Electrochemical Study of Titanium Dioxide Based Nanostructured Catalysts

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Titanium dioxide (TiO_2) nanomaterials have been widely investigated as photocatalysts due to their biological and chemical inertness, cost effectiveness, high corrosion resistance, and strong oxidizing power of the photogenerated holes [1]. TiO_2 nanotubes may be synthesized via several approaches, including through the use of nanoporous alumina templates, sol-gel processes, seeded growth methods, hydrothermal techniques, and the anodization of titanium within fluoride-based electrolytes. On the other hand, platinum-based nanomaterials with high surface areas have been receiving increased attention because of their unique properties and a number of impressive applications in catalysis, fuel cells and chemical sensors [2]. Recently, my research team has fabricated and studied a number of novel TiO_2-based and platinum-based nanomaterials [3-5]. In this presentation, we report on a facile photoassisted method for the modification of TiO_2 nanotubes with various Pt, PtAu, and PbO_2 nanoparticles and their electrocatalytic activity.

The TiO_2 nanotube arrays were grown directly on titanium plates (1.25cm x 0.8cm x 0.5mm, 99.2%, purchased from Alfa Aesar) using anodic oxidation. The Ti plates were initially sonicated in acetone, rinsed with pure water and then etched in 18% HCl at 85°C for 10 minutes. The etched titanium plate was then submerged in a one compartment two-electrode cell containing DMSO + 2% HF and was electrochemically treated via anodization at 20 V for 24 h. To ensure that the anatase crystal structure of TiO_2 was obtained, the plates were annealed in an oven at 450°C for 3h. The fabricated TiO_2 nanotubes were further modified with Pt, PtAu, and PbO_2 nanoparticles.

The as-fabricated different TiO_2-based nanostructured electrode materials were characterized by field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and electrochemical methods. A three-electrode cell system was employed for the electrochemical studies. A Pt coil with a 10 cm^2 surface area was used as the auxiliary electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The electrochemical measurements were carried out at room temperature (20±2 °C) using a Voltalab 40 Potentiostat (PGZ301).

The TiO_2-supported Pt nanoparticles exhibit interesting kinetic behaviors in the formation and reduction of Pt oxide during electrochemical cycling, spanning the potential range between −0.225 and +1.35 V. The peaks for oxide formation and reduction incrementally decrease and then completely disappear after 800 cycles, whereas the integrated charge for hydrogen adsorption and desorption reaches a constant, ~70% of the initial value. An S-shaped cyclic voltammogram was observed for methanol oxidation on the electrochemically treated TiO_2/Pt electrode. In comparison to the Pt nanoparticles, the fabricated TiO_2-supported PtAu nanoparticles with the Au composition between 30% and 50% exhibit not only a more negative onset potential, but also a much higher current density for formic acid oxidation. The results of impedance measurements of these two electrodes (PtAu33% and PtAu50%) show very small charge transfer resistances and a much higher activity for the oxidation of formic acid. In addition, the PbO_2 nanoparticles photoelectro-deposited on the TiO_2 nanotubes are effective for lignin oxidation. The electrochemical oxidation of lignin is a promising approach for the conversion of lignin into valuable products such as vanillin and vanillic acid, which enhance the potential utility of lignin that is found in the pulp and paper industrial wastewater. Our electrochemical studies have shown that the TiO_2 nanotubes are promising substrates in the development of high-performance electrocatalysts for environmental and renewable energy applications. Potential electronic interactions and synergistic effects between the TiO_2 nanotubes and the supported nanoparticles are discussed.

Acknowledgments

This work was supported by a discovery grant from the Natural Sciences and Engineering Research Council of Canada (NSERC). A. Chen acknowledges the Canada Foundation of Innovation (CFI) and NSERC for the Canada Research Chair Award in Material and Environmental Chemistry.

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