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# Ni<sub>2</sub>P hollow microspheres for electrocatalytic oxygen evolution and reduction reactions

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Ni<sub>2</sub>P hollow microspheres were synthesized and examined as an electrocatalyst for both  $O_2$  evolution and reduction reactions. This hollow microsphere structure, assembled by ultrathin nanosheets, has a high surface-to-volume ratio and is beneficial for fast charge transfer and mass diffusion. This Ni<sub>2</sub>P material is efficient for water oxidation by getting a 10 mA cm<sup>-2</sup> current at 280 mV overpotential. It is also effective in catalyzing the reduction of  $O_2$  with an onset potential of 0.92 V, representing a rare example of Ni phosphides as  $O_2$  reduction catalysts.

Hydrogen generated by solar-driven water splitting is a clean and environmentally benign fuel and is an ideal alternative to replace fossil fuels, whose uses have caused a series of energy and environmental issues.<sup>1-3</sup> The oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are the half reactions in the generation (via water splitting) and the use (via fuel cell) of H<sub>2</sub>, respectively.<sup>4-6</sup> However, these two reactions are sluggish and thus limit the overall progress to realize a hydrogen-based society.<sup>1</sup> Developing efficient OER and ORR catalysts have attracted extensive attention. Materials of noble metals are active for OER (i.e., RuO<sub>2</sub> and IrO<sub>2</sub>) and ORR (i.e., Pt),<sup>7-9</sup> but their uses are restricted due to the high cost and low natural abundance of noble metal elements. Recently, materials of earth-abundant transition metal elements, including Mn,<sup>10,11</sup> Fe,<sup>12,13</sup> Co,<sup>14-19</sup> Ni,<sup>20-23</sup> and  ${\rm Cu,}^{\rm 24,25}$  have been shown to be active for OER and ORR. However, Ni-based materials that are active for both OER and ORR have seldom been reported.

Transition metal phosphides have high electrical conductivity<sup>26,27</sup> and are widely studied as electrocatalysts for water reduction to evolve  $H_2$ .<sup>28-30</sup> In addition to the metallic property, metal phosphides are beneficial for water reduction due to the strong electron-donating ability of phosphorus. This feature makes metal center electron-rich to assist the binding and reduction of protons. Although considerable progress has been made by using metal phosphides as water reduction

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catalysts, only a few of them are active for  $O_2$  reduction.<sup>31,32</sup> On the other hand, metal phosphides have been studied as OER catalysts.<sup>33,34</sup> During electrocatalysis, the outmost spheres of metal phosphides will be converted in situ to metal oxides/hydroxides, which perform better catalytic activity than their corresponding initial phosphides and are real OER catalysts. It is likely that roughening and micro-structural reconstruction during the electrolysis process give more active sites. In addition, the phosphate, which is converted from phosphide during surface oxidation, may adjust coordination modes of the metal ion during redox switching processes to facilitate the OER process. The interior metal phosphides, which have better electronic conductivity than metal oxides, can be maintained and can facilitate fast electron transfer between the surface catalytic sites and the electrode. Based on the above factors, we expect that Ni phosphides will be effective in catalyzing both OER and ORR. However, until very recently, Dai and co-workers reported the first example of Ni phosphide acting as a bifunctional catalyst for OER and ORR.<sup>35</sup>

Herein, we report the synthesis of  $Ni_2P$  and its catalytic properties for OER and ORR. The as-prepared  $Ni_2P$  material has a hollow microsphere structure, which has a very high surfaceto-volume ratio and is beneficial for fast charge transfer and mass diffusion. These features are useful for electrocatalysis. The high activities and stabilities of this  $Ni_2P$  material for both OER and ORR were confirmed, representing a rare example of bifunctional OER and ORR catalysts among Ni phosphides.

The Ni<sub>2</sub>P hollow microsphere was synthesized via a facile two-step strategy, including hydrothermal synthesis of Ni(OH)<sub>2</sub> followed by phosphorization with NaH<sub>2</sub>PO<sub>2</sub> under argon. In a typical synthesis, Ni(NO<sub>3</sub>)<sub>2</sub> and oleylamine were dissolved in ethanol and were heated at 180 °C for 12 h.<sup>36</sup> The blue-green Ni(OH)<sub>2</sub> precipitate that formed was collected, washed, and was then subjected to phosphorization to give Ni<sub>2</sub>P black powders. The powder X-ray diffraction (XRD) patterns of the Ni(OH)<sub>2</sub> precursor and Ni<sub>2</sub>P are shown in Fig. 1a. XRD results suggested the formation of pure  $\alpha$ -Ni(OH)<sub>2</sub> (JCPDS 380715). For Ni<sub>2</sub>P, its characteristic diffraction peaks at 40.6°, 44.5°, 47.3°, 54.1°, 54.9°, 66.2°, 72.6° and 74.7° were identified (pure Ni<sub>2</sub>P, JCPDS 030953), corresponding to the crystal face (111), (201), (210), (300), (211), (310), (311) and (400), respectively. The disappearance of Ni(OH)<sub>2</sub> peaks and the strong peaks of

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 $Ni_2P$  at 40.6° and 47.3° in XRD indicate the complete conversion of  $Ni(OH)_2$  to  $Ni_2P$  under the synthetic conditions. Energy-dispersive X-ray spectroscopy (EDX) gave an elemental Ni/P atomic ratio of 2:1, which is consistent with the  $Ni_2P$ formulation (Fig. S1). This Ni/P atomic ratio was further confirmed by inductively coupled plasma mass spectrometry (ICP-MS). For comparison, the EDX analysis of the  $Ni(OH)_2$ precursor was provided in Fig. S2.

The X-ray photoelectron spectroscopy (XPS) spectrum of Ni<sub>2</sub>P shows the characteristic peaks of Ni and P (Fig. 1b). The narrow scan spectrum of Ni 2p displays peaks centered at 853.1 and 870.4 eV, which can be assigned to the Ni 2p<sub>3/2</sub> and Ni 2p<sub>1/2</sub> of metallic Ni<sub>2</sub>P, respectively (Fig. 1c).<sup>28,30,37</sup> The peaks at 856.4 and 874.2 eV can be ascribed to NiO<sub>x</sub> species arisen from surface oxidation of Ni<sub>2</sub>P in air. In the narrow scan spectrum of P 2p (Fig. 1d), an intensive peak can be fitted into two peaks at 129.3 and 130.5 eV, which are assigned to the P 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks in Ni<sub>2</sub>P, respectively.<sup>28,30,37</sup> The peak at 133.6 eV is attributed to oxidized P species. Importantly, peaks at 853.1 for Ni 2p<sub>3/2</sub> and 129.3 eV for P 2p<sub>3/2</sub> are identical to the binding energy values of Ni and P in Ni<sub>2</sub>P reported previously.<sup>28,30,37</sup>



Fig. 1 (a, b) XRD patterns and XPS survey spectra of  $Ni_2P$  and  $Ni(OH)_2$ . (c, d) XPS narrow scan spectra of Ni 2p and P 2p of  $Ni_2P$ .

The structure and morphology of the Ni(OH)<sub>2</sub> precursor and Ni<sub>2</sub>P were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. S3, Ni(OH)<sub>2</sub> precursor has a hollow microsphere structure with a typical diameter of 2.1  $\mu$ m. After phosphorization, the hollow microsphere structure can be maintained (Fig. 2a and 2b). The high-magnification TEM images of the resulted Ni<sub>2</sub>P confirmed the hollow structure and showed that the microsphere is built up by numerous ultrathin nanosheets (Fig. 2c and 2d). In addition, the homogeneous dispersion of Ni, P and O elements was confirmed by elemental mapping analysis (Fig. 2e, 2f and Fig. S4). These results are significant to show (1) the successful conversion of Ni(OH)<sub>2</sub> to Ni<sub>2</sub>P and (2) the maintenance of the hollow microsphere structure after the phosphorization process. Similar Brunauer-Emmett-Teller (BET) surface areas of  $Ni(OH)_2$  and  $Ni_2P$  (> 230 m<sup>2</sup> g<sup>-1</sup>) were obtained, confirming that the high surface area of the hollow structure was reserved after phosphorization.



**Fig. 2** (a, b) SEM, (c) TEM, (d) high-magnification TEM, and (e, f) elemental mapping images of the Ni<sub>2</sub>P microsphere.

First, we investigated the electrocatalytic OER activity of Ni<sub>2</sub>P in 1.0 M KOH. The catalyst was drop-casted onto a carbon cloth electrode with a loading of 0.20 mg cm<sup>-2</sup>. Fig. 3a shows the linear sweep voltammetry (LSV) of Ni<sub>2</sub>P. Significantly, in successive scans, the OER onset (current density  $j = 5 \text{ mA cm}^{-2}$ ) potential decreased and the catalytic current increased, indicating the formation of active catalytic species on the surface of Ni<sub>2</sub>P microspheres during LSV scans. An irreversible anodic peak at 1.28 V vs reversible hydrogen electrode (RHE, all potentials are versus RHE unless otherwise stated) was identified, which was assigned to the Ni<sup>III</sup>/Ni<sup>II</sup> redox progress.<sup>20,38-41</sup> No further activity enhancement was observed after 20 scans, suggesting the complete oxidation of surface Ni<sub>2</sub>P to active NiO<sub>x</sub>. Fig. S5 shows the cyclic voltammetry (CV) of Ni<sub>2</sub>P after 20 LSV scans, which is consistent with the data from LSV. Fig. 3b presents the LSV of Ni<sub>2</sub>P after 30 and 500 scans, showing their almost the same behaviors. This result suggests that the activated material is stable for catalytic water oxidation.

For comparison, LSV of electrode without catalyst or with Ni(OH)<sub>2</sub> precursor are provided in Fig. 3c. The current density of 10 mA cm<sup>-2</sup>, an approximate value expected for reaching a 12.3% solar-to-hydrogen efficiency,<sup>42</sup> can be achieved at 280-mV overpotential for Ni<sub>2</sub>P, while it is 390 mV for the Ni(OH)<sub>2</sub> precursor. Comparison of Ni<sub>2</sub>P with other metal phosphides shows that it is among the most active metal phosphide OER catalysts (Table S1). The Tafel slope of Ni<sub>2</sub>P material was 115 mV per decade (Fig. S6). The durability of this catalyst material was confirmed by chronopotentiometry (Fig. 3d). Constant overpotentials are required for maintaining current densities

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at 5, 10 and 20 mA cm<sup>-2</sup> during 10-h measurements, which is supportive of the catalyst stability for water oxidation. During electrolysis, numerous  $O_2$  gas bubbles were generated on the electrode surface. By using a gastight electrochemical cell, the amount of  $O_2$  formed on the headspace can be determined by gas chromatography, which gave a Faradaic efficiency > 93%.

Electrochemically active surface area (ECSA) analysis showed similar double layer capacitance ( $C_{dl}$ ) values for Ni<sub>2</sub>P (41 µF) and Ni(OH)<sub>2</sub> (44 µF) (Fig. S7). The ECSA of Ni<sub>2</sub>P and Ni(OH)<sub>2</sub> can be calculated to be 1.52 and 1.63 cm<sup>2</sup>, respectively (see ESI for details). Electrochemical impedance spectroscopy (EIS) measurements showed that Ni<sub>2</sub>P has a smaller resistance and thus a higher charge transfer ability than Ni(OH)<sub>2</sub> does (Fig. S8). This result is consistent with the metallic property of Ni<sub>2</sub>P. On the basis of these results, it is concluded that the better OER performance of Ni<sub>2</sub>P as compared with Ni(OH)<sub>2</sub> is largely due to its better electrical conductivity.



**Fig. 3** (a) LSV scans of Ni<sub>2</sub>P, showing the anodic activation of Ni<sub>2</sub>P. (b) LSV scans of Ni<sub>2</sub>P after 30 and 500 scans, showing almost identical behaviors. (c) LSV scans of electrode loaded without catalyst or with Ni<sub>2</sub>P or Ni(OH)<sub>2</sub>. (d) Chronopotentiometry plots of Ni<sub>2</sub>P to get current densities of 5, 10 and 20 mA cm<sup>-2</sup>. Conditions: 1.0 M KOH; 5 mV s<sup>-1</sup> scan rate.

The catalyst material after electrolysis was analyzed. The XPS narrow scan spectra of Ni 2p and P 2p are displayed in Fig. S9. Significant differences between the XPS spectra before and after electrolysis can be identified. The disappearance of Ni 2p peaks at 853.1 and 870.4 eV and P 2p peak at 129.3 eV indicates the surface oxidation of Ni<sub>2</sub>P. Importantly, the comparison of the grazing-incidence XRD patterns of the catalyst loaded on an indium tin oxide (ITO) electrode before and after electrolysis confirmed the presence of Ni<sub>2</sub>P in the catalyst bulk phase (Fig. S10). Based on these results, we can conclude that the outmost spheres of Ni<sub>2</sub>P are oxidized to NiO<sub>x</sub> during electrocatalysis, which is the real OER catalyst.

Next, we evaluated the ORR activity of Ni<sub>2</sub>P in an O<sub>2</sub>saturated 0.1 M KOH solution. Catalyst materials were dropcasted onto a rotating-disk electrode (RDE). As shown in Fig. 4a, Ni<sub>2</sub>P and carbon black alone showed poor ORR activities. However, the hybrid material of Ni<sub>2</sub>P and carbon black (Ni<sub>2</sub>P/C) exhibited a pronounced catalytic ORR current with the onset (current density  $j = 80 \ \mu A \ cm^{-2}$ ) and half-wave potentials of 0.92 V and 0.81 V, respectively. The use of carbon black as a support for Ni<sub>2</sub>P was aimed to prevent the agglomeration of Ni<sub>2</sub>P microspheres during electrocatalysis and also to facilitate the diffusion of O<sub>2</sub> to the catalyst.<sup>40,41</sup> More importantly, this activity is one of the best reported for metal phosphide ORR catalysts (Table S2). We also compared the ORR activity of Ni<sub>2</sub>P with the Ni(OH)<sub>2</sub> precursor. In order to compare their intrinsic activities, we loaded pure Ni<sub>2</sub>P and Ni(OH)<sub>2</sub> without carbon black on the electrode and measured their LSV for ORR under the same conditions. As shown in Fig. S11, Ni(OH)<sub>2</sub> is much less active than Ni<sub>2</sub>P to catalyze ORR.



**Fig. 4** (a) LSV scans of Ni<sub>2</sub>P, carbon black, Ni<sub>2</sub>P/C and Pt/C in an O<sub>2</sub>saturated 0.1 M KOH at 1600 rpm. (b) The *n* values of O<sub>2</sub> reduction with Ni<sub>2</sub>P, carbon black, Ni<sub>2</sub>P/C and Pt/C. (c) RDE measurements of Ni<sub>2</sub>P/C at various rotation rates. (d) K-L plots of Ni<sub>2</sub>P/C. (e) Controlled potential electrolysis of Ni<sub>2</sub>P/C and Pt/C at 0.6 V in O<sub>2</sub>saturated 0.1 M KOH solutions. (f) Chronoamperometric responses of Ni<sub>2</sub>P/C and Pt/C upon the introduction of methanol.

The number of electrons (*n*) transferred for O<sub>2</sub> reduction was obtained by RDE and rotating ring-disk electrode (RRDE) measurements. In RRDE, the disk electrode was scanned from 1.1 V to 0.3 V with a rate of 10 mV s<sup>-1</sup>, while the ring potential was held at 0.5 V. The measured H<sub>2</sub>O<sub>2</sub> yields are 17.5% (Ni<sub>2</sub>P), 33.4% (carbon black), and 8.7% (Ni<sub>2</sub>P/C) over the potential range of 0.45-0.75 V. The *n* value of 3.8 was calculated for Ni<sub>2</sub>P/C (Fig. 4b). The same *n* value of 3.8 was also calculated from the RDE Koutecky-Levich (K-L) method for Ni<sub>2</sub>P/C (Fig. 4c and 4d). The linearity and near parallelism of the fitting lines suggest a first-order reaction kinetics on the concentration of dissolved O<sub>2</sub> and similar electron transfer numbers for ORR at different potentials from 0.35 V to 0.65 V.

The stability of  $Ni_2P$  for ORR was then studied. Controlled potential electrolysis at 0.6 V showed that  $Ni_2P/C$  had only a

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10% current decay in 10-h electrolysis while Pt/C had a 28% current decay (Fig. 4e). Moreover, in methanol crossover tests, the current of Ni<sub>2</sub>P/C showed a negligible change upon addition of 2 M methanol, but Pt/C showed an exaggerated current jump due to the methanol oxidation reaction (Fig. 4f). These results suggest that Ni<sub>2</sub>P/C is an efficient and stable catalyst for the four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O.

In summary, Ni<sub>2</sub>P hollow microspheres were synthesized and were identified as active electrocatalysts for both OER and ORR. Our results show that Ni<sub>2</sub>P can catalyze water oxidation to get 10 mA cm<sup>-2</sup> current density at 280-mV overpotential and can catalyze the selective four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O at an onset potential of 0.92 V, making it one of the most active metal phosphide catalysts for OER and ORR. Its high efficiency is likely attributed to the intrinsic feature of Ni<sub>2</sub>P and the hollow microsphere structure assembled by many ultrathin nanosheets. This structure has a high surface area to expose more active sites and is beneficial for fast charge transfer and mass diffusion for electrocatalysis. This work is significant to demonstrate the potential use of well-designed metal phosphides for OER and ORR.

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The Ni<sub>2</sub>P hollow microsphere is synthesized via a facile two-step strategy and is shown to be active bifunctional electrocatalyst for oxygen evolution and reduction reactions.