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# Phase transformation of iron phosphide nanoparticles for hydrogen evolution reaction electrocatalysis

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## ARTICLE INFO

### Article history:

Received 1 December 2017

Received in revised form

31 January 2018

Accepted 7 February 2018

Available online xxx

### Keywords:

Hydrogen evolution reaction

Iron phosphide nanoparticles

Phase transformation

Fe<sub>2</sub>P

FeP

## ABSTRACT

Transition metal phosphides have emerged as alternative electrocatalysts for hydrogen evolution reaction (HER) due to their high activity and low cost compared to the conventional HER electrocatalysts such as Pt. However, the dependency of HER activity on different crystal phases is not well-understood. Here, we synthesized iron phosphide nanoparticles with two distinct phases via chemical transformation from iron metal to iron phosphides. During the development of iron phosphide phases by varying the synthesis conditions such as reaction temperature and time, the HER activities of the nanoparticle were examined. The HER activities of the iron phosphide nanoparticles were found to be phase-dependent.

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## Introduction

Hydrogen is one of the most promising alternate energy sources due to its clean and high energy density [1–3]. There are several methods to produce hydrogen, such as partial oxidation from oil, coal gasification, and steam reforming from hydrocarbon, of which water electrolysis is the most environmentally-friendly method [2]. For efficient hydrogen evolution reaction (HER) through water electrolysis, developing highly active electrocatalysts is the key to obtaining high current density with low overpotential. Pt-based catalysts have exhibited excellent catalytic activity in HER, but high cost and limited reserves hinder the commercialization

of these precious metal catalysts [2,4,5]. Accordingly, non-noble metal-based or metal-free catalysts have been studied to overcome the limitation of the traditional Pt-based electrocatalysts for HER [6–10]. Among numerous candidates, transition metal phosphides have emerged as alternative electrocatalysts due to their high HER catalytic performance [8,11,12].

Various transition metal phosphides, such as cobalt phosphides [13–22], iron phosphides [23–33], molybdenum phosphides [34–36], and nickel phosphides [37–45], have been utilized for HER catalyst. To enhance the HER catalytic activity of transition metal phosphides, much effort has been devoted such as phase transformations [20,26,40,41], support changes [18,20,42] and diverse morphology controls including

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<https://doi.org/10.1016/j.ijhydene.2018.02.197>

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nanoparticles [15,19,23,27,35,37], nanowires [17,24,26,39], nanorods [13], and nanosheets [16,28,38]. Among these transition metal phosphides, iron phosphides have been reported as one of the most active HER catalysts showing low overpotential [23]. Specifically, FeP nanoparticles (NPs) exhibited high stability in strongly acidic aqueous solutions while requiring overpotentials of only  $-50$  and  $-61$  mV (at a loading density of  $\sim 1$  mg cm $^{-2}$ ) to produce current densities of  $-10$  and  $-20$  mA cm $^{-2}$ , respectively [23]. Fe $_2$ P, structurally different from FeP, has also been analyzed as active HER catalysts [25]. However, only a few studies have been performed to evaluate the HER catalytic activities of iron phosphides with phase changes, which are crucial for fully understanding the mechanism of their HER activities and to further improve their catalytic performance [26]. Additionally, the structural evolution and corresponding catalytic properties during the phase transformation from iron to iron phosphides are not well studied yet.

Secondary phase transformation of NPs such as cation/anion exchange [46–49], galvanic replacement [50–53], and redox addition [54–56] is an efficient and powerful route to precisely control the phases and isolate the metastable structures. For example, spherical or rod-shaped CdSe nanocrystals were converted into Cu $_2$ Se through a cation exchange reaction, which resulted in metastable phases of Cu $_2$ Se [57]. Anion exchange can be used to synthesize metal sulfide/selenide from metal oxide, while preserving the wurtzite crystal structure [58,59]. Among the various phase transformation reactions, phosphorization of transition metal has also been studied. The phase transformation from  $\epsilon$ -Co to Co $_2$ P to CoP was reported for colloidal NPs, resulting in control over their magnetic properties [60]. CoS $_2$  was also converted to CoPS with a similar crystal structure, leading to an enhanced HER catalytic activity [61]. However, a systematic study on the phase transition of iron phosphide NPs from iron is not well-established.

Herein we developed a synthesis method to control the morphology and phases of iron phosphide NPs through a secondary transformation pathway and evaluated the correlation between their HER catalytic activities and their phase/crystallinity. The phosphorization of iron NPs was controlled by the reaction temperature and time and resulted in phase transformation from iron to Fe $_2$ P to FeP. The nanorod (NR) shape was preserved during the phase transformation of iron phosphide NPs from Fe $_2$ P to FeP, which is ideal for comparing their catalytic activities. The FeP NPs with enhanced crystallinity show higher HER catalytic activity than Fe $_2$ P NPs.

## Experimental

### Chemical and materials

Iron pentacarbonyl (Fe(CO) $_5$ , >99.99% trace metal basis, Sigma-Aldrich), oleylamine (OLA, 70%, Sigma-Aldrich), tri-*n*-octylphosphine (TOP, 90%, Sigma-Aldrich), 1-octadecene (ODE, 90%, Acros), squalane (98%, Alfa-Aesar), chloroform (99.8%, Alfa-Aesar), ethanol (99.9% anhydrous, Daejung), hexane (95%, Daejung), titanium foil (Sejin), and sulfuric acid (H $_2$ SO $_4$ , 95% Extra Pure, JUNSEI) were purchased and used as received.

### Iron phosphide nanoparticle synthesis

Iron phosphide NP synthesis was modified from previous reports [23,62]. Iron NPs were first synthesized to generate the phase transformation to iron phosphides. ODE (10 mL) and OLA (0.2 mL) were added to a 25 mL three-necked flask, which was equipped with a condenser, thermometer, thermometer adapter, rubber septum and magnetic stir bar. The solution was stirred and heated to 120 °C under vacuum condition for 40 min to remove impurities (water and volatile chemicals). Then, the flask was kept under nitrogen atmosphere and heated up to 190 °C. When the solution temperature reached 190 °C, Fe(CO) $_5$  (0.35 mL) was rapidly injected into the flask. The suspension was maintained at 190 °C for 20 min.

To convert iron NPs to iron phosphide NPs, TOP (3 mL) and squalane (7 mL) were added to a 25 mL three-necked flask. The impurities in this mixture were also removed through a degassing process before heating up to 300 °C. At 300 °C, ODE/OLA containing iron NPs solution was injected and the reaction was left to proceed at 300–340 °C for 1–2 h. After the reaction with the desired temperature and time, the reaction mixture was then divided into centrifuge tubes. NPs were collected by adding hexane and ethanol, followed by centrifugation. NPs were then re-suspended to hexane, and this process was repeated twice. Finally, NPs were dispersed and kept in chloroform.

### Electrochemical measurement

To perform electrochemical measurements, iron phosphide NPs were dispersed in chloroform with a concentration of 2 mg mL $^{-1}$ . 20  $\mu$ L of the NP solution was deposited onto a 0.38 cm $^2$  Ti foil and then dried. The resulted NP film was heated to 450 °C under a H $_2$  (5%)/Ar (95%) gas flow for 30 min to remove organic ligands which were originally covering the surface of the NPs. The electrochemical measurements were performed using Autolab PGSTAT302F. The electrolyte solution was prepared using deionized water and H $_2$ SO $_4$ . Saturated calomel electrode (SCE) and graphite rod were employed as a reference and a counter electrode, respectively. The potentials were iR-corrected with the resistance obtained from electrochemical impedance spectroscopy. Cyclic voltammetry (CV) experiments were performed in 0.5 M H $_2$ SO $_4$  at a sweep rate of 50 mV/s. In addition, electrochemical measurement of Pt/C was also carried out for comparison. The Pt/C was mixed with isopropyl alcohol to make a catalyst ink. Then Pt/C (40 wt %) catalyst was drop-casted on a Ti electrode with the same amount of iron phosphide NPs. The CV scans were performed in N $_2$ -saturated 0.5 M H $_2$ SO $_4$  at 50 mV/s.

### Materials characterization

Transmission electron microscopy (TEM) images were acquired using a JEOL-2100 operating at 200 kV. High-resolution TEM (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) images were collected by an FEI Tecnai G $^2$  F30 S-Twin at an accelerating voltage of 300 kV. Approximately 100 particles were analyzed for all the samples to obtain a size distribution. Microscope samples were prepared by drop-casting of NP samples dispersed in hexane on a carbon-coated copper grid.

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