This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
High catalytic activity for water oxidation based on nanostructured nickel phosphide precursors

Ali Han, Huanlin Chen, Zijun Sun, Jun Xu, Pingwu Du*

For the first time, noble-metal-free nickel phosphide (Ni$_2$P) was used as an excellent catalyst precursor for water oxidation catalysis. The lowest onset potential was observed at ~1.54 V (vs. RHE) and a Tafel slope of 60 mV/dec was obtained in alkaline solution (pH =13.6).

Hydrogen production through photo- and electro-catalytic water splitting has attracted much attention in the last few decades. The water splitting reaction contains two half-reactions: hydrogen evolution reaction (HER) and water oxidation reaction. Catalysts play very important roles in highly promoting both HER and water oxidation. In nature, the CaMn$_2$O$_4$ active site in the oxygen evolution center of photosystem II serves as the catalyst for water oxidation, in that it can assist the O-H bond breaking and the formation of O-O to evolve O$_2$. Inspired by nature, a variety of materials and molecular metal complexes made of earth-abundant elements have been widely studied as catalysts for the water oxidation reaction, such as the materials based on the elements Mn, Co, Ni, Fe, and Cu elements. Despite these studies, for the purpose of future application, there is still a demand for highly efficient, robust, and low-cost water oxidation catalysts.

Nickel phosphide, a material made of earth-abundant nickel element, has been recently reported as an efficient HER catalyst with low overpotentials under different pH values. Nickel phosphide was not expected to have good prospects for catalytic water oxidation because it was usually used for reduction reaction. And to the best of our knowledge, the use of nickel phosphide for catalytic water oxidation has not received prior investigation. There are a few metal oxide and metal sulfide materials, such as CoO$_x$, NiO$_x$, and NiS$_x$, reported as bifunctional catalysts for catalyzing both HER and water oxidation reaction. Inspired by these studies, herein we report on the use of Ni$_2$P nanowires and nanoparticles as highly active catalysts precursors for water oxidation. Our results indicated that the nanowire-based catalyst showed a low onset potential at ~1.54 V (vs. RHE) at pH 13.6 and a Faradic efficiency of ~92% was achieved under an overpotential of 360 mV. All of our results demonstrate that Ni$_2$P nanowires have high activity for water oxidation in alkaline solution.

Nanostructured nickel phosphide (Ni$_2$P) materials with two different morphologies (nanowires and nanoparticles) were successfully synthesized and the experimental details can be found in supplementary information. The morphologies of the as-prepared Ni$_2$P nanowires and Ni$_2$P nanoparticles were investigated by transmission electron microscopy (TEM). Figure 1a shows the TEM images of Ni$_2$P materials, demonstrating the nanowire morphology with a diameter of 4~7 nm and a length of 100-300 nm. A high-resolution TEM image of the nanowire material is shown in the inset of Figure 1b. The average length is ~5 nm, which is consistent with the result from the TEM image. In addition, the HR-TEM image gave a crystal lattice spacing of ~0.34 nm, corresponding to the (001) plane of Ni$_2$P (PDF#74-1385) (Figure 1b, inset). The TEM image of the Ni$_2$P nanoparticles is shown in Figure S1a. The nanoparticles are aggregated with each other and the size of nanoparticles is in a range of 20-50 nm. The high-resolution TEM (HR-TEM) image in Figure S1b also shows a lattice spacing of 0.34 nm of Ni$_2$P (001).

Figure 1. (a) and (b) TEM images of Ni$_2$P nanowires. The inset image is the HRTEM image of Ni$_2$P nanowires.

Powder X-ray diffraction (XRD) patterns of the as-synthesized Ni$_2$P nanowires and Ni$_2$P nanoparticles are shown in Figure 2a. The appreciable diffraction peaks at 2θ = 40.77, 44.59, 47.45, 54.16, 66.54, 72.64, and 74.34 are assigned to the (111), (201), (210), (300), (310),...
(311), and (400) planes of hexagonal Ni$_3$P (PDF#74-1385), respectively. It should be noted that the diffraction peaks of Ni$_3$P nanowires (black plot) are much broader than Ni$_3$P nanoparticles (red plot). In addition, the intensity of the (300) peak in Ni$_3$P nanowires is relatively higher. These observations probably result from the anisotropic nanostructure, in particular the increased dimension in the long axis of Ni$_3$P nanowires. The peak of (300) is also a feature of the increased dimension in the long axis of the nanocrystals. Such a distinctive peak has also existed in other nanowire samples.\(^{23,24}\)

![Figure 2.](image)

Figure 2. (a) X-ray diffraction patterns of the as-prepared Ni$_3$P nanowires (black) and Ni$_3$P nanoparticles (red); (b) XPS survey data of Ni$_3$P nanowires (black) and Ni$_3$P nanoparticles (red); (c) high resolution XPS spectra of Ni 2p; (d) high resolution XPS spectra of P 2p.

The XPS spectra of Ni$_3$P samples were measured to identify the surface chemical composition and valence states. The XPS survey scans in Figure 2b show the presence of Ni, P, O, and C elements. The binding energies were corrected according to the C element at 285.0 eV. The high resolution XPS spectra of Ni and P elements from Ni$_3$P nanowires are shown in Figures 2c and 2d. The peaks at 852.79 eV and 129.89 eV are assigned to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ binding energies, respectively.\(^{18,25}\) The high resolution spectrum of P 2p shows two peaks located at 129.12 eV and 129.89 eV, corresponding to P 2p$_{3/2}$ and P 2p$_{1/2}$, respectively. The other peak at 133.49 eV was probably from partial oxidation of Ni$_3$P.\(^{23,26-27}\) As for the Ni$_3$P nanoparticles, the peaks for Ni 2p have features similar to those of the Ni$_3$P nanowires although the peak of P 2p at 134.32 eV showed a slight shift compared to P 2p of Ni$_3$P nanowires at 133.49 eV.

![Figure 3.](image)

Figure 3. (a) CV scans using FTO electrode loading 0.1 mg/cm$^2$ Ni$_3$P nanowires as the working electrode in 1.0 M KOH (pH = 13.6). The scan rate was 50 mV s$^{-1}$ and iR drop was applied; (b) CV scans using FTO electrode loading 0.1 mg/cm$^2$ Ni$_3$P nanoparticles as the working electrode in 1.0 M KOH (pH = 13.6). The scan rate was 50 mV s$^{-1}$ and iR drop was applied; (c) Polarization curves for Ni$_3$P nanoparticles, and nanoparticles on FTO after CV scans for 500 cycles in 1.0 M KOH. Base FTO electrode was used for comparison. (d) The Tafel plots of Ni$_3$P nanowires and nanoparticles obtained from the polarization curves in Figure 3c.

For comparison, Ni$_3$P nanoparticles on FTO were used for CV scans, as shown in Figure 3b. During the scans, appreciable catalytic waves for water oxidation appeared but the catalytic current densities were much lower than that for nanowires. In the beginning, the oxidation wave presented a quite high onset potential of 1.67 V for water oxidation was decreased and the catalytic current density was enhanced under the same applied potential, indicating that the electroactive species formed on the electrode surface during CV scans. A stable current density was achieved after 200 cycles and no deactivation was observed from the first cycle to the 500th cycle. The lowest onset potential of ~1.54 V was achieved for Ni$_3$P nanowires, a figure which is comparable to many metal oxide-based water oxidation catalysts such as Co$_3$O$_4$/graphene (1.63 V vs. RHE, pH 14),\(^{28}\) NiC$_x$–NiO$_x$ (1.7 V vs. RHE, pH 13),\(^{29}\) NiCo$_2$O$_4$ (1.52 V vs. RHE, pH 13.6),\(^{30}\) and Zn$_x$Co$_{3-x}$O$_x$ (1.55 V vs. RHE, pH 14).\(^{31}\) Therefore, the present Ni$_3$P nanowire material is among the most efficient reported noble-metal-free electrocatalysts for water oxidation in alkaline solutions.
same as the observations by CV scans. Note that bare FTO electrode without loading Ni$_3$P materials shows negligible catalytic current under an applied potential less than 1.88 V, indicating the important role of Ni$_3$P for catalytic water oxidation. From the LSV data in Figure 3c, we can see that a current density of 10 mA/cm$^2$ can be achieved with an overpotential of only ~400 mV for Ni$_3$P nanowires and ~500 mV for Ni$_3$P nanoparticles. For comparison, a simple nickel salt (NiCl$_2$) was used as a precursor for water oxidation. However, NiCl$_2$ was not soluble in strong basic solution. Then, we initially used NiCl$_2$ (~1.34 μmol) as the precursor in 0.1 M KPi (pH = 7.0) to obtain NiO$_x$-based catalyst film. After 2 h of electrolysis under a potential of 1.3 V (vs. Ag/AgCl), the film was cleaned and after electrolysis (bottom) for 10 h.

The reaction kinetics of Ni$_3$P nanomaterials can be studied by the Tafel plot. The current density ($j$) under various potentials was obtained from the LSV data. The Tafel plots were then calculated by a function of the overpotential ($\eta$) vs. the Nernstian potential for water oxidation (Figure 3d). The slope of the Tafel plot for Ni$_3$P nanowires is ~60 mV/dec, indicating a very efficient kinetics for the water oxidation process. From the plot, an appreciable current density at $\eta$ = 250 mV is observed. A current density of ~ 1.0 mA/cm$^2$ required $\eta$ = 310 mV. In contrast, the Ni$_3$P nanoparticles show a higher Tafel slope of ~70 mV/dec, indicating that Ni$_3$P nanoparticles material is less active than Ni$_3$P nanowire material. The high activity of Ni$_3$P nanowires for water oxidation activity can probably be attributed to its one dimensional (1D) structural feature providing more active sites than nanoparticles. The Faraday efficiencies for O$_2$ evolution of Ni$_3$P-based catalysts on FTO (0.5 cm$^2$ surface area, 0.1 mg/cm$^2$ loading) were estimated under an overpotential of 360 mV for 1.5 h. The electrolysise experiments resulted in evolution of 18.7 μmol O$_2$ for Ni$_3$P nanowires. The amounts of evolved O$_2$ showed a Faradic efficiency of >92% (Figure 4a). A large amount of gas bubbles on the surface of the working electrode were produced during electrolysis for the Faradic efficiency measurement (Figure 4b).

To further investigate the composition and valence states of the Ni$_3$P-based catalysts, XPS spectra were examined after bulk electrolysis for 10 h (Figures 4c and 4d). Significant differences can be seen from the high resolution spectra of Ni 2p and P 2p. The binding energies of Ni 2p at 855.7 eV (2p$_3/2$) and 873.0 eV (2p$_1/2$) indicate the formation of NiO$_x$ (~855.6 eV).$^{11}$ As for P 2p, an obvious oxidation peak at 133.6 eV appears, suggesting that P in Ni$_3$P is probably oxidized to produce phosphate species (~133.6 eV),$^{23, 26-27}$ which might help proton transfer during water oxidation catalysis.$^7$ Therefore, Ni$_3$P materials served as active catalyst precursors to catalyze water oxidation at low overpotentials. SEM images of Ni$_3$P after electrolysis were also measured (Figure S4). The NiO$_x$ obtained from Ni$_3$P nanoparticles showed aggregated nanoparticles (Figure S4a) and the morphology of the NiO$_x$ from Ni$_3$P nanowires still showed many nanowires and short nanowires have been observed (Figure S4b).

Conclusions

In summary, this is the first report that nanostructured Ni$_3$P materials have been studied for water oxidation catalysis. The results show that Ni$_3$P nanowires material is more active than Ni$_3$P nanoparticle material and the lowest onset potential of ~1.54 V can be achieved using Ni$_3$P nanowires. The Faradic efficiency was more than 92% under an overpotential of 360 mV. The electrochemical measurements demonstrated that Ni$_3$P nanoparticle material is an excellent electrocatalyst for water oxidation under alkaline conditions. Further XPS analysis indicated that Ni$_3$P is probably a catalyst precursor during water oxidation catalysis.

This work was financially supported by NSFC (21271166, 21473170), the Fundamental Research Funds for the Central Universities, the Program for New Century Excellent Talents in University (NCET), and the Thousand Young Talents Program.

Notes and references

*Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences, Department of Materials Science and Engineering, (CHEM) Collaborative Innovation Center of Chemistry for Energy Materials, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui Province, 230026, P. R. China. Fax: 86-551-63606207; E-mail: dupingwu@ustc.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details, figures and so on. See DOI: 10.1039/c000000x/