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The nature of active sites of Ni_2P electrocatalyst for hydrogen evolution reaction

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ABSTRACT

Nano-scaled Ni_2P particles were synthesized by ligand stabilization method and applied for hydrogen evolution reaction (HER). X-ray diffraction (XRD), transmission electron microscope (TEM), and X-ray absorption fine structure (XAFS) spectroscopy were employed to examine structural properties of Ni_2P nanoparticles. The electrocatalytic HER activity and stability for the Ni_2P nanocatalyst were tested in 0.5M H_2SO_4, and the Ni_2P electrocatalyst exhibited a low onset potential for the HER at around −0.02 V vs. RHE, a little more negative compared to the Pt catalyst which shows almost 0 V vs. reversible hydrogen electrode (RHE), and the Tafel slope of 75 mV per decade, i.e. following Volmer step as a rate-determining step. Density functional theory (DFT) calculations for hydrogen adsorption over Ni_2P surfaces (001) and (002) revealed that the hydrogen adsorption might occur via two reaction pathways: consecutive or simultaneous hydrogen adsorption. The consecutive hydrogen adsorptions on threefold hollow (TFH)-Ni site followed by on P(II) site on a Ni_2P (001) surface led to a lower reaction barrier than simultaneous hydrogen adsorption. These results thus demonstrated that the Volmer step might follow consecutive adsorption mechanism over the Ni_2P surface.

1. Introduction

The growing interest in the production of hydrogen as a promising alternative to the conventional fossil fuel has spurred much research on the electrolysis of water [1,2]. The water-splitting reaction can occur via two half reactions: the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). As introduced by Bockris et al., the HER is a reductive half-reaction of the electrolysis of water, and it requires an active catalyst to lower the overpotential and finally to facilitate the hydrogen production [3]. Pt has been known as the most active catalyst for the HER under acid condition to exhibit the lowest overpotential [4].

However, the high cost and the lack of Pt reserve have limited its commercialization for the HER process. The development of cost-effective, highly active, and stable HER electrocatalysts has thus become an urgent need [5]. Transitional metal chalcogenides such as metal sulfides [6] and carbides [7] have recently drawn considerable attention as alternative electrocatalysts for the HER because of the low cost, high chemical stability, and excellent electrocatalytic properties.

Although micron-sized metal sulfides or carbides have shown poor activity in the HER [8], nano-sized MoS_2 catalysts have exhibited much enhanced activity as reported by Bonde et al. [9], Wang et al. [10], and Chung et al. [11]. Similar results were also reported for the metal carbides such as WC and Mo_2C by Chen et al. [12] and Zheng et al. [13], respectively. These metal chalcogenides are also known to be active for hydrodesulfurization (HDS), where reversible hydrogen adsorption and desorption are of great importance. In the similar manner, metal phosphides such as Ni_2P, MoP, and WP have been introduced by Oyama et al. as a new catalyst group for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) [14–19]. Among them Ni_2P catalyst has shown the best activity in the HDS [19]. Regarding the active phase of the Ni_2P catalyst, the atomic-scale images of a Ni_2P(0001) surface have been firstly observed by Moula et al. with using a scanning tunneling microscope (STM) [20]. The image showed an ordered hexagonal symmetry of the (0001) face, which was assigned to phosphorus atoms on Ni_3P_2- and Ni_3P_1-terminated surface, corresponding to Ni_2P (001) and (002) plane, respectively. More recently, Schaak et al. reported that nano-sized Ni_2P catalysts exhibited a high density of exposed (001) facets and showed a good activity in HER [21].

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In this study, we synthesized nano-sized Ni_2P for the HER and conducted density functional theory (DFT) calculations to elucidate the active sites of Ni_2P and to verify the HER mechanism over the surface of Ni_2P (001) and (002).

2. Experimental and computational methods

2.1. Synthesis of the nanostructured Ni_2P

All procedures were conducted under inert atmosphere using an Ar-filled glove box and Schlenk line. The chemicals used in the synthesis were nickel acetylacetonate($Ni(acac)_2$, Alfa Aesar, 95%), trioctylphosphine (TOP, Alfa Aesar, 90%), trioctylphosphine oxide (TOPO, Sigma Aldrich, 90%), methanol (Samchun, 98%), and acetone (Samchun, 98%). Ni-containing TOP solution was prepared by mixing $Ni(acac)_2$ (0.196 g) and TOP (5 ml) at 70 °C in the glove box with Ni:P ratio of 1:20. TOPO of 11.6 g was heated to 310 °C, and the Ni-TOP solution was rapidly combined with TOPO under vigorous stirring at 310 °C. Before the injection of Ni-TOP solution, the color was yellow, and then, the solution became dark brown within few minutes after introducing Ni-TOP solution. Finally the color changed to black. The mixing was maintained at 310 °C for 2 h and then cooled down to 60 °C. The resulting precipitation was separated by addition of 30 ml of methanol followed by centrifugation at 3000 rpm.

2.2. Characterization

X-ray diffraction (XRD) patterns of the samples were measured using a diffractometer (Rigaku DMAX-2500) operated at 60 kV and 300 mA with Cu Kα radiation ($\lambda = 0.15418$ nm). Transmission electron microscope (TEM) images were collected on a JEOL JEM-2010 electron microscope operating at 200 kV. The TEM samples were prepared by dropping the suspension of the nanoparticles dispersed in hexane onto carbon-coated copper grid and then dried in a vacuum oven

2.3. Activity in HER

The synthesized Ni_2P nanoparticles (5 mg) were mixed with Vulcan carbon black (VB, 5 mg) and Nafion resin (28.6 mg) as a binder and dissolved in 2-propanol. Then, 5 μL of the mixed solution was loaded onto a glassy carbon electrode with the area of $0.196\ cm^2$. Autolab potentiostat (PGSTAT) in a standard three-electrode cell was used for electrochemical measurements with Pt as a counter electrode and saturated calomel electrode as a reference electrode. The polarization curves of the HER were measured using a rotating disk electrode (RDE) with a scan speed of 2500 rpm at a scan rate of $5\ mV\ s^{-1}$ in a saturated hydrogen gas. All the potentials presented the reversible hydrogen electrode (RHE) calibrated to confirm the hydrogen oxidation potential. HER measurements were conducted using 0.5 M H_2SO_4 solution with 293 K. For measuring the resistance, electrochemical impedance spectroscopy was performed from 200 kHz to 50 mHz at an open-circuit voltage (OCV) of 25 mV. All HER data have been corrected for an ohmic drop (9.4 Ω) based on the impedance spectroscopy. In order to confirm the durability of the electrocatalyst, we conducted the acceleration durability test (ADT) by the cyclic voltammetry (CV) with a scan rate of $50\ mV\ s^{-1}$ between 0.1 and $-0.4\ V_{RHE}$ for 500 cycles.

2.4. Computational methods

Density functional theory (DFT) calculations were performed using $DMol^3$ module in the Material Studio package from Accelrys (version 5.5). The double-numerical plus polarization (DNP) basis set with a real space cutoff radius of 4.5 Å and PW91 exchange–correlation functional were used. Effective core potentials were used to treat the core electrons of nickel.

First, Ni_2P unit cell was calculated according to the crystallographic data [22], and geometry was optimized under three-dimensional periodic boundary conditions to further refine the structure. Fig. 1 shows the unit cell and periodic supercell models of Ni_2P used in this study. There are two types of Ni and P sites in the Ni_2P crystal, denoted as Ni(I), Ni(II), P(I), and P(II). The Ni (I)

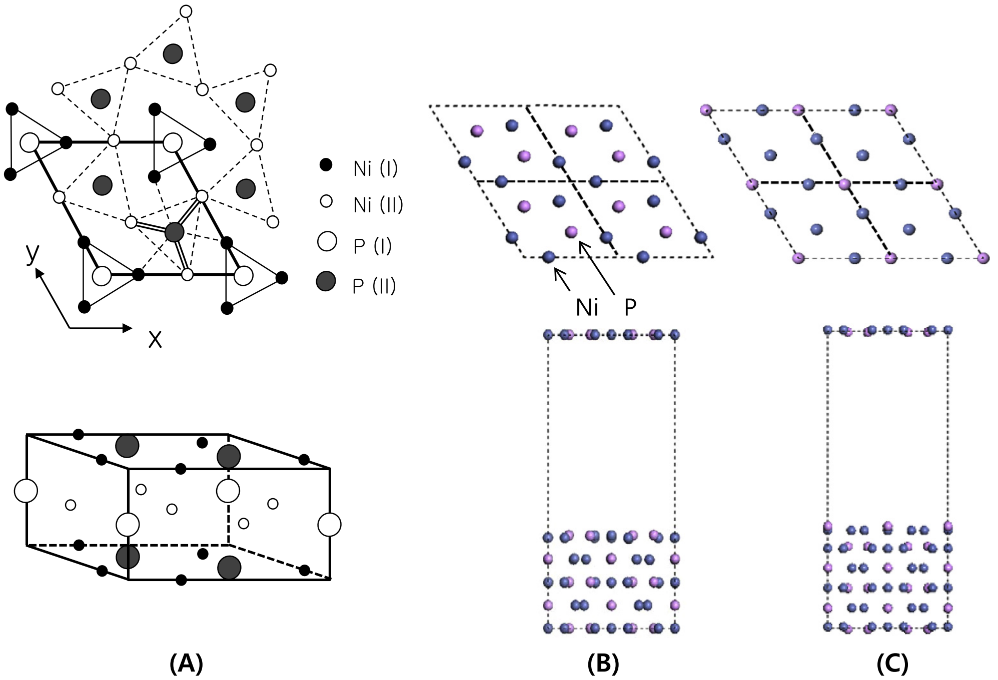

Fig. 1. (A) Unit cell of Ni_2P, (B) supercell model of Ni_2P (001) surface, and (C) supercell model of Ni_2P (002) surface.