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Effect of atomic-layer-deposited TiO_2 on carbon-supported Ni catalysts for electrocatalytic glycerol oxidation in alkaline media

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ABSTRACT

Thin TiO_2 layers were deposited onto a carbon-supported Ni catalyst (Ni/C) through atomic layer deposition (ALD) and the resulting TiO_2-coated Ni/C (ALD(TiO_2)-Ni/C) was utilized for electrochemical glycerol oxidation in alkaline media. X-ray photoelectron spectroscopy analysis demonstrated that the Ni surface phase of ALD (TiO_2)-Ni/C mainly consisted of $Ni(OH)_2$ while that of uncoated Ni/C was a mixed phase of NiO and $Ni(OH)_2$. The ALD(TiO_2)-Ni/C exhibited electrocatalytic activity at least 2.4 times higher than that of Ni/C. Density functional theory calculations were used to investigate how the modified Ni surface with the TiO_2 coating affects the adsorption/desorption of glycerol.

1. Introduction

Atomic Layer Deposition (ALD) has been used to effectively control the preparation of materials at the atomic scale [1–4] and can be used to synthesize new types of atomically-controlled catalytic materials. It has been shown that an ALD coating of Al_2O_3 or TiO_2 can prevent dissolution of base metal nanoparticles such as Cu or Co in aqueous phase catalytic reactions [5,6]. Previous studies have also demonstrated that coating metal oxides by ALD can improve the longevity of semiconductor photoelectrodes and increase their activity in photoelectrochemical applications [7–9]. We recently reported that an ALD TiO_2 coating can enhance the catalytic activity and stability of non-precious-metal-based catalysts for electrochemical water oxidation [10]. TiO_2 was chosen as it is a well-known material having high stability under electrochemical conditions. In addition, this ALD technique could be used to design atomically-controlled electrocatalysts with increased activity or selectivity for electrocatalytic alcohol oxidation using e.g. biomass-derived ethanol or glycerol.

Herein, we report that a thin TiO_2 coating on Ni/C by ALD strongly affects the electrocatalytic activity of Ni/C toward glycerol electrooxidation in an alkaline medium. The ALD(TiO_2)-Ni/C exhibits high activity and stability, and both are superior to the activity and stability of uncoated Ni/C. The enhanced electrocatalytic performance of ALD (TiO_2)-Ni/C can be explained by the TiO_2 coating modifying the surface oxidation state of nickel, thus affecting the adsorption/desorption of glycerol.

2. Experimental

TiO_2 layers were deposited on commercial Ni/C (20%, Premetek) by the ALD technique using a similar method to that described in our previous work [10]. High-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma-optical emission spectrometry (ICP-OES), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were used to characterize the prepared samples. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometry (CA) were carried out in a three-electrode system consisting of a Hg/HgO (MMO, 1 M KOH) and a Pt wire as the reference and counter electrodes, respectively; glassy carbon (0.07 cm^2) or carbon paper (2 cm^2) was used as the working electrode. The catalysts were blended with a Nafion solution (catalyst:Nafion = 90:10 wt %) and loaded onto the glassy carbon or carbon paper (0.65 mg cm^{-2}). The electrochemical impedance spectra (EIS) were measured under a

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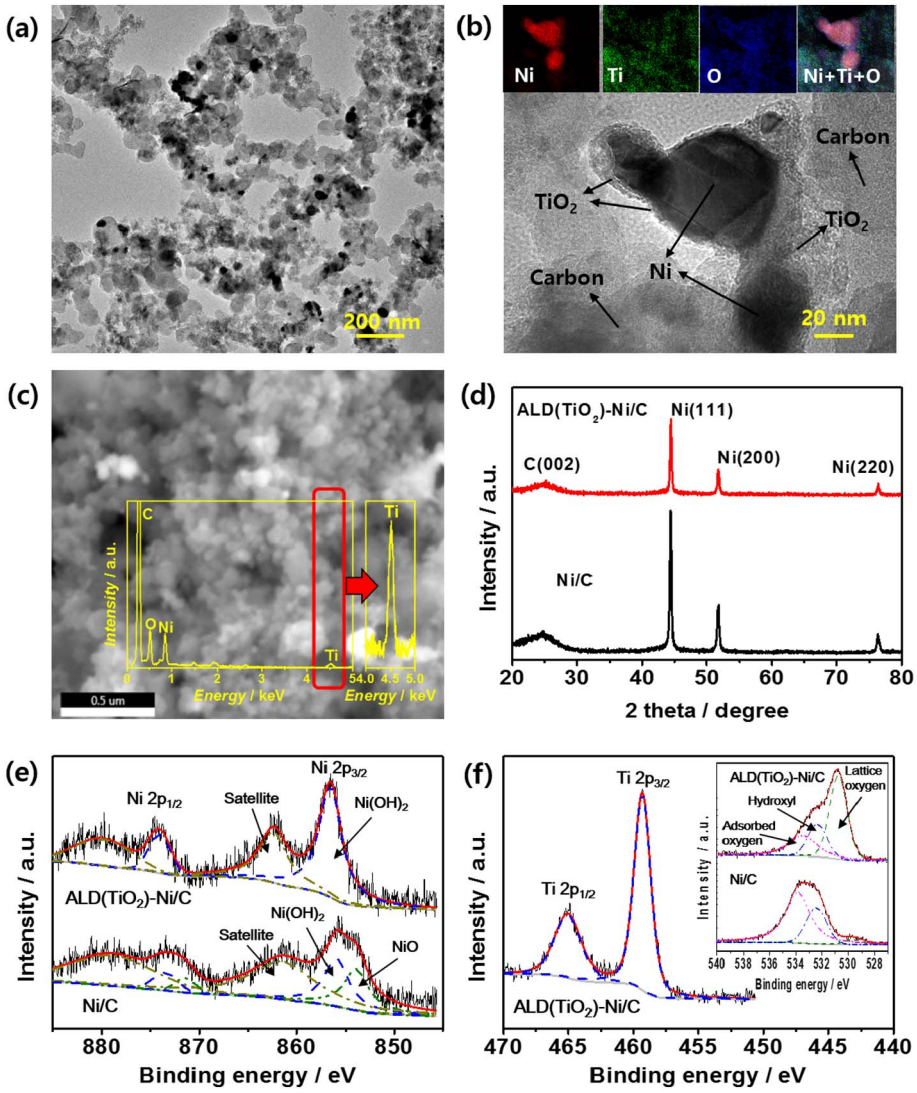

Fig. 1. (a) TEM, (b) HRTEM, and (c) SEM images of ALD (TiO_2)-Ni/C. Inset: EDS spectrum. (d) XRD patterns of Ni/C and ALD(TiO_2)-Ni/C. XPS spectra of Ni/C and ALD(TiO_2)-Ni/C in (e) the Ni 2p and (f) the Ti 2p regions. Inset: XPS spectra in the O 1 s region.

constant voltage of 0.6 V at frequencies from 100 kHZ to 0.1 Hz with an AC amplitude of 5 mV. After the electrochemical reaction with the carbon paper electrode, each phase of the reaction mixture was analyzed with a Waters 2535 high performance liquid chromatograph (HPLC) equipped with a RI detector and a UV–vis detector (220 nm). The column used was a Biorad Aminex HPX-87H sugar column. All density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP) [11,12]. Computational settings not listed here were the same as in our previous study [13]. We modeled oxidized Ni (111) surfaces by subtracting electrons without changing the lattice parameters of the optimized neutral Ni (111) surface (14.6 × 14.6 × 27.9 $Å^3$). The solvation effect was implicitly considered within the VASPsol code [14]. Atomic partial charges were estimated from a Bader analysis [15–16].

3. Results and discussion

Fig. 1a and b show TEM and HRTEM images of the prepared ALD (TiO_2)-Ni/C which has Ni particles 29 ± 8 nm in size distributed on the carbon support. The elemental maps of Ni, Ti, and O revealed that both Ti and O were evenly deposited on the surface of Ni/C (inset of Fig. 1b). The EDS spectrum from SEM also confirms the existence of Ti in the ALD(TiO_2)-Ni/C sample (Fig. 1c). The mass fraction of Ti in the sample determined by ICP-OES was approximately 7 wt% (TiO_2 thickness measured by XPS [17]: *ca.* 2.3 nm). The XRD patterns reveal that both Ni/C and ALD(TiO_2)-Ni/C (Fig. 1d) have the characteristic peaks of a crystalline face-centered-cubic (fcc) phase of Ni. The broad peaks at *ca.* 25 °C correspond to the hexagonal structures of the carbon support. For the ALD(TiO_2)-Ni/C, we could not find any diffraction peak for the crystalline TiO_2 phase, implying that the TiO_2 grown on the Ni/C surface is amorphous in this sample. The HRTEM image in Fig. 1b also shows that amorphous TiO_2 forms a thin film over the nickel particles during the ALD process. Fig. 1e shows the Ni 2p region of the XPS spectra for Ni/C and ALD(TiO_2)-Ni/C. The Ni $2p_{3/2}$ core level of Ni/C could be deconvoluted into two contributions at 854.0 eV and 856.0 eV, attributable to NiO and $Ni(OH)_2$, as well as a satellite peak at 861.7 eV [18]. In the case of ALD(TiO_2)-Ni/C, the NiO contribution is negligible and the surface layer of Ni is mainly present in the form of $Ni(OH)_2$, indicating the formation of $Ni(OH)_2$ due to the change in the nature of surface Ni after TiO_2 ALD deposition. The Ti 2p XPS spectrum of the ALD(TiO_2)-Ni/C is shown in Fig. 2f. The peak location of Ti $2p_{3/2}$ at 459.3 eV and spin orbit splitting between Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks of 5.8 eV are consistent with the reported values of electron orbitals for TiO_2 (Ti^{4+}) [19]. The O 1 s spectra (inset of Fig. 2f) can be fitted with three peaks at binding energies of *ca.* 530.8, 532.4, and 533.5 eV, which could be assigned to lattice oxygen in TiO_2, a surface hydroxyl group, and adsorbed oxygen, respectively, further confirming the formation of TiO_2 in the ALD(TiO_2)-Ni/C [18].

CV tests for the ALD(TiO_2)-Ni/C and Ni/C in 0.1 M KOH without glycerol were performed to probe the electrochemical interaction