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2018

Zhang, Y., Ouyang, B., Xu, K., Xia, X., Zhang, Z., Rawat, R. S., & Fan, H. J. (2018).
Pre-reduction of metal oxides via carbon plasma treatment for efficient and stable
electrocatalytic hydrogen evolution. *Small*, 14(17), 1800340-. doi:10.1002/sml.201800340

<https://hdl.handle.net/10356/105548>

<https://doi.org/10.1002/sml.201800340>

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Pre-reduction of Metal Oxides via Carbon Plasma Treatment for Efficient and Stable Electrocatalytic Hydrogen Evolution

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Supporting Information is available online from Wiley InterScience or from the author.

Keyword: electrocatalysis; hydrogen evolution reaction; Carbon shell; metal oxide; plasma treatment

Abstract:

Pre-reduction of transition metal oxides is a feasible and efficient strategy to enhance their catalytic activity for hydrogen evolution. Unfortunately, the pre-reduction via the common H₂ annealing method is unstable for nano-materials during the hydrogen evolution process. In this study, using NiMoO₄ nanowire arrays as the example, we demonstrate that carbon plasma (C-plasma) treatment can greatly enhance both the catalytic activity and long-term stability of transition metal oxides for hydrogen evolution. The C-plasma treatment has two functions in one go; it induces partial surface reduction of the NiMoO₄ nanowire to form Ni₄Mo nanoclusters, and simultaneously deposits a thin graphitic carbon shell. As a result, the C-plasma treated NiMoO₄ can maintain its array morphology, chemical composition and catalytic activity during long-term intermittent hydrogen evolution process. This work may pave a new way to simultaneous activation and stabilization of transition metal oxide based electrocatalysts.

Hydrogen evolution from water splitting offers a sustainable method to acquire molecular hydrogen (H_2) fuel, an ideal alternative to fossil fuels without CO_2 emission.^[1-4] To make this technology viable, the catalyst in an electrolysis device should exhibit both high electrocatalytic activity and long-term durability. In this regard, catalysts based on precious metals, such as Pt, meet the above-mentioned characteristics, but their scarcity, high cost and poor stability are hindrance to any large-scale industrial H_2 production.^[5-7] Therefore, the realization of hydrogen economy relies largely on the development of high-efficiency, cost-effective and durable alternatives as HER electrocatalysts.

In the past few decades, intensive research efforts have been focused on transition metal based materials, such as nitrides,^[8, 9] carbides,^[10, 11] sulfides^[12-14], phosphides^[15-17] as efficient candidates for hydrogen evolution reaction (HER) catalysts due to their low cost, earth abundance and optimal strength of metal hydride bond (M-H). Nevertheless, most of the above catalysts are fabricated from high-temperature annealing in harsh environments that involve poisonous feedstock and byproduct. Even worse, the indispensable high temperature annealing process makes it nearly impossible to maintain the high-specific-area nanostructures, which is important for an efficient catalyst. In contrast, transitional metal oxides are easily available compound materials with a wide variety of nanostructures with high specific surface area.^[18] However, most of them fail to play an important role in hydrogen evolution due to their low electrical conductivity, sluggish catalytic kinetics and poor long-term stability. In this regard, it is highly desirable to improve the HER performance of transition metal oxides.

Recently, there has been a few reports that modulation of the local atomic structure via introducing oxygen vacancy could improve the HER activity for certain metal oxides ^{[19] [20]}. For example, Yang et. al. reported that the commercial WO_3 nanoparticles can show enhanced HER activity after annealing under H_2 atmosphere.^[20] In addition, we found that metal oxides (herein, $NiMoO_4$, Co_3O_4 and NiO) show a self-activation effect during the continuous hydrogen evolution process (**Figure S1**). The activity improvement is probably due to the surface reduction of metal oxides by the highly active hydrogen atoms that are produced on their surface during the HER process. This phenomenon is similar to the surface oxidation of some non-oxide catalysts during oxygen evolution reaction (OER) process.^[21, 22] However, this *in-situ* improvement by self-activation is slow (takes a few hours), transient, and extremely unstable; the catalytic activity degrades quickly when the H_2 evolution is interrupted (Figure S1d). So pre-reduction of metal oxides should be a more feasible and efficient strategy to improve their HER catalytic activity. H_2 annealing is a commonly employed for pre-reduction of metal oxides. Unfortunately, the high temperature and long annealing time may destroy the nanostructure. Also the reduction is still unstable and obvious degradation of HER catalytic activity is observed for the H_2 -annealed $NiMoO_4$, Co_3O_4 and NiO (see Figure S1d). Zhang et al. ^[23] and Chen et al. ^[24] treated $NiMoO_4$ nanorods by reducing under a H_2 atmosphere. While the electrodes after H_2 reduction show good catalytic

performance in both studies, the nanorod surfaces were directly exposed and might be subject to oxidation during operation in the KOH electrolyte. This has been demonstrated in our experiment (Figure S1d). Therefore, it becomes necessary that a surface modification to the transition metal oxides should simultaneously improve the catalytic activity and stability, and maintain the nanostructures.

Herein, we report a more efficient method to boost the HER catalytic activity of metal oxides with more stable performance via carbon plasma modification. Plasma treatment has been reported recently as a powerful approach for surface conversion reaction and modification of the electrode materials.^[25-30] In this work, we take NiMoO₄ nanowire arrays on carbon cloth as a case study. As show in the **Scheme 1**, after the C-plasma treatment, active species of Ni₄Mo nanoparticles are produced due to reduction of the NiMoO₄. And the nanowire array structure is well preserved due to a very short process time (30 s). In the meantime a thin outer layer of carbon shell is deposited on the nanowire surface, which assures the chemical stability by preventing oxidation. Benefiting from the high exposed surface active sites (nanowire array), the generated active Ni-Mo alloy nanoparticles and the protection of carbon shell, the C-plasma treated NiMoO₄ nanowire electrode displayed a low overpotential of 76 mV to reach 10 mA cm⁻² in 1 M KOH and superior duration in intermittent operation condition. This strategy is generic and also effective for Co₃O₄ nanowire arrays. Our work offers a feasible plasma-assisted strategy towards activation and stabilization of transition metal oxide based electrocatalysts.

Scheme 1. The preparation of C-plasma treated and H₂ annealed NiMoO₄.

To prepare the C-plasma treated NiMoO₄ electrocatalyst, the common NiMoO₄ nanowire arrays were fabricated via a solvothermal method. And then the obtained NiMoO₄ were treated under C-plasma atmosphere at different plasma discharge duration: 15, 30, and 60 s, corresponding to the products of C-15s, C-30s and C-60s, respectively, and presented in **Figure S2**. **Figure 1** shows the detailed morphological structures of the C-30s. The morphology of nanowire arrays was preserved and many nanoparticles with the diameter of 5-10 nm were separated out on the surface of nanowires (Figure 1a and b). In the high magnified transmission electron micrograph (TEM) images (Figure 1c and d), *d*-spacing of 0.208 nm and 0.180 nm were measured for the nanoparticles, which

corresponds to the (121) and (310) plane of the Ni_4Mo alloy (PDF# 65-5480). This indicates that Ni_4Mo alloy could be separated under the reductive atmosphere, which is in agreement with previous reports.^[23, 31] About 1-2 layers of carbon were coated on the surface of nanowire. By their nature of catalytic decomposition of ethanol, Ni_4Mo nanoparticles have a thicker carbon shell, which is around 2 nm, corresponding to 4 graphitic layers. Furthermore, a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image further confirmed that the metal nanoparticles decorated nanowires were formed (Figure 1e). As presented in the corresponding energy-dispersive X-ray (EDX) mappings, the Mo, O and C elements were homogeneously distributed throughout the whole nanowire, while the Ni element was distributed granularly on the surface with distinguishable particle boundaries. The STEM-EDX line analysis of the C-30s along the noted path in **Figure S3** further reveals the enrichment of Ni element. The energy dispersive spectroscopy confirms that the molar ratio of Ni to Mo is $\sim 1.05:1$ (Figure S3c). The X-ray diffraction (XRD) patterns in **Figure S4** confirm that NiMoO_4 was converted into Ni_4Mo and MoO_2 after 30 s C-plasma treatment.

Figure 1. Electron micrographs of C-30s: (a) SEM, (b-d) TEM and (e) STEM image and EDX elemental mapping.

Figure 2. High-resolution XPS for NiMoO₄ and C-30s (a) Ni 2p_{3/2}; (b) O 1s; (c) Mo 3d, and (d) C 1s.

The surface chemical composition and valence states of samples were further characterized by X-ray photoelectron spectroscopy (XPS; **Figure 2** and **Figure S5**). Four elements including Ni, Mo, O and C were identified from the XPS spectra (Figure S5a), consistent with EDX mapping results. With the increasing treatment duration, the peak intensities of Ni, Mo and O became weaker, while the peak intensities of C became stronger. For C-60s, the layer of carbon was too thick to detect the signal of Ni, Mo and O. For the high resolution spectra of Ni 2p (Figure 2a), the peak at 855.6 eV and its broad satellite peak at 861.8 eV belongs to Ni²⁺. After 30 s C-plasma treatment, the new peak at 852.4 is indexed to metallic Ni.^[32] The partial reduction of NiMoO₄ under C-plasma treatment could also be seen from the O 1s spectra (Figure 2b). As exhibited, the intensity of the peak at 530.7 eV, corresponding to the O²⁻ ions in the crystal line of NiMoO₄, decreased for the C-30s sample.^[21] A new peak from the surface groups of carbon shell appeared at 531.8 eV. The Mo 3d spectra in Figure 2c displays a new peak at low binding energy at 229.4 eV after C-plasma treatment, which attributes to low valence Mo^{δ+} species ($\delta=0, 1, 2, 3$).^[33] The percentage of Mo^{δ+} in C-30s is 40.2%, which is higher than that of C-15s (12.7%) as compared in Table S1 (Figure S5b). The ratio of Ni:Mo is around 1.1:1 based on the XPS spectra of Ni 2p and Mo 3d. The slight higher ratio of Ni element is probably due to the enrichment of Ni on the surface. The C 1s spectra in Figure 2d only manifest the graphitic carbon at 284.3 eV, and no carbide peak (lower binding energy, ≈ 282.7 eV) was observed.

Figure 3. Electrochemical test of all samples: (a) LSV curves; (b) Tafel slopes; (c) Comparison of η_{10} values (potentials required to reach 10 mA cm⁻² and Tafel slopes for all catalysts; (d) Nyquist plots at 10 mA cm⁻².

The electrocatalytic activity of all samples for HER were evaluated by a three-electrode system in 1 M KOH (**Figure 3**) and compared to the state-of-the-art Pt/C electrocatalysts. Carbon rod was used as the counter electrode to avoid the possible contamination of Pt. The polarization curves at a sweep rate of 5 mV s⁻¹ after iR-correction show an increase in the HER activity in the following order: NiMoO₄, C-15s, C-60s, C-30s and Pt/C. The overpotential of only 76 mV is required for C-30s sample to reach a current density of 10 mA cm⁻² (η_{10}), which is slightly higher than that of Pt/C (45 mV) and obviously lower than that of NiMoO₄ (406 mV), C-15s (135 mV) and C-60s (152 mV). The inferior HER activity of C-60s attributes to the thicker and hollow carbon shell, which blocks the active sites from electrolyte. In addition, the overpotential of C-30s is only 287 mV to reach a high current density of 300 mA cm⁻² (**Figure S6**). The Tafel slope, as one of the experimental descriptor to study the HER kinetics, were obtained by plotting the overpotential versus the logarithm of the absolute value of current density (Figure 3b). The Tafel slope of C-30s (78 mV dec⁻¹) is smaller than those of NiMoO₄ (130 mV dec⁻¹), C-15s (106 mV dec⁻¹) and C-60s (103 mV dec⁻¹). The comparison of Tafel slope versus η_{10} value for all of the studied catalysts in Figure 3c has clearly shown that the C-plasma treated NiMoO₄ had significantly improve the HER catalytic activity (larger current density and faster HER rates). The C-30s electrode exhibits comparable HER catalytic activity to those transition metal-based materials reported in the literature (Table S2). To better understand the superior HER activity of C-plasma treated NiMoO₄, their electrochemical impedance spectroscopies (EIS) were carried out to study the kinetics occurring at the electrode/electrolyte surface under HER conditions. The typical Nyquist plots in Figure 3d depict the diameter of the semicircles decreased in the following order: NiMoO₄, C-15s, C-60s and C-30s, indicating that C-30s has the fastest electron transfer and HER activation.

Figure 4. Stability test. (a) Pristine NiMoO₄ nanowire, and C-30s sample, as well as another sample after H₂ treatment. (b) LSV curves of the C-30s electrode under different HER test stage. (c) C-30s at different overpotentials (without iR-correction).

The C-30s sample also exhibits an excellent long-term electrochemical stability. As shown in **Figure 4**, Electrolysis at three constant current densities (10, 30 and 50 mA cm⁻²) was carried out sequentially over 36 h (Figure 4a). The overpotentials at different current densities show a relatively small fluctuation after each 12 h electrolysis (-4, 8 and 17 mV at 10, 30 and 50 mA cm⁻², respectively). The slight decrease of overpotential at 10 mA cm⁻² was probably due to the penetration of electrolyte to expose more active sites. The degradation at 30 and 50 mA cm⁻² was partially due to reduced active sites caused by the physical adsorption of the generated H₂. As shown in Figure 4b, the linear sweep voltammetry (LSV) curves after electrolysis at different current densities almost overlap with the original one. In addition, a multistep chronoamperometric curve was recorded in a wide overpotential range (from 50 mV to 500 mV) with an increment of 50 mV (Figure 4c). The response current densities remain constant at each step, implying the excellent mass transportation, conductivity, and mechanical robustness of the C-30s electrode.

The electrode also maintains its morphology and chemical composition after the 36 h stability test (**Figure 5**). The nanowire array morphology and the layer of carbon shell were well preserved, as shown by SEM and TEM images in Figure 5a and b. The Ni₄Mo nanoparticles are clearly observed in nanowires, owing to the protection provided by the carbon shell. We also compare the XPS spectra of Ni and Mo before and after stability test (Figure 5c and 5d). The peaks due to both Ni⁰ and Mo^{δ+} remain except for slight decrease in their intensities. This verifies that the C-30s sample is not only a highly active but also a very stable electrocatalyst for HER in alkaline medium.

Figure 5. C-30s sample after stability test. a) SEM, b) TEM, c) Ni 2p_{3/2} XPS spectra, and d) Mo 3d XPS spectra

In order to verify the contribution of C shell, we intentionally synthesized a hydrogen-reduced NiMoO₄ nanowires film in gas ambient (H₂-1h) and investigated its catalytic enhancement and stability. Surface treatment of the NiMoO₄ nanowires in a H₂ gas ambient can also improve the catalyst activity, but cannot solve instability problem. The synthetic and structural details of H₂-1h were presented in the Experimental Section and **Figure S7**. The SEM image (Figure S7a) and XRD pattern (Figure S7b) confirmed that indeed Ni₄Mo nanoparticles were formed on the surface of nanowires, similar to carbon-plasma reduction. Furthermore, the surface chemical composition and valence states of H₂-1h were the same as those of C-30s (XPS of Ni and Mo in Figure S8d and e). A current density of 10 mA cm⁻² was achieved with an overpotential of only 60 mV in 1 M KOH, which was better than that of C-30s (76 mV) (Figure S7c). However, it is quite unstable. After 1-2 h stability test at 10 mA cm⁻², the overpotential of H₂-1h was higher than that of C-30s (Figure 4a). If soaking the H₂-1h in electrolyte for only 30 min, the η_{10} would sharply increase to ~223 mV (Figure S7c). The XPS spectra of Ni and Mo, after the 30 min soaking (Figure S8d and e), showed that both peaks for Ni⁰ and Mo^{δ+} disappeared. So the active sites are most likely Ni₄Mo and low valence (Mo^{δ+}).^[34] To further check their chemical stability, the NiMoO₄, H₂-1h and C-30s samples were immersed in 1 M KOH solution for 12 h (without electrochemical measurement). We found the nanowire arrays of the NiMoO₄ and H₂-1h samples almost disappeared, but not the C-30s (**Figure S8**). This indicates that the carbon shell effectively protects the active materials from dissolution in KOH solution.

Finally, to further demonstrate the versatility of our fabrication strategy, we also used C-plasma to treat Co₃O₄ nanowire arrays (data presented in **Figure S9**). After the C-plasma treatment, the

nanowire morphology was retained and lower valence CoO phase was generated. Similarly, a thin layer of graphitic carbon shell formed on the CoO nanowire surface. Compared with H₂ annealing, the pre-reduction of Co₃O₄ via C-plasma treatment not only improve the HER catalytic activity but also the longtime stability.

In summary, we have demonstrated that pre-reduction of transition metal oxides is an efficient method to greatly improve their catalytic activity for hydrogen evolution. Compared with the common H₂ annealing, the C-plasma treatment not only has a reduction reaction function, but also leads to a concurrent encapsulation of the whole nanowire with a thin layer of graphitic carbon. Benefiting from the protection of carbon shell, the modified metal oxide exhibits outstanding physical and chemical stability under longtime and intermittent operation for hydrogen evolution. We show that this strategy is generic and also effective to other metal oxides (such as Co₃O₄), which paves a new way to exploit transition metal oxide materials as highly activity and stable HER catalysts to compete against precious metals.

Experimental details

Material synthesis: Nickel acetate (NiAc₂·4H₂O, 1.24 g) and ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, 1 g) were added to a mixed solution (30 mL deionized (DI) water and 30 mL ethylene glycol) under magnetic stirring to give a green solution. Then, the solution was transferred into a Teflon-lined stainless steel autoclave liner. A piece of clean carbon cloth was immersed into the reaction solution. The liner was sealed in a stainless steel autoclave and maintained at 140 °C for 10 h. After cooling to room temperature, samples were washed with DI water and ethanol in sequence, dried in oven at 60 °C and then annealed in furnace at 450 °C under Ar atmosphere for 30 min to remove moisture. The average mass was about 1.2 mg cm⁻². Finally, the NiMoO₄ were directly subjected to C-plasma to be modified. After NiMoO₄ was inserted into the reactor chamber, the temperature of chamber was increased to 450 °C and the pressure was pumped down to 0.2 mbar. Subsequently, a feedstock of ethanol was introduced. The RF-plasma discharge was conducted at 300 W and 13.56 MHz for different treatment time, i.e., 15, 30 and 60 s and the resulting products were denoted as C-15s, C-30s and C-60s, respectively.

For comparison, the obtained NiMoO₄ was partially reduced via heating under H₂/Ar (2:98) atmosphere at 450 °C for 1 h with 100 sccm.

Co₃O₄ nanowire arrays grown on Ni foam were fabricated as previous report.^[21] And the plasma parameters are the same as that for NiMoO₄ and the treatment time was 30 s.

Sample characterization: The morphology and phase of samples were characterized by field emission scanning electron microscopy (FESEM, FEI SIRION), X-ray diffraction (XRD, 6000 Shimadzu), high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 20), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Theta Probe).

Electrochemical characterization: All electrochemical measurements were performed on an electrochemical workstation (Zahner zennium, Germany) in a glass cell with a three-electrode setup. The samples were used as the working electrode; carbon rod (D=8 mm) and Ag/AgCl (3 M KCl) were used as the counter electrode and reference electrode, respectively. 1 M KOH solution (pH=13.6) was used as the electrolyte. All potential were calculated with respect to reversible hydrogen electrode (RHE) via the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \text{ pH} + 0.210 \text{ V}$. All samples were firstly conducted the

cyclic voltammetry (CV) test to get a stable curve at 50 mV s⁻¹. Linear sweep voltammetry (LSV) and chronoamperometric tests were conducted to evaluate the HER catalytic activity of the samples. The LSV tests were carried out at a scan rate of 5 mV s⁻¹. The Tafel plots were derived from LSV curves which were tested at the scan rate of 1 mV s⁻¹. The electrochemical impedance spectroscopies (EIS) were conducted at the current density of 10 mA cm⁻², in a frequency from 100 kHz to 50 mHz with an AC amplitude of 5 mV.

Acknowledgement

This work is supported by National Natural Science Foundation of China (Grant. No. 51728204). It is also supported by the Singapore MOE AcRF Tier 1 grant (RG98/15) and Tier 2 grant (MOE2017-T2-1-073). We thank Qiaobao Zhang for the STEM image and EDS elemental mapping measurement (Xiamen University).

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