobalt/manganese co-doped TONTAs. The results show that the cobalt/manganese co-doped TONTAs have good photocatalytic efficacy (Fig.3(b)).

The initial process for photocatalytic decomposition is the generation of electron-hole pairs on the semiconductor surface. In aqueous solutions, holes in valence band typically form hydroxyl radicals OH$^\bullet$, while electrons in the conduction band mainly reduce dissolved molecular oxygen to super-oxide O$_2^-$ anions. These species (in particular OH$^\bullet$ radicals) possess such high oxidation power (redox potential) that they can oxidize essentially all organic molecules in the solution into carbon dioxide and water. The recombination of electrons and holes is unfavorable to the efficiency of the photocatalysts. The doping of Mn and Co cations on a semiconductor surface can change the photocatalytic process by modifying the semiconductor surface properties. The metal cations can enhance the yield of a particular product or the rate of photocatalytic reaction. The mechanism needs further study.

Generally, the highly ordered and vertically oriented pure TONTAs were synthesized by anodic oxidation of titanium foils in fluoride-based electrolytes under different experimental conditions and heat treated at different temperatures. The cobalt-doped, manganese-doped and cobalt-manganese co-doped TONTAs were also successfully fabricated by heat treatment at different temperatures.

The anodic oxidation temperature has great effect on the pore size and wall thickness. The lower anodic oxidation temperature will result in the smaller pore size and wall thickness. The results indicate that the structure of TONTAs is anatase at 500 °C. With the temperature increasing to 700 °C, the most of anatase will transform to rutile, and the nanotube arrays form granular titanium oxide, while at 900 °C, anatase transforms to rutile completely. The doped TONTAs suggest that the excessive doped cations will form metal oxides themselves. The experimental results of photocatalytic degradation of methylene blue solution show that the cobalt-manganese co-doped TONTAs have good photocatalytic degradation

efficiency. The mechanism needs further study.

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