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*Supplementary Information*

# High catalytic activity for water oxidation based on nanostructured nickel phosphide precursors

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## Experimental Methods

**Materials.** All chemicals, including nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), nickel (II) acetylacetonate ($Ni(acac)_2$), Sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$), oleic acid, trioctylphosphine (TOP, $P(C_8H_{16})_3$), tri-n-octylamine (TOA, $N(C_8H_{16})_3$), and potassium hydroxide (KOH) were purchased from Aldrich or Acros and used without further purification. All electrolyte solutions were prepared using millipore water (resistivity: ~18 MΩ·cm).

**Sythesis of $Ni_2P$ nanowire.** The $Ni_2P$ nanowires were prepared according to the reported procedure.[1] $Ni(acac)_2$ (128.5 mg, 0.5 mmol) was added into a 50 mL three-necked, round-bottom flask containing a high-temperature resistance stirring bar. Then oleic acid (0.38 mL, 1.2 mmol) and TOA (10 mL) were mixed to prepare a stock solution. The stock solution was degassed by argon and heated to 120 °C under stirring. Next, the stock solution was slowly injected (0.05 mL/min) using a syringe pump into a stirring mixture containing TOA (5 mL) and TOP (1.2 mL, 2.4 mmol) heated at 300 °C under argon. The solution was maintained at 300 °C until titration was finished. The flask was then removed from the heating mantle to cool to room temperature. The products were collected by centrifugation at 10000 rpm for 3 min. The resulting powder was washed using a mixture of hexane and ethanol, separated by centrifugation for 3 times. Finally, the product was dried under vacuum at room temperature for 6 h.

**Synthesis of $Ni_2P$ nanoparticles.** The $Ni_2P$ nanoparticles were prepared by a modified method.[2] In a typical procedure, 20 mmol $NiCl_2 \cdot 6H_2O$ and 80 mmol $NaH_2PO_2 \cdot H_2O$ were mixed together in an agate mortar and ground to a fine mixture. The mixture was transferred to a ceramic boat and heated to 400 °C for 2 h at a heating rate of 2 °C $min^{-1}$ under an argon atmosphere in a tube furnace. After cooling to room temperature, the sample was washed with water and ethanol three times each and dried at 80 °C for 6 h to result in the $NiO_x$ materials. The same phosphidiation procedure was

Applied again to convert $NiO_x$ into $Ni_2P$ nanoparticles.

**Electrochemical methods**

The electrochemical experiments were operated in a three-electrode electrochemical cell at ambient temperature with a 660D CH Instrument potentiostat (Shanghai Chen Hua Instrument Co., Ltd.). An Ag/AgCl electrode (3 M KCl, the potential is 0.21V vs. NHE) was used as the reference electrode. The working electrode was $Ni_2P$/FTO or bare FTO plates. 1.0 M KOH (pH ~13.6) were used as the electrolytes except as otherwise noted. There were several iR drops applied for compensation and no stirring were used for the cyclic voltammetry and linear sweep voltammetry. Bulk Electrolysis experiment for faraday efficiency was performed under an overpotential of 360 mV. The reference electrode was placed a few millimeters from the working electrode. All the potentials reported in this paper were converted to the reversible hydrogen electrode (RHE). The $Ni_2P$/FTO working electrode was prepared as follows: 5 mg of $Ni_2P$ was added into 0.9 mL EtOH and 0.1 mL 5% Nafion solution and ultrosonicated for 3-5 minutes to prepare the $Ni_2P$ ink. Then 10 μL of the ink was loaded onto the FTO plate (~0.1 mg/$cm^2$) and the plate was dried at room temperature for more than 1 h.

**Characterization of $Ni_2P$ materials**

The $Ni_2P$ materials were characterized by powder X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° $min^{-1}$ from 20° to 80° in 2θ. The chemical compositions and valence states of the $Ni_2P$ nanomaterials were examined by ESCALAB 250 X-ray photoelectron spectroscopy (XPS). The spectra are referenced to the C1s peak (285.0 eV). The TEM images were obtained by using transmission electron microscope (TEM). Samples for TEM analysis were prepared by sonicating the materials in alcohol and dropped onto a carbon-coated copper grid. The crystalline phases of the $Ni_2P$ samples were identified by high-resolution transmission electron microscopy (HR-TEM). Energy dispersive X-ray spectroscopy (EDS) data were obtained using JSM-6700F field emission scanning electron microscope (FE-SEM). The materials were analyzed in several local spots to ensure their chemical homogeneity. The samples were sprayed with Pt to improve their conductivity before loading into the instrument.

## References

1. Y. Z. Chen, H. D. She, X. H. Luo, G. H. Yue, D. L. Peng, *J. Cryst. Growth.* 2009, ***311***, 1229-1233.
2. N. Jiang, L. Bogoev, M. Popova, S. Gul, J. Yano, Y. J. Sun, *J. Mater. Chem. A.* 2014, ***2***, 19407-19414.

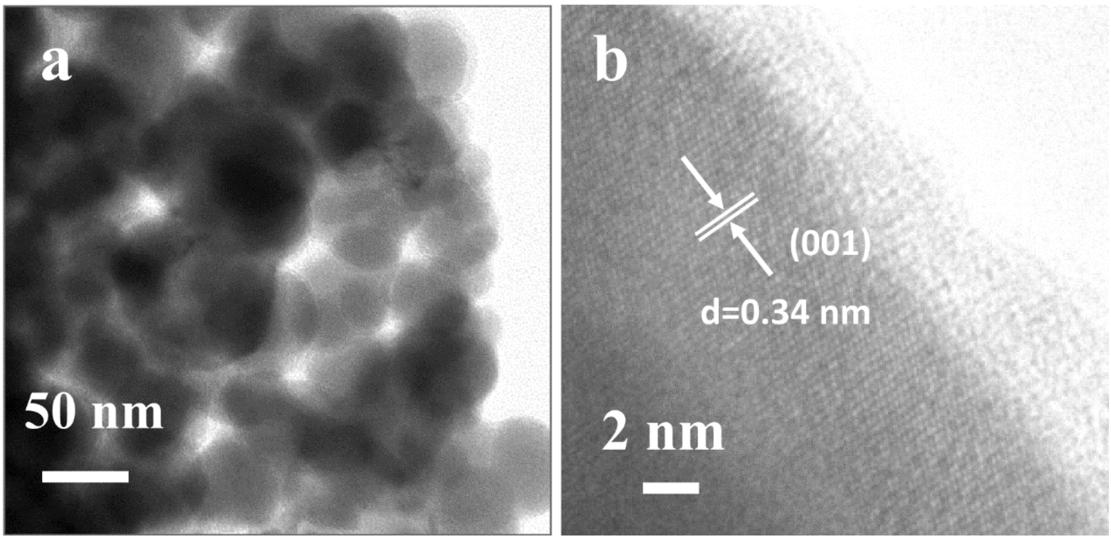

**Figure S1.** (a) TEM image of $Ni_2P$ nanoparticles; (b) HR-TEM image of $Ni_2P$ nanoparticles.

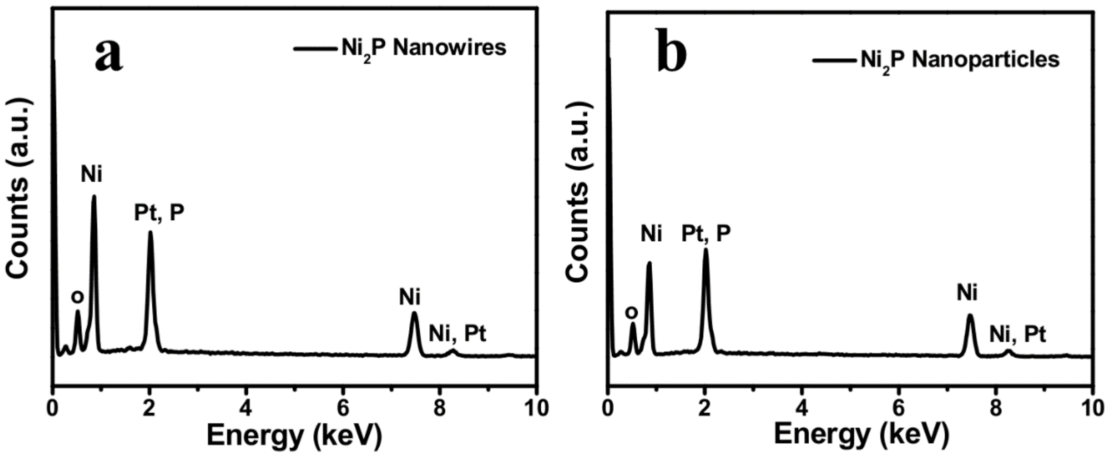

**Figure S2.** (a) EDX spectrum of the as-prepared $Ni_2P$ nanowires and the atom ratio of Ni and P is 33.74:17.77. (b) EDX spectrum of the as-prepared $Ni_2P$ nanoparticles and the atom ratio of Ni and P is 42.37:20.55.

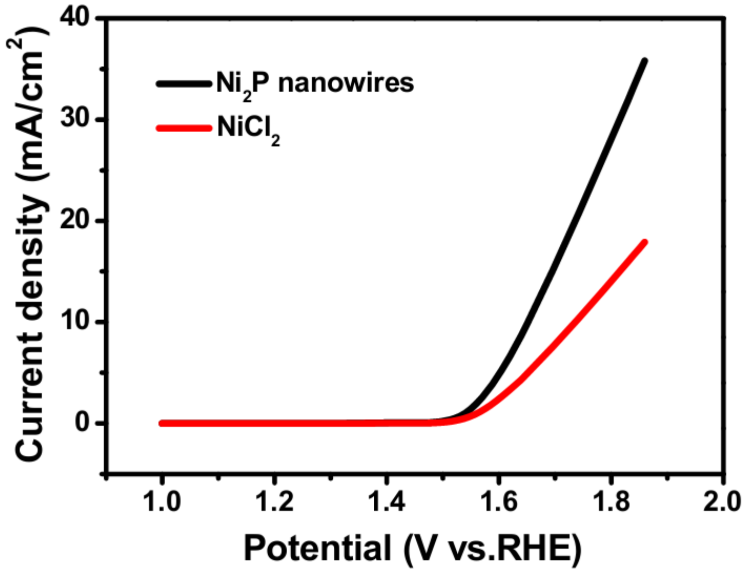

**Figure S3.** Linear sweep voltammetry (LSV) scans of water oxidation catalyst derived from different precursors in 1.0 M KOH. Black plot: $Ni_2P$ nanowires, red plot: $NiCl_2$.

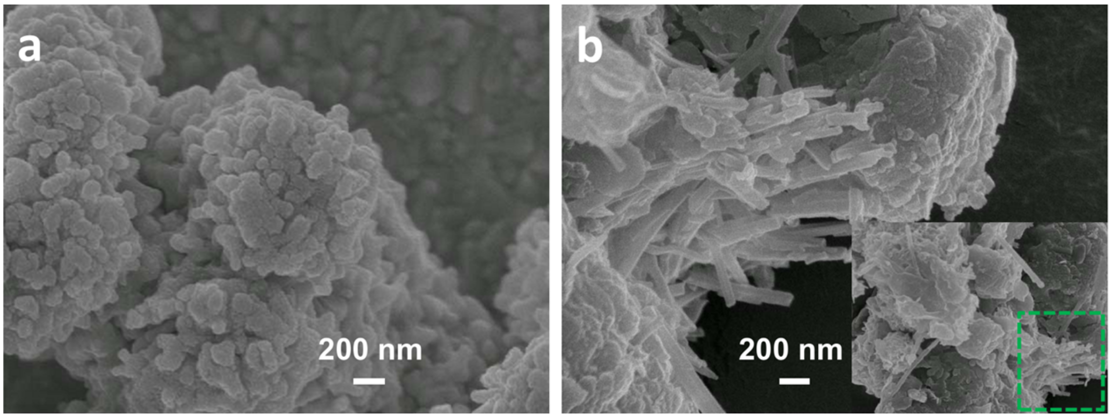

**Figure S4.** SEM images of $NiO_x$ derived from $Ni_2P$ nanoparticles and nanowires after bulk electrolysis for 5 h under an applied potential of 1.60 V (vs.RHE).