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Silver nanoparticles supported on TiO_2 nanotubes as active catalysts for ethanol oxidation

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ABSTRACT

Silver (Ag) nanoparticles were successfully assembled in self-organized TiO_2 nanotubes by the polyol process. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy as well as Fourier transform infrared spectroscopy were used for the characterization of surface morphology, phase composition, microstructure, and valent state of the Ag—TiO_2 catalysts. It was found that these catalysts showed improved dispersion and increased catalytically active sites. The electrocatalytic properties of Ag—TiO_2 catalysts for ethanol oxidation were investigated by cyclic voltammetry. The results showed that the Ag doped anatase TiO_2 composites exhibited excellent catalytic activity in electrocatalytic ethanol oxidation in alkaline media. Hence, the composites look promising in direct ethanol fuel cell applications.

1. Introduction

With the energy shortage becoming more and more serious, people are looking for environmentally friendly transportation fuels to replace conventional fossil fuels. At present, considerable research is focused on the development of high surface area electrocatalysts, which has high catalytic activity for methanol oxidation and resistance to catalyst poisoning [1]. In the past decades, ethanol has received increased attention because it has fuel characteristics similar to those of methanol. However, from an energy storage point of view, ethanol appears to be a preferable fuel over methanol. Also, ethanol is much less toxic and expensive than methanol; thus, the threat to the environment can be dramatically attenuated [2]. For these reasons, ethanol was adopted to evaluate the catalytic activity in this study. Nanosized TiO_2, one of the most popular catalyst materials, has the advantages of physical and chemical stability, high activity, and low price. Among various TiO_2 morphologies, TiO_2 nanotubes are attractive substrates because of their large specific surface areas, thermal stability, chemical inertness, and nontoxicity [3]. In addition, noble metal catalysts also attract considerable attention due to their unique nature. Therefore, metals such as Au, Pt, Rh, and Pd deposited on the surface of TiO_2 have shown excellent performance in the activity and stability [4–7]. However, these noble metals are too expensive to use at an industrial scale. Recently, silver doped TiO_2 (Ag—TiO_2) nanocomposite structures have attracted much attention not only because TiO_2 is a promising material with desirable electronic and optical properties, but also because Ag displays some unique activities in chemical and biological sensing compared with the other noble metals mentioned above [8]. Thus, the study of Ag modified TiO_2 has significant practical value. To date, it has been shown in many reports that impregnating TiO_2 with noble metals, such as Pd, Au, or Pt could effectively improve the photocatalytic activity of TiO_2 [9,10]. However, the electrocatalytic activity of Ag doped TiO_2 nanotubes has not been subjected to intensive study. It is well known that TiO_2 has three crystal phases (anatase, rutile, and brookite). However, the influence of TiO_2 crystal phase on the electrocatalytic activity has not been reported in detail.

The photoreduction method was usually employed to synthesize Ag doped TiO_2 nanotube composites [11]. It was observed that photoreduced Ag cannot be highly dispersed on the surface of TiO_2. Hence, the amount of active sites on the Ag—TiO_2 surface cannot be increased significantly. Other methods involving sol–gel, ‘wet’ chemical and ceramic methods, where drying, heating or annealing at high temperatures are important steps in the preparation process [12–14], are too complicated for large-scale production. It is well known that the polyol process is a convenient, versatile and low-cost method for the synthesis of metal nanostructures on a large scale. Based on this technique, a number of metal nanostructures, such as gold nano-octahedra [15], gold nanoplates [16], Ag nanowires [17] and Ag nanopowder [18], have been successfully synthesized in ethylene glycol (EG) solution.

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In order to modify the TiO_2 nanotubes by Ag nanoparticles, a polyol method at low-temperature has been developed to overcome the difficulties and disadvantages mentioned above. The Ag^+ ions from silver nitrate ($AgNO_3$) can be reduced to metallic Ag, some of which can be deposited onto the nanotube surface, while the others may react with the small amount of ruitle TiO_2 to form the silver titanate. We have found no study on the preparation of simultaneously doped and deposited Ag on TiO_2 nanotubes using this method.

In order to prepare Ag—TiO_2 composite nano-material, a small amount of sodium borohydride ($NaBH_4$) was added to an EG solution of polyvinylpyrrolidone (PVP) prior to the addition of $AgNO_3$ aqueous solution. In this process, the $AgNO_3$ solution serves as the metal salt precursor, $NaBH_4$ as the reductant, and EG as both a solvent for the precursors and a reductant for the reaction. Previous studies revealed that the surfactant PVP could act not only as a stabilizer to prevent the aggregation of the products but also as a shape controller to assist the formation of anisotropic metal nanostructures. The advantage of this method is that the EG can serve not only as solvent but also as reducing reagent. The use of EG may lead to a more environment-friendly production of Ag nanoparticles deposited on TiO_2 surfaces as well as to an increase in stability of the obtained Ag—TiO_2 colloids [19]. In this study, the Ag nanoparticles were deposited successfully on different crystal phases of TiO_2. Furthermore, the electrocatalytic activity of the Ag—TiO_2 catalysts was also evaluated.

2. Experimental

2.1. Synthesis of self-organized TiO_2 nanotube arrays on Ti substrate

TiO_2 nanotubes on Ti substrates were fabricated by anodic oxidation according to a method reported in the literature [20]. Briefly, commercial pure titanium sheets (11 mm × 9 mm × 0.6 mm, Tianjin Pengbo Company, China) were used as the substrate electrode. Prior to anodic oxidation, the titanium sheets were ground with different types of emery paper (600#, 1000#, and 2000#) and then degreased in an ultrasonic bath in ethanol and deionized (DI) water followed by air drying. Samples were anodized in water/glycerol (1:1 Vol.%) mixtures containing 0.3 M NH_4F at a potential of 30 V for 3 h. Finally, the as-prepared TiO_2 nanotube electrode was annealed at 723 and 923 K under oxygen atmosphere for 1 h.

2.2. Chemical assembly of Ag nanoparticles in TiO_2 nanotubes

PVP was added to water/ EG (1:1 Vol.%) mixtures in a beaker. The mixture was stirred for about 5 min, and then, $NaBH_4$ was introduced under stirring. After 1–2 min, $AgNO_3$ was added. These operations were performed at room temperature. The solution appeared deep brown owing to the presence of Ag^+ ions. The concentrations of Ag^+ ions, $NaBH_4$ and PVP were about 0.035, 0.026, and 0.001 M, respectively. All reagents were analytical grade. The as-prepared TiO_2 nanotube sample was immersed in this electrolyte under static conditions at 40 °C for 3, 7, and 11 h, and subsequently rinsed with DI water and air dried. The surface morphology and structure of samples were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), X-ray diffraction (XRD, RIGAKU/DMAX), and transmission electron microscopy (TEM, Philips Tecnai G2 F20). Surface chemical analysis of Ag—TiO_2 coatings were performed by X-ray photoelectron spectroscopy (XPS) using a PHL1600ESCA instrument equipped with a monochromatic Mg Ka X-ray source ($E = 1253.6$ eV) source operated at 250 W. The analysis spot had a diameter of 200 μm, and the detection angle relative to the substrate surface was 45°. In such conditions, the probed depth was estimated to be around 3 nm. Peak position was internally referenced to the C1s peak at 284.5 eV. Fourier transform IR Spectra (FTIR) of Ag—TiO_2 coatings were measured by Fourier transform IR Spectrometer (WQF-510) to study the chemical interactions between PVP molecules and $AgNO_3$ as well as the composition evolution during the Ag formation processes. The obtained Ag—TiO_2 coatings were first removed from the titanium substrate and dried under vacuum in a desiccator prior to the FTIR analysis. Then, the samples were grinded into fine powder, which involves mixing thoroughly the material to be tested with KBr before forming a pellet at high pressure.

2.3. Characterization of electrocatalytic properties of Ag—TiO_2 nanotubes

The effect of ethanol on the catalytic activities of the catalysts was determined by cyclic voltammetry (CV) in acidic medium containing C_2H_5OH (0.5 M)—H_2SO_4 (0.1 M) and alkaline medium containing C_2H_5OH (0.5 M)—NaOH (0.1 M). All the electrochemical measurements were performed on an electrochemical workstation (Gamry Reference 600, Gamry, USA). The electrochemical measurements were carried out with a conventional three-electrode system. The Ag—TiO_2 nanotube electrode was used as the working electrode, a platinum electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode in all cases.

3. Results and discussion

Fig. 1 shows the SEM images of the as-formed TiO_2 nanotubes (a, b), Ag-fresh TiO_2 (c, d), Ag—TiO_2/723 K (e, f), and Ag—TiO_2/923 K (g, h) coatings in the top, bottom and cross-sectional views after 7 h deposition. The morphology of the synthesized TiO_2 nanotubes is shown in Fig. 1a and b. The nanotubes (with diameter of 120 nm and length of 1.2 μm) are vertically aligned on the Ti substrate by anodization. The bottoms of the tubes have a flute-shape structure. It is apparent from Fig. 1c the ordered and evenly distributed Ag nanoparticles with average diameter of 20 nm are formed preferentially on the exterior mouth of the amorphous TiO_2 nanotubes. After the nanotubes were annealed at 723 K, the Ag nanoparticles were deposited on them under the same method (see Fig. 1e). Some Ag nanoparticles were dispersed on the pore openings and showed a distribution less dense than that in Fig. 1c, while some were deposited into the nanotubes, as indicated by the arrows. It can be presumed that the nanotubes annealed at 723 K facilitate the Ag formation on the tube surface, leading to high electrocatalytic activity as discussed later. However, the nanotubes annealed at 923 K seem to exhibit unfavorable properties for depositing ordered Ag nanoparticles, as shown in Fig. 1g. It is obvious that some particle aggregates are located on the tube surface, while some were not formed completely. This result may be due to the incomplete reaction of $AgNO_3$, which will be further confirmed by XPS results in a later section. Meanwhile, images of the bottom and cross-section of the Ag doped samples are also shown in Fig. 1d, f and h. According to the SEM image of the bottom shown in Fig. 1d, the space between two nanotubes is filled by Ag nanoparticles. Also, the Ag nanoparticles can permeate into the flutes of tube bottoms by passing through their interstices. Apparently, the boundary between the Ag nanoparticles and the nanotubes disappear and become gradually integrated after annealing at 723 K, as shown in Fig. 1f. In addition, the cross-sectional image in Fig. 1f shows that the sidewall of the nanotubes was almost entirely covered by Ag nanoparticles. But the inset in Fig. 1d shows that Ag nanoparticles mainly adhere to the upper