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Synthesis, characterization, and application of CuO-modified TiO_2 electrode exemplified for ammonia electro-oxidation☆

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ABSTRACT

In this study, a copper nanoparticle-modified titanium dioxide (CuO–TiO_2) catalyst was synthesized using the coprecipitation method with $Cu(NO_3)_2$ as the active component for the electrochemical oxidation (ECO) of ammonia (NH_3). The voltammetric behavior and characterization of the electrocatalyst, including oxidation behavior, were investigated using linear sweep voltammetry (LSV), polarization, and chronoamperometric measurements, combined with SEM, FTIR, XRD, EEFM and XPS. SEM and XRD spectroscopy revealed that CuO particles were highly dispersed on the anatase phase of the TiO_2-supported surface. The XPS and FTIR analysis indicated that CuO was firmly deposited through the linkage of Cu—O—Ti bonding to the TiO_2 base and the sample exhibiting the stretching vibration mode associated with the Cu—O bonds of the CuO nanoparticle. Results of EEFM analysis indicate that significant excitation/emission plots located at 218/280 nm is associated with the CuO nanoparticle. The LSV oxidation ability could explain the catalytic activities of the CuO–TiO_2 electrocatalysts, and NH_3 oxidation peak current on the CuO–TiO_2 electrocatalyst increased as scan rates increased, indicating that the adsorption-controlled process occurred at the electrocatalyst.

1. Introduction

Ammonia (NH_3) nitrogen is a major nitrogen-containing pollutant; it is recently receiving increasing attention from researchers because it is a corrosive and carcinogenic inorganic gas, which exudes a pungent odor, and is emitted from both biogenic and anthropogenic sources under ambient conditions (Endo et al., 2004; Galloway et al., 2008; Lei et al., 2009; Zhang et al., 2010; Birch et al., 2011; Yuan et al., 2016). Moreover, it has recently been proven that NH_3 nitrogen is potentially harmful to public health and the environment. NH_3 nitrogen is emitted during numerous processes, including biomass gasification, urea manufacturing, nitrogen fertilizer production, petroleum refining, refrigeration, livestock waste and animal agriculture. Studies have suggested removing NH_3 from gaseous and waste streams and decreasing worldwide NH_3 emissions to ensure a healthy environment. Several approaches have been developed to treat NH_3 through biological, physical, and chemical processes. In particular, the application of the catalytic concept for NH_3 decomposition has been proposed as a new technology to improve and simplify the impact of nitrogen on the environment and supply clean H_2 gas rather than CH_3OH for fuel cell applications (Wojcik et al., 2003; Fournier et al., 2006; Halseid et al., 2006).

Vidal-Iglesias et al. (2007) and Yao et al. (2016) have reported that the electrocatalytic oxidation of ammonia (ECO-NH_3) is the most widely used approach for reducing NH_3 pollution. Based on the fundamental viewpoint of shortening reaction times and having molder operating conditions, this technology which features a heterogeneous catalytic process, has garnered significant attention because of the increasing effectiveness of the oxidation process using certain catalysts. Thus, further development of highly active and durable catalysts is demanded for the ECO-NH_3 process that can be selective for nitrogen or hydrogen and can prevent further oxidation of nitrogen. Regarding the ECO-NH_3 process, Pt-based alloy catalysts have been found to be the

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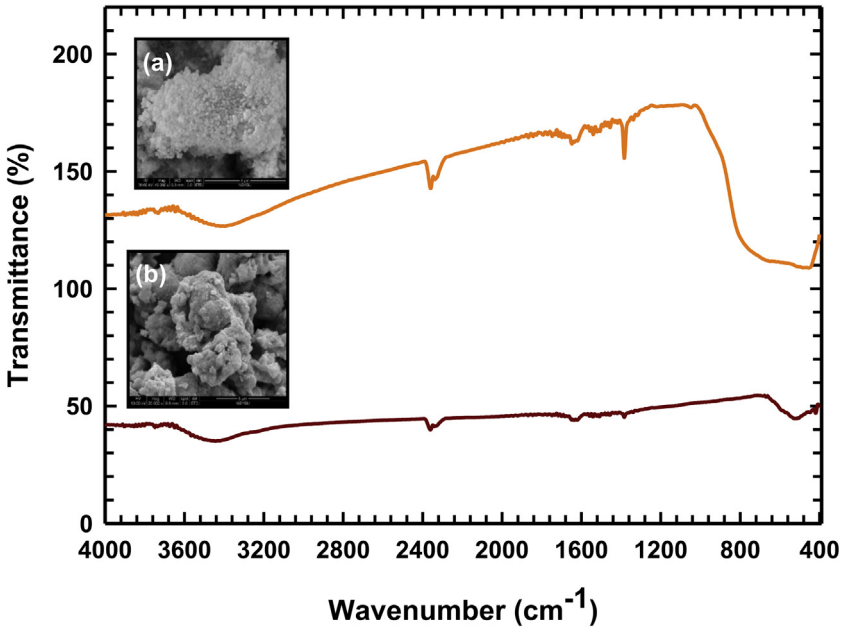

Fig. 1 – SEM and FTIR spectra of the (a) CuO and (b) CuO–TiO_2 electrocatalyst.

most promising catalysts that applied to oxidize NH_3, such as the polymer electrolyte membrane fuel cells with the NiPt catalyst for selective conversion of NH_3 to H_2 between temperatures of 793 and 963 K in the hydrogen oxidation reaction process (Chellappa et al., 2002). Vidal-Iglesias et al. (2003) demonstrated that excellent selective electrocatalysis can convert NH_3 into H_2 in the catalytic oxidation process with an alkaline medium over Pt(100) catalyst sites. Boggs and Botte (2009) developed an NH_3 electrolytic cell consisting of Ti-carbon fiber paper catalysts. Ti-based catalysts exhibit relatively high NH_3 electrochemical oxidation (ECO) activity and selectivity. Michels et al. (2010) performed differential electrochemical mass spectrometry (DEMS) and chronoamperometry of boron-doped diamond (BDD) electrodes to oxidize NH_3. The application of a numerical model of H_2 production in fuel cells in catalytic packed-bed reactor systems for NH_3 decomposition over an $NiPt/Al_2O_3$ catalyst was adopted inspected, and reported to perform efficiently (Chein et al., 2010). In the catalytic decomposition process, Zheng et al. (2008) applied CeO_2 into the Ni/Al_2O_3 catalyst at 823 K and found it to be suitable for the selective conversion of NH_3 to H_2, revealing that CeO_2 considerably improved the catalytic activity and stability of Ni/Al_2O_3 catalysts for NH_3 decomposition to CO_x-free H_2. Recently, Chaudhari and Mishra (2016) used 0.1 mol% CuO-doped TiO_2 nanocomposites for sensing NH_3 and reported that it showed the highest sensitivity to 50 ppm of NH_3 (97%) with a response time of 2 s at room temperature. Silva et al. (2016) reported that Pt/C-ITO catalysts have the highest catalytic activity for NH_3 electro-oxidation reactions; they attributed this finding to the presence of indium oxide (In_2O_3) in the ITO ($In_2O_3{\cdot}SnO_2$) support, which provides oxygenated or hydroxide species and results in the removal of atomic nitrogen (N_{ads}) poisonous intermediates and the promotion of NH_3 electro-oxidation.

Related studies have demonstrated that cupric copper (CuO) possessing highly active transition metals is a promising p-type semiconductor suitable for various applications, such as a potential substitute for noble metal-based emission control catalysts (Zhu et al., 2006; Hung, 2011; Bhuvaneshwari and Gopalakrishnan, 2016). CuO doped with titanium dioxide (TiO_2) is an efficient catalyst for various reactions, such as the catalytic reduction of NO + CO reaction (Jiang et al., 2004), CO oxidation (Huang et al., 2006), direct hydrogen production from photocatalytic (Xu and Sun, 2009) and photoelectrochemical (PEC) cells (Ganesh et al., 2014), and the degradation of methyl orange (Nourbakhsh et al., 2016). Meanwhile, copper and TiO_2 exhibit

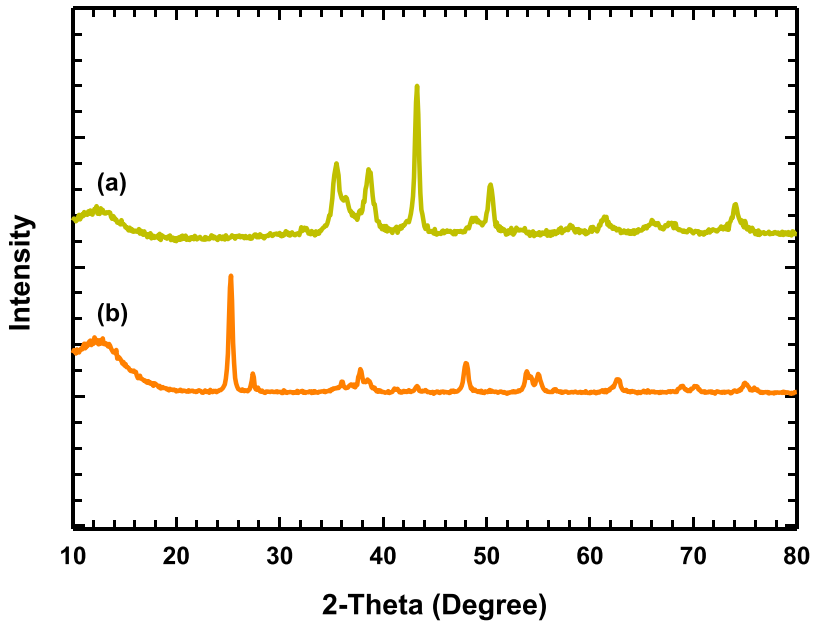

Fig. 2 – XRD spectra of the (a) CuO and (b) CuO–TiO_2 electrocatalyst.

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