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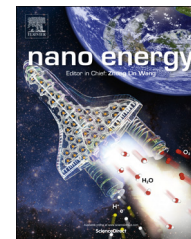
Cobalt phosphide nanorods as an efficient electrocatalyst for hydrogen evolution reaction

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Abstract
Cobalt phosphide (Co_2P) nanorods are found to exhibit efficient catalytic activity in hydrogen evolution reaction (HER), with the overpotential required for the current density of 20 mA/cm^2 as small as 167 mV in acidic solution and 171 mV in basic solution. In addition, the Co_2P nanorods can work stably in both acidic and basic solution during hydrogen production. This performance can be favorably comparable to typical high efficiently non-precious catalysts, and suggest the promising application potential of the Co_2P nanorods in the field of hydrogen production. The HER process follows a Volmer–Heyrovsky mechanism, and the rates of the discharge step and desorption step appear to be comparable during the HER process. The similarity of charged natures of Co and P in the Co_2P nanorods to those of the hydride-acceptor and proton-acceptor in high efficient Ni_2P catalyst, [NiFe] hydrogenase, and its analogues implies that the HER catalytic activity of Co_2P nanorods might be correlated with the charged natures of Co and P.
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Introduction

The solar-driven splitting of water into molecular hydrogen and oxygen is one of the most promising possibilities for simultaneously solving the global energy crisis and current environmental issues [1–3]. Because of the intrinsically slow hydrogen evolution reaction (HER) kinetics of semiconductors, photocathodes must be decorated with HER catalysts

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for efficient hydrogen production. Though platinum remains the most effective HER catalyst, having been shown to significantly enhance the hydrogen production capability of photocathodes several decades ago [4,5], it is a limited resource and expensive, and so its widespread practical application in the field of solar-driven hydrogen production may be limited. There is therefore a demonstrable need for non-precious HER catalysts.

Recently, a variety of new HER catalysts have been reported, including molybdenum sulfide [6,7], molybdenum carbide [8-10], molybdenum nitride [10], molybdenum boride [8], tungsten carbide [11,12], tungsten carbonitride [13], first-row transition-metal dichalcogenides [14,15], nickel selenide [16], nickel phosphide [17], cobalt phosphide (CoP) [18-20], molybdenum phosphide [21,22], etc. The first-row transition-metal dichalcogenides have similar coordination structure as the active centers in efficient hydrogenase [15], and the charged natures of metal and P in metal phosphides are similar to those of the hydride-acceptor and proton-acceptor in [NiFe] hydrogenase and its analogues ([Ni(PS3*)(CO)]$^{1-}$ and [Ni(PNP)$_2$]$^{2+}$) [23].

Here the HER performance of cobalt phosphide (Co$_2$P) nanorods is introduced. Although their structure and composition are different from all heretofore reported HER catalysts, the Co$_2$P nanorods exhibit efficient and stable HER catalytic activity in both acidic and basic solutions. The overpotential required for a current density of 20 mA/cm^2 (η_{20}) is as small as 167 mV in acidic solution and 171 mV in basic solution. The η_{20} of the Co$_2$P nanorods lies in the top 10 of the reported values of non-precious HER catalysts. It is worth noting that the four reported η_{20} better than that of the Co$_2$P nanorods were obtained from the composites of catalysts and nanostructured conductive supports, including Mo$_1$So$_y$ particles loaded on reduced graphene oxide (Mo$_1$So$_y$/rGO) [10], CoP nanoparticles loading on carbon nanotube (CoP/CNT) [18], CoP nanowires loaded on carbon cloth (CoP/CC) [20], and MoS$_2$ loaded on mesoporous graphene foam (MoS$_2$/MGF) [24]. The nanostructured conductive supports have been well known to improve the electron transport among catalysts and therefore the performance of catalyst [25]. The charged natures of Co and P in the Co$_2$P nanorods are similar to those of the hydride-acceptor and proton-acceptor in Ni$_2$P catalyst, [NiFe] hydrogenase, and its analogues. Such similarity might afford the efficient catalytic activity of the Co$_2$P nanorods.

Materials and methods

Synthesis of Co$_2$P nanorods

Cobalt acetate tetrahydrate (0.50 g, 2 mmol) was mixed with oleylamine (12 g, 45 mmol) in a 100 mL round-bottom flask. The flask was heated via a heating mantle. Dispersion was obtained by stirring the mixture at 70 °C. The dispersion was then heated to 120 °C and triphenylphosphine (5.246 g, 20 mmol) was added to the mixture. The flask was pumped under vacuum at 120 °C for 30 min to remove water, and then refilled with N$_2$. The temperature of the heating mantle was increased to 370 °C and maintained at this value for 10 min. The flask was removed from the heating mantle and cooled to room temperature. The black product

was isolated and washed by repeated centrifugation/ultra-sonication, with hexane as good solvent and ethanol as non-solvent. Finally, the product was dried under vacuum at room temperature.

Characterization

The morphology of Co$_2$P nanorods was assessed by transmission electron microscopy (TEM, 200 kV, JEM2100, JEOL) and scanning electron microscopy (SEM, 7001F, JEOL). The energy-dispersive X-ray spectroscopy (EDX) spectrum was recorded using a GENESIS 2000 XM 30T (EDXA) on a JEM2100. For the TEM investigation, the Co$_2$P nanorods were dispersed in hexane by ultrasonication. The dispersion was dropped onto a carbon-coated copper grid (300-mesh). The copper grid was then dried at 100 °C for 5 min before the TEM characterization. Powder X-ray diffraction (XRD) patterns were collected using a D8 Advance diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ=1.54178 Å). The X-ray photoelectron spectroscopy (XPS) experiments were carried out on an ESCALAB250Xi System (ThermoFisher) equipped with a monochromatic Al $K\alpha$ (1486.6 eV) source and a concentric hemispherical energy analyzer. The binding energy C 1s peak from surface adventitious carbon (284.8 eV) was adopted as a reference for the binding energy measurements.

Electrochemical performance

Co$_2$P nanorods (15 mg) were dispersed in hexane (0.5 mL) with the aid of an ultrasonic horn (2 mm diameter, 130 W, 60 min). The dispersion (17 μL) was dropped onto a clean Ti foil (0.5 cm^2) and dried naturally. The Ti foil was polished by sandpaper (7000 mesh), and then cleaned by acetone, ethanol, de-ionized water (15 min each) prior to the drop-coating of the Co$_2$P nanorods. The Co$_2$P nanorods loaded on the Ti foil were annealed in 5% H$_2$/N$_2$ at 450 °C for 30 min to remove surface ligands.

All electrochemical measurements were carried out with an electrochemical workstation (CHI 614D, CH Instrument) in a three-electrode configuration, with Co$_2$P (loaded onto Ti foil) as a working electrode, a graphite rod (6 mm diameter) as a counter electrode, and a mercury/mercurous sulfate electrode (MSE) or mercury/mercury oxide electrode (MMO) as a reference electrode. The samples were assembled into a homemade electrochemical cell, with only a defined area ($\sim$0.07 cm^2) of the front surface of the sample exposed to solution during the measurements. The counter electrode was separated from working chamber by porous glass frit.

H$_2$SO$_4$ aqueous solution (0.5 M) or KOH aqueous solution (1 M) was used for electrochemical measurements. The MSE is used as the reference electrode in H$_2$SO$_4$ solution, and the MMO is used in KOH solution. The solutions were purged with high purity H$_2$ (99.999%) for 30 min prior to electrochemical measurements. The reversible hydrogen evolution potential (RHE) was determined by the open circuit potential of a clean Pt electrode in the solution of interest bubbled with H$_2$ (99.999%), being $-$0.694 V vs. MSE for the 0.5 M H$_2$SO$_4$ solution and $-$0.876 V vs. MMO for the 1 M KOH solution. A potential measured with respect to the MSE electrode was therefore referenced to the RHE by adding