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# A one-dimensional porous carbon-supported Ni/Mo<sub>2</sub>C dual catalyst for efficient water splitting†

Zi-You Yu, Yu Duan, Min-Rui Gao, Chao-Chao Lang, Ya-Rong Zheng  
and Shu-Hong Yu\*

The development of active, stable and low-cost electrocatalysts towards both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) for overall water splitting remains a big challenge. Herein, we report a new porous carbon-supported Ni/Mo<sub>2</sub>C (Ni/Mo<sub>2</sub>C-PC) composite catalyst derived by thermal treatment of nickel molybdate nanorods coated with polydopamine, which efficiently and robustly catalyses the HER and OER with striking kinetic metrics in alkaline electrolyte. The catalyst affords low onset potentials of −60 mV for the HER and 270 mV for the OER, as well as small overpotentials of 179 mV for the HER and 368 mV for the OER at a current density of 10 mA cm<sup>−2</sup>. These results compare favorably to Mo<sub>2</sub>C-PC, Ni-PC, and most other documented Ni- and Mo-based catalysts. The high activity of Ni/Mo<sub>2</sub>C-PC is likely due to electron transfer from Ni to Mo<sub>2</sub>C, leading to a higher Ni valence and a lower Mo valence in the Ni/Mo<sub>2</sub>C-PC catalyst, as these are HER and OER active species and thus account for the enhanced activity. Remarkably, our home-made alkaline electrolyser, assembled with Ni/Mo<sub>2</sub>C-PC as a bifunctional catalyst, can enable a water-splitting current density of 10 mA cm<sup>−2</sup> to be achieved at a low cell voltage of 1.66 V.

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## Introduction

With the rapid depletion of fossil fuels, the production of clean hydrogen fuels from water *via* electro/photochemical water splitting has become a very promising approach.<sup>1–8</sup> The electrochemical water-splitting reaction includes a cathodic hydrogen evolution reaction (HER) and an anodic oxygen evolution reaction (OER), both of which have substantial overpotential ( $\eta$ ) requirements.<sup>3,5,9</sup> Diverse catalysts have been designed and prepared to reduce the  $\eta$  value for more economical utilization of energy.<sup>3,5,10,11</sup> Currently, Pt-based metals show the best activity for the HER, and Ru/Ir-based materials are the benchmark catalysts for the OER.<sup>12–16</sup> However, the low earth abundance and high cost of these metals significantly limit their widespread use, and thus the development of cost-effective and efficient alternative catalytic materials is highly demanded.<sup>17</sup>

Recently, 3d metal-based materials (*e.g.*, Ni, Co, Fe and Mn) have been intensively developed as HER catalysts, among which it was established that Ni-based catalysts exhibited optimum

performance in alkaline electrolyte, owing to the optimum OH–Ni<sup>2+ $\delta$</sup>  ( $0 \leq \delta \leq 1.5$ ) bond strength that allows favorable intermediate adsorption.<sup>5</sup> Ni and its alloy composites have been applied as alkaline HER catalysts in the water-splitting industry for decades.<sup>18–20</sup> However, the main drawback of this catalyst is that its activity is easily lost after long-term operation because of the agglomeration and dissolution of the catalyst components.<sup>21,22</sup> Therefore, substantial improvements in activity and stability are greatly needed. Substantial studies have revealed that coupling different functional species together can lead to significant performance gain owing to synergistic effects, such as the synergism occurring in the CoSe<sub>2</sub>/Mn<sub>3</sub>O<sub>4</sub> and CoSe<sub>2</sub>/MoS<sub>2</sub> composite catalysts developed by our group.<sup>6,12</sup> Very recently, molybdenum carbide (Mo<sub>2</sub>C) has attracted great attention as a HER catalyst, because of its good stability, high electrical conductivity, and its similar electronic structure to Pt-group metals.<sup>23–27</sup> In view of the above considerations, chemically coupling Ni with Mo<sub>2</sub>C is supposed to result in an improved HER catalytic activity.<sup>28</sup> Moreover, such combination is also likely to realize outstanding OER performance owing to the presence of OER-active Ni.<sup>29–32</sup> This catalyst design eventually will lead to a new bifunctional catalyst for efficient overall water splitting application, which is highly desirable for electrolyser development.<sup>33</sup>

Herein, we report the synthesis of a new composite catalyst by embedding Mo<sub>2</sub>C and Ni nanoparticles into porous carbon nanorods (Ni/Mo<sub>2</sub>C-PC) through thermal treatment of nickel molybdate (NiMoO<sub>4</sub>) nanorods coated with polydopamine,

Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Collaborative Innovation Center of Suzhou Nano Science and Technology, CAS Center for Excellence in Nanoscience, Hefei Science Center of CAS, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: shyu@ustc.edu.cn; Fax: +86-551-63603040; Tel: +86-551-63603040

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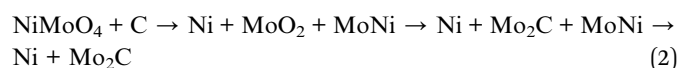
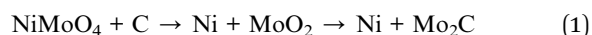
which is cost-effective and delivers highly active and stable performance for the HER with a low onset potential of  $-60$  mV and a high exchange current density of  $0.20$  mA cm $^{-2}$ . Meanwhile, Ni/Mo $_2$ C-PC was found to be active as an OER catalyst with an onset potential of 270 mV and it can offer a current density of  $10$  mA cm $^{-2}$  at a small  $\eta$  value of 368 mV. Intriguingly, our home-made alkaline electrolyser using Ni/Mo $_2$ C-PC as both cathodic and anodic catalysts can operate at a current density of  $10$  mA cm $^{-2}$  with a small cell voltage of merely 1.66 V, and performs robustly. Our results suggest methods of designing and synthesizing efficient bifunctional catalysts based on low-cost nickel and molybdenum carbide, which could open the way to economic electrolyzers for large-scale production of H $_2$  fuels.

## Results and discussion

An illustration of the synthesis of the Ni/Mo $_2$ C-PC catalyst is shown in Fig. 1a (see the ESI for details $^\dagger$ ). We first prepared NiMoO $_4$  nanorods with a diameter of 40–80 nm by a simple hydrothermal process as described in our previous work (Fig. 1b and S1, ESI $^\dagger$ ). $^{34}$  Then a uniform polydopamine (PDA) shell was coated on the NiMoO $_4$  nanorods in a Tris buffer solution (pH 8.5), and well-defined NiMoO $_4$ @PDA nanorods were obtained after polymerization for 24 h (Fig. 1c). Then the obtained dried powder was transferred into a tube furnace and annealed at 800 °C for 2 h under an Ar atmosphere, which eventually led to the generation of the black Ni/Mo $_2$ C-PC catalyst (Fig. 1d).

In order to understand the phase transformation during the annealing process, powder X-ray diffraction (XRD) was performed for NiMoO $_4$ @PDA samples annealed at different temperatures ranging from 500 °C to 900 °C (Fig. S2a, ESI $^\dagger$ ). The XRD pattern at lower temperature was not recorded because of the very weak diffraction resulting from uncarbonized PDA. The strong metallic Ni phase (JCPDS no. 04-0850) and weak MoO $_2$  phase (JCPDS no. 32-0671) can be detected for the sample annealed at 500 °C. Upon increasing the temperature to 600 °C, the diffraction peaks from MoO $_2$  became obvious. This MoO $_2$  phase, however, disappeared upon further increasing the temperature to 700 °C, while a new Mo $_2$ C phase (JCPDS no. 35-0787) appeared, which remained unchanged even when increasing temperatures to 800 °C and 900 °C. The metallic Ni

phase existed in all samples from 500 °C to 900 °C. Based on these results, the formation of the Ni/Mo $_2$ C-PC composite with increased annealing temperature can be reasonably speculated to be the reaction described in eqn (1). Transmission electron microscope (TEM) images (Fig. S2b–e, ESI $^\dagger$ ) showed that the core of nanorods was maintained at 500 °C, and started to be destroyed from 600 °C. Along with the temperature increasing to 900 °C, these one-dimensional (1D) nanorods became porous and nanoparticles were formed and embedded in the carbon nanorods. Of note, the mass ratio of dopamine and NiMoO $_4$  greatly affected the morphology and phase composition of the prepared samples (Fig. S3, ESI $^\dagger$ ). During the annealing process, the increasing carbon content will switch the reaction to eqn (2) for the formation of Ni/Mo $_2$ C-PC. The optimal mass ratio and temperature for achieving the Ni/Mo $_2$ C-PC composite were 1.5 and 800 °C, respectively. For comparison, Mo $_2$ C-PC, Ni-PC, and PC can be prepared using similar methods (Fig. S4 and S5, ESI $^\dagger$ ).



Scanning electron microscopy (SEM) and TEM images showed that the as-obtained 1D Ni/Mo $_2$ C-PC composite has a diameter of 150–200 nm and a length of up to 2–4  $\mu$ m (Fig. 2a–c). The rod-like structure has a smooth surface with particulate Ni and Mo $_2$ C encapsulated within the carbon shells. Enlarged TEM images (Fig. 2d and e and S6a, ESI $^\dagger$ ) revealed the interesting porous structure of Ni/Mo $_2$ C-PC, which might benefit the access of electrolyte and reactants to active sites and thereby offer improved catalytic performance. $^{35-37}$  N $_2$  adsorption-desorption isotherms and pore size distribution curves showed that the mesoporous composite has a Brunauer-Emmett-Teller surface

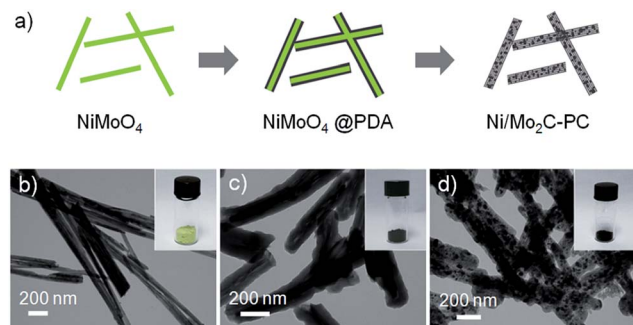


Fig. 1 (a) Illustration of the synthesis of Ni/Mo $_2$ C-PC from NiMoO $_4$  nanorods. (b–d) TEM images of (b) NiMoO $_4$ , (c) NiMoO $_4$ @PDA, and (d) Ni/Mo $_2$ C-PC. Insets are the corresponding digital photographs.

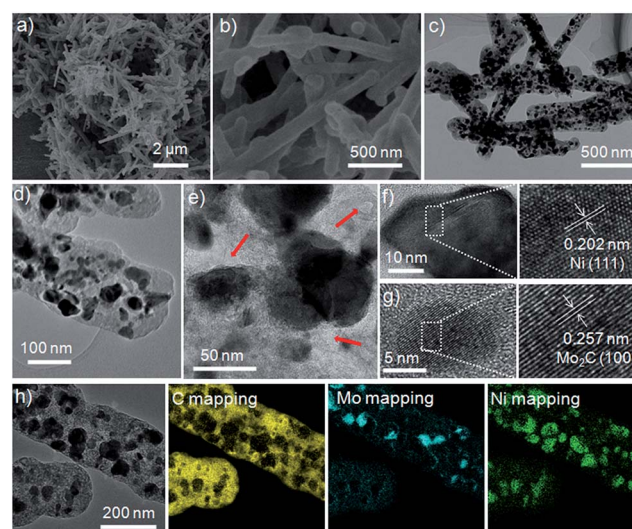


Fig. 2 (a) Low and (b) high magnification SEM images of Ni/Mo $_2$ C-PC. (c) Low and (d and e) high magnification TEM images of Ni/Mo $_2$ C-PC; the arrows in (e) show the porosity. (f and g) HRTEM images of (f) Ni and (g) Mo $_2$ C. (h) EELS elemental mapping images of C, Mo, and Ni.





To understand the potential HER enhanced mechanism behind this new composite catalyst, we performed X-ray photoelectron spectroscopy (XPS) studies on the relevant catalysts (Fig. S12, ESI†). We found that our Ni/Mo<sub>2</sub>C-PC composite catalyst was doped with nitrogen, owing to the use of a nitrogen-containing precursor. However, our results showed that the nitrogen content in the studied catalysts had little effect on the HER activity, although the nitrogen content in nitrogen-doped carbon was described to be crucial to the HER activity.<sup>50,51</sup> Therefore, we reasoned that the nitrogen dopant is not the main reason for the enhanced HER activity of Ni/Mo<sub>2</sub>C-PC (Fig. S12, ESI†). Due to the HER activity being sensitive to the valence states of metal element, we investigated the electronic structures of the Ni and Mo atoms with XPS.<sup>1,5</sup> Ni 2p XPS spectra showed that the Ni-PC sample mainly contained metallic state Ni, whereas the majority of surface Ni in Ni/Mo<sub>2</sub>C-PC was oxidized with a +2 oxidation state (Fig. 4a).<sup>52,53</sup> It is worth noting that Ni<sup>2+</sup> species are believed to be effective active sites for water dissociation (the Volmer step), which is the critical HER step and consistent with the Tafel slope.<sup>1,5</sup> Fig. 4b showed that the Mo 3d peaks in Ni/Mo<sub>2</sub>C-PC shifted to a lower binding energy as compared to Mo<sub>2</sub>C-PC, suggesting a lower Mo valence in the Ni/Mo<sub>2</sub>C-PC. Deconvolution of the Mo 3d XPS peaks (Fig. S12c, ESI†) provided detailed information on the Mo valence (0, +2, +3 and +4 for Ni/Mo<sub>2</sub>C-PC, and +2, +3, +4 and +6 for Mo<sub>2</sub>C-PC). Among these valence states of the Mo element, the Mo<sup>6+</sup> species were documented to be inactive for the HER,<sup>25,26</sup> suggesting that Ni/Mo<sub>2</sub>C-PC possibly has more HER active sites. According to these insights, we proposed that coupling Ni with Mo<sub>2</sub>C might enable electron transfer from Ni to Mo<sub>2</sub>C, leading to a higher Ni valence and lower Mo valence for the Ni/Mo<sub>2</sub>C-PC catalyst, as they were HER active and thus accounted for the enhanced HER activity.

Furthermore, Ni/Mo<sub>2</sub>C-PC was also found to be active for the OER in alkaline electrolyte (Fig. 5a). This composite catalyst delivered an onset potential of 270 mV and  $\eta_{10}$  of 368 mV, which are substantially superior to those of Ni-PC. Although the Ni content in Ni/Mo<sub>2</sub>C-PC (20.9 wt%) was lower than that in Ni-PC (47.6 wt%), Ni/Mo<sub>2</sub>C-PC had a higher content of Ni<sup>2+</sup> species based on the XPS studies, which can act as OER active sites. This is consistent with the observed larger redox peak (Ni<sup>2+</sup>/Ni<sup>3+</sup>) during the OER operation (Fig. S13, ESI†).<sup>5,52</sup> Therefore, the enhanced OER activity of Ni/Mo<sub>2</sub>C-PC can be ascribed to its

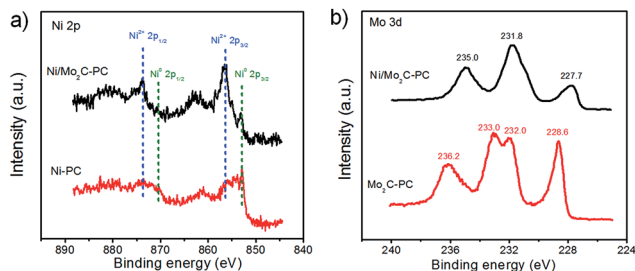


Fig. 4 (a) High-resolution Ni 2p XPS spectra for Ni/Mo<sub>2</sub>C-PC and Ni-PC. (b) High-resolution Mo 3d XPS spectra for Ni/Mo<sub>2</sub>C-PC and Mo<sub>2</sub>C-PC.

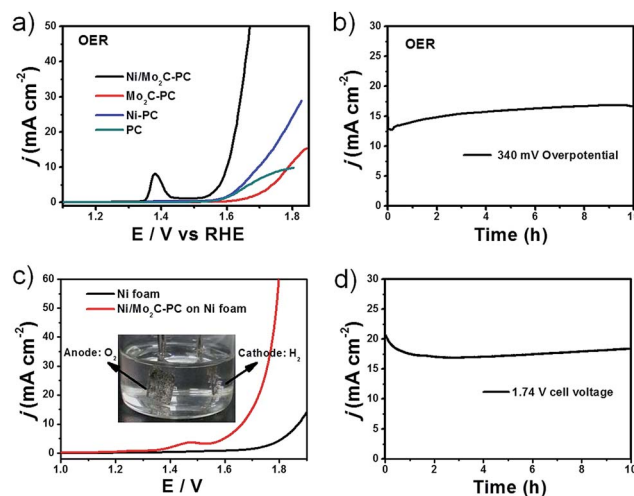


Fig. 5 OER and water-splitting tests in 1 M KOH. (a) OER polarization plots with a loading of 0.50 mg cm<sup>-2</sup> supported on a GC electrode. (b) The OER stability test for Ni/Mo<sub>2</sub>C-PC on Ni foam with a loading of 2 mg cm<sup>-2</sup>. (c) LSV curves of overall water splitting in a two-electrode configuration. The inset is the digital photo of H<sub>2</sub> and O<sub>2</sub> bubbles. (d) The stability of water splitting at an applied bias of 1.74 V for 10 h. The loadings of both cathode and anode for water splitting are 2 mg cm<sup>-2</sup> supported on Ni foam.

higher Ni valence resulting from the strong electron transfer. We note that the OER activity of Ni/Mo<sub>2</sub>C-PC is remarkable, even if compared with documented Ni-based OER catalysts (Table S2, ESI†). Moreover, this composite catalyst is extremely stable. Long-term stability tests demonstrated that it can catalyze the OER without any current loss but a certain increase for 10 h under harsh OER running conditions (Fig. 5b).

Its excellent bifunctional catalytic properties inspired us to examine the possibility of using Ni/Mo<sub>2</sub>C-PC for practical water splitting. In commercial alkaline electrolyzers, Ni foam was often used to support a catalyst, in view of its low cost, high conductivity and three-dimensional framework structure.<sup>33</sup> We thus loaded the Ni/Mo<sub>2</sub>C-PC catalyst on Ni foam and used it as both the cathode and anode for a home-made electrolyser (Fig. 5c and S14, ESI†). Water-splitting current densities of 10 and 50 mA cm<sup>-2</sup> can be achieved by applying cell voltages of 1.66 and 1.79 V, respectively, on the constructed device. The performance of Ni/Mo<sub>2</sub>C-PC as a dual catalyst for overall water splitting is excellent, performing better or comparably to other reported bifunctional water-splitting catalysts (Table S3, ESI†). Obvious H<sub>2</sub> and O<sub>2</sub> bubbles can be observed on the surface of both electrodes (inset in Fig. 5c). The long-term stability of the water-splitting reaction was evaluated by continuous operation at 1.74 V for 10 h (Fig. 5d). There was only a little degradation at the first hour, and after that the activity remained stable or even increased, demonstrating the excellent chemical stability and its great potential for real electrolyser systems. Lastly, we performed XRD and XPS measurements to analyze the variation of the Ni/Mo<sub>2</sub>C-PC catalyst after cyclic tests (Fig. S15, ESI†). Both the HER and OER cyclic tests didn't change the valence state of Ni, showing the high stability of Ni during the cyclic test. However, the Mo species wasn't very stable after long-term tests.



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