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Short communication

Preparation and characterization of TiO_2-nanotube/Ti plates loaded Cu_2O nanoparticles as a novel heterogeneous catalyst for the azide–alkyne cycloaddition

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ABSTRACT

Cu_2O-NPs/TiO_2-NTs/Ti plates were fabricated via electrodeposition of Cu_2O nanoparticles on TiO_2 nanotubes previously formed by anodizing of titanium. Microstructure studies show that nanoparticles of Cu_2O having high surface area have been deposited on the walls of as-prepared TiO_2 nanotubes. The catalytic activity of plates was tested for azide–alkyne cycloaddition. The results of catalytic experiments demonstrate that the Cu_2O-NPs/TiO_2-NTs/Ti plate exhibits significantly enhanced catalytic activity for the azide–alkyne cycloaddition.

1. Introduction

The copper(I)-catalyzed Huisgen [3 + 2] dipolar cycloaddition (CuAAC) between organic azides with alkynes has arguably become the most popular ligation reaction that has been widely applied in a variety of chemical disciplines including organic synthesis, the modification of biological macromolecules and in polymer and materials chemistry [1–10]. Because the recycling of the recovered catalyst in successive reuses allows processes interesting from an economical point of view, much attention has been paid to the development of heterogeneous copper(I) catalytic systems for CuAAC reactions [11–16].

The mesoporous properties of plate as substrate can significantly affect microstructures of Cu_2O, leading to low size and therefore high active catalyst surface which can improve the performance of Cu_2O as catalyst. Among various types of plates, TiO_2-NTs/Ti fabricated by anodizing of titanium plate can be used as a suitable substrate because of its high surface area, thermal stability, controlled pore structure, relatively low cost and especially the excellent reusability relative to other powdery TiO_2 nanomaterials [17,18]. The results of our previous works have confirmed that the TiO_2-NTs/Ti plates having high surface area can be used as appropriate substrate for deposition of various types of materials at electrocatalysts, photocatalysts and supercapacitors [19–21].

In this work, Cu_2O-NPs/TiO_2-NTs/Ti plates were fabricated via electrodeposition of Cu_2O nanoparticles onto TiO_2 nanotubes fabricated by anodizing of titanium. The properties of fabricated plates were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). The catalytic activity of Cu_2O-NPs/TiO_2-NTs/Ti plates was examined in the azide–alkyne cycloaddition and the experimental results were discussed (Scheme 1). To the best of our knowledge, this work is the first report about electrodeposition of Cu_2O nanoparticles on the TiO_2-NTs/Ti plates for catalytic applications.

2. Experimental

2.1. Preparation of the Cu_2O-NPs/TiO_2-NTs/Ti plates

Titanium dioxide nanotubes were grown on stripes of Ti plate (99% purity) with a geometric area of 9 cm^2. Very briefly, Ti stripes were polished with emery papers no 400 to 3000 to obtain a mirror finish and subsequently cleaned in acetone and deionized water in an ultrasonic bath. The cleaned samples were anodized at 40 V for 2 h in ethylene glycol containing 0.5 wt.% ammonium fluoride and 2.5 wt.% of water at room temperature in a two-electrode cell using a platinum foil as a counter electrode. The anodized samples were further washed with deionized water and ultrasonically cleaned for 60 s in deionized water to remove surface debris and subsequently dried in air. The anodized samples were annealed at 450 °C for 2 h to form the anatase phase. The growth of nanotubes by anodizing of titanium can be described as a

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selective etching, and the method can be related to a top down approach. In the simplest approach, such nanotube growth can be described in terms of a competition between several electrochemical and chemical reactions including: anodic oxide formation:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e \quad (1)$$

chemical dissolution of the titanium oxide as soluble fluoride complexes, e.g.:

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{-2} + 2H_2O \quad (2)$$

and direct complexation of Ti^{+4} ions migrating through the film:

$$Ti^{+4} + 6F^- \rightarrow [TiF_6]^{-2}. \quad (3)$$

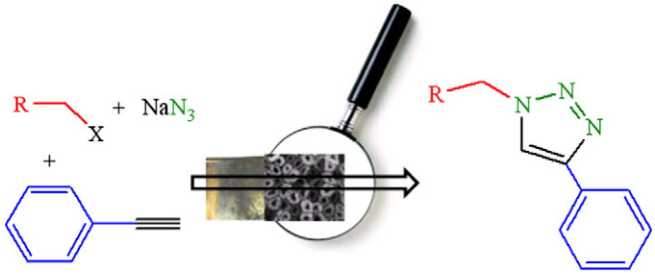
Reaction in Eq. (1) describes the oxide growth on an anodized metal surface in a fluoride-free electrolyte. Firstly, a layer of anodically formed oxide is formed. Further oxide growth is controlled by the migration of O^{-2} and Ti^{+4} ions through the growing oxide film. As the system is under a constant applied voltage, the electric field within the oxide is progressively reduced by the increasing oxide thickness; the process is self-limiting [22,23].

Electrochemical reduction of Cu_2O onto the annealed TiO_2-NTs/Ti plates was carried out potentiostatically at a constant potential of −0.4 V vs. SCE electrode for the duration of 1000 s in a three-electrode cell using TiO_2-NTs/Ti plate as a working electrode, Pt as a counter electrode and a saturated calomel (SCE) as a reference where the electrolyte was 0.4 mol·l^{-1} copper sulfate and 3 mol·l^{-1} lactic acid solution. Bath composition and electrodeposition conditions are given in Table 1. The yellow colored, homogeneous and adherent Cu_2O film were successfully obtained on the TiO_2-NTs/Ti plates and denoted as Cu_2O-NPs/TiO_2-NTs/Ti plates. After the electrodeposition, the plates were immediately removed from the electrolyte and sequentially rinsed with DI water. The obtained Cu_2O-NPs/TiO_2-NTs/Ti plates were then annealed at 200 °C for 60 min in nitrogen atmosphere. The weights of the plates were measured by a microbalance. The mass of Cu_2O-NPs deposited on a plate was about 0.05 g. Surely, error of around ±5% is expected. The electrodeposition mechanism for the formation of Cu_2O can be explained through the electrogeneration of base route [24–26]. According to the pourbaix diagram relating to Cu–H_2O, at −0.4 V vs. SCE electrode, the measured cathodic current can be sustained by the following reduction process:

$$Cu^{+2} + e^- \leftrightarrow Cu^+. \quad (4)$$

The Cu^{+1} ions present in the solution migrate to the cathode to form copper hydroxide:

$$Cu^+ + OH^- \rightarrow Cu(OH). \quad (5)$$



Scheme 1. Cycloaddition of alkyl halides with phenyl acetylene and NaN_3.

Table 1
The optimized bath composition and electroplating conditions.

Bath composition	Concentration (mol·l^{-1})	Electroplating conditions
Copper sulfate	0.4	T = 35 °C
Lactic acid	3.00	
H_2SO_4	For adjusting of pH	pH = 11
KOH	For adjusting of pH	
		Counter electrode: Pt(6 cm^2)
		Potential: −0.4 V vs. SCE
		Electrodeposition time: 1000 s

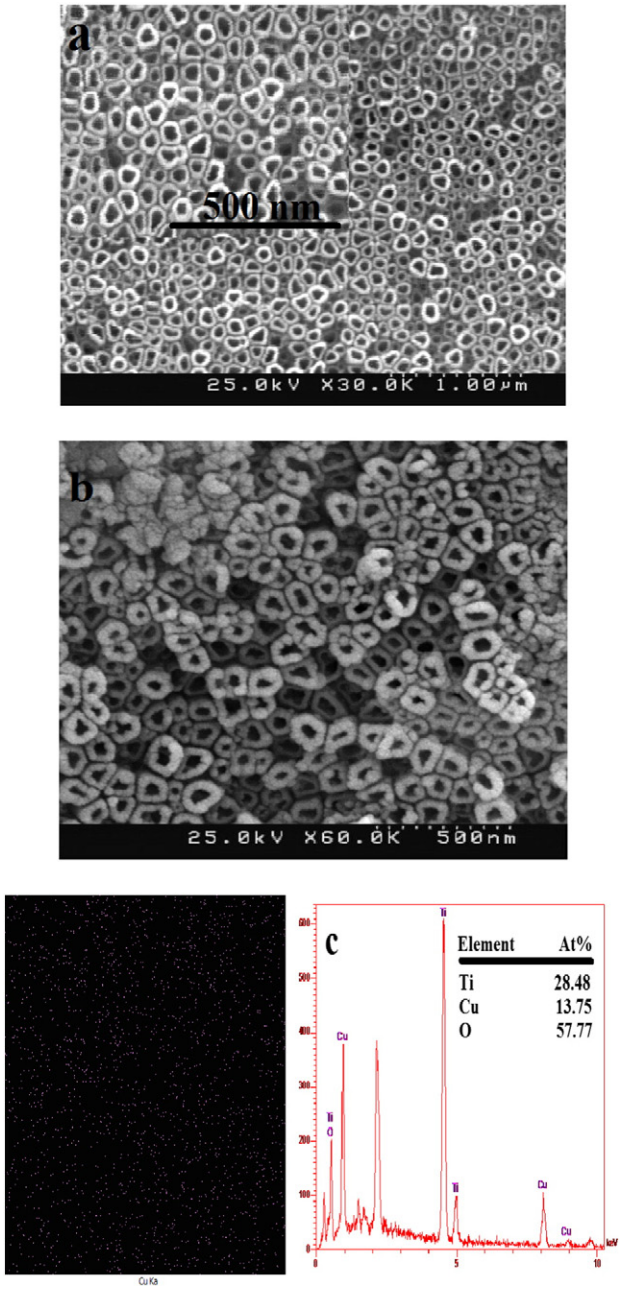


Fig. 1. SEM images of bare TiO_2-NTs/Ti plate (a), Cu_2O-NPs/TiO_2-NTs/Ti plate (b) and EDX spectra obtained of Cu_2O-NPs/TiO_2-NTs/Ti plate as well as elemental analysis maps for Cu (c).