Pomegranate-like molybdenum phosphide@phosphorus-doped carbon nanospheres coupled with carbon nanotubes for efficient hydrogen evolution reaction

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ABSTRACT

Rational design and synthesis of low-cost electrocatalysts with high-performance is of urgency for hydrogen evolution reaction (HER). Herein, we report a facile synthetic approach to construct a pomegranate-like MoP@P-doped porous carbon nanospheres coupled with carbon nanotubes (CNTs) composite using metal-organic frameworks-CNTs hybrid as precursor, which was successfully employed as a robust electrocatalyst for the HER. Ascribed to the distinct nanostructure together with the synergistic coupling, the resultant composite exhibits highly efficient electrocatalytic performance, featured by a low onset overpotential of 75 mV, small Tafel slope of 55.9 mV dec⁻¹, as well as long-term stability for 10 h, which is comparable or even superior to the best MoP-based catalysts toward HER up to now. More importantly, this strategy can provide a new route in the construction of highly efficient Pt-free electrocatalysts for energy conversion fields.

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1. Introduction

To overcome environmental crisis and energy shortage issues, hydrogen (H₂), as clean, sustainable, and renewable energy, has stimulated extensive research. In terms of large-scale H₂ production, electrochemical water splitting is widely regarded as an effective approach to produce high-purity H₂ [1,2]. Currently, the highest performing electrocatalysts toward hydrogen evolution reaction (HER) are platinum-based nanomaterials owing to their extraordinary catalytic activity. Unfortunately, the low-abundance and high-cost critically limited their widespread applications [3,4]. As a consequence, seeking and exploring earth-abundance and inexpensive non-precious metal HER catalysts with high efficiency become a hot subject in the catalytic field.

In the past few years, 3d transition metal (TM)-based materials such as sulfides [5–9], carbides [10–14], nitrides [15–17], and phosphide [18–22], have attracted great interest as potential alternatives for HER, due to their abundance and favorable activity. Especially, molybdenum phosphide (MoP)-based composites as outstanding HER electrocatalysts have been a focus of research owing to their high activity and electrical conductivity [23–29]. Regrettfully, their electrocatalytic performance is still far from satisfactory in comparison with noble metal-based nanomaterials, which is associated with aggregation and surface oxidation of MoP nanoparticles during preparation and long-term storage. To further boost their catalytic activity, coupling TM-based catalysts with carbon materials (graphene, carbon nanotubes (CNTs), etc.) is frequently identified as a hopeful strategy to increase the conductivity and facilitate the electron transfer [30–36]. Although substantial progress have been achieved in enhancing HER catalytic performance, rational design and development of high-efficiency catalysts toward HER is still at its infancy stage.

Metal-organic frameworks (MOFs)-derived functional materials have received much attention due to their fascinating physical and chemical properties [37–43]. Noteworthily, polyoxometalate-based MOFs (POMOFs), as a new class of MOFs, can be considered as ideal...
candidates to synthesize Mo, W, and V-contained materials, which are almost impossible to implement using sole MOFs as precursors [44]. Despite a considerable development in the field of POMOFs, until now there have been few reports of the exploration of Mo-based electrocatalysts derived from POMOFs for HER [45–48]. In particular, to the best of our knowledge, little attention has been paid to the investigation of MoP-based materials utilizing POMOFs-CNTs composite as precursor toward HER.

Inspired by the above-mentioned, we herein have ingeniously conceived and fabricated pomegranate-like Mo@P-doped porous carbon nanospheres accompanied with CNTs nanocomposite (denoted as Mo@PC-CNTs) through a POMOFs-assisted method. Impressively, the resultant Mo@PC-CNTs is endowed with three prominent features: (1) small-sized Mo nanoparticle seeds can be confined in P-doped carbon shell as peel; (2) porous structures; (3) the introduction of CNTs can not only boost the interfacial contact between nanospheres, but offer more sufficient catalytic sites. Benefitting from these merits, the composite exhibits superior electrocatalytic properties and prominent long-term stability for the HER, which can even compete the recently reported MoP-based electrocatalysts for hydrogen production.

2. Experimental

2.1. Materials

Copper acetate monohydrate (Cu(OAc)2·H2O), phosphomolybdic acid (H3PMo12O40·nH2O), phosphotungstic acid (H3PW12O40·nH2O), polyvinylpyrrolidone (PVP, K30), l-glutamic acid (C5H9NO4), 1,3,5-benzenetricarboxylic acid (H3BTC, 98%), iron (III) chloride hexahydrate (FeCl3·6H2O) and diammonium hydrogen phosphate ((NH4)2HPO4) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Synthesis of pretreatment of CNTs

2 g of pristine CNTs were refluxed in a 300 mL mixture of sulfuric acid and nitric acid (1:3) in a water bath at 80 °C for 3 h with stirring. And then, the resulting sample was collected by filtration and rinsed with ultra-purified water until the pH value was 7.0, then dried at 80 °C for 12 h.

2.3. Synthesis of NENU-5-CNTs and NENU-5

In a typical procedure, 10 mg of pretreated CNTs and 200 mg of PVP were first added in 40 mL of ultra-purified water. After sonication for 2 h, 0.2 g of Cu(OAc)2·H2O, 0.3 g of H3PMo12O40·nH2O and 0.07 g of C6H3NO4 were dissolved into form solution A. H3BTC (0.14 g) was dispersed in an equal amount of water, and then added dropwise into A. After vigorous stirring for 16 h, the product was cleansed with alcohol/water for several times and dried at 70 °C in vacuum (defined as NENU-5-CNTs).

For comparison, NENU-5 was synthesized under the same condition without adding CNTs.

2.4. Synthesis of MoO2@PC-CNTs and MoO2@PC

The NENU-5-CNTs was calcined at 600 °C for 6 h under Ar gas flow; and then, the sample was dispersed in 0.1 M FeCl3 solution and stirred for 6 h to remove metallic Cu. The resulting sample was collected by filtration, washed with ultra-purified water and dried under vacuum at 70 °C (termed MoO2@PC-CNTs).

In control experiment, MoO2@PC was gained by the identical method as that for MoO2@PC-CNTs using NENU-5 as precursors.

2.5. Synthesis of MoP@PC-CNTs and MoP@PC

The prepared MoO2@PC-CNTs (100 mg) was placed in a tube furnace, and (NH4)2HPO4 (500 mg) was put at the upstream side. Under H2/Ar, the heating temperature was elevated to 850°C for 2 h, and the final product was named as MoO2@PC-CNTs. In control experiments, MoP@PC-CNTs (5 mg) and MoP@PC-CNTs (15 mg) were also synthesized by identical condition except that the content of CNTs is 5 and 15 mg, respectively.

In addition, the MoP@PC was prepared by a similar approach, but utilizing MoO2@PC as raw materials, respectively.

2.6. Instruments

The surface morphologies of these materials were characterized by transmission electron microscopy (TEM, JEOL-2100F), scanning electron microscope (SEM, JSM-7600F). The powder X-Ray diffraction (XRD) patterns were carried out on a D/max 2500VL/PC diffractometer equipped with Cu Kα line (λ = 1.5406 Å). X-ray photon spectroscopy (XPS) analysis was performed on PHI 5000 Versa using Al Kα X-ray source. Nitrogen sorption isotherms were measured on a Micromeritics ASAP 2050 system. Surface area was determined according to Barret-Joyner-Halenda (BJH) model.

2.7. Electrochemical study

The electrochemical evaluations were conducted by an electrochemistry workstation (CHI 760D). A saturated calomel electrode (SCE) is utilized as a reference electrode. A graphite rod is used as a counter electrode. The sample-coated glassy carbon electrode (GCE, 0.0706 cm2) is adopted as a working electrode. The sample ink is composed of 4 mg sample dispersed in 2 mL of ultra-purified water/ethanol solution (3:1 v/v %) and sonicated for 12 h. Subsequently, 5 µL sample ink was dropped on the GCE and dried at ambient condition. Finally, the working electrode was achieved by dropping 5 µL Nafion solution (0.1 wt%) on the surface of GCE. The sample loading is ~0.14 mg cm−2. The measured potentials were converted to a reversible hydrogen electrode (RHE) without IR correction. In 0.5 M H2SO4 (pH = 0), E RHE = E SCE + 0.241 V.

Linear sweep voltammetry (LSV) at a scan rate of 2 mV s−1 was performed in 0.5 M H2SO4 (pH = 0) with high-purity N2. Stability was tested by cyclic voltammograms (CVs) at 100 mV s−1. Meanwhile, the accelerated durability was also characterized by chronoamperometry (CA) at 10 mA cm−2 current density. The electrochemical active surface areas of these catalysts were measured by using CV within −59 - 41 mV with various scan rates ranging from 20 to 200 mV s−1.

3. Results and discussion

As exhibited in Fig. 1, a multi-step method was performed to fabricate well-defined MoP@PC-CNTs composite. Firstly, the NENU-5-CNTs achieved by a facile solution method at ambient temperature were carbonized at 600 °C for 6 h, where PMo12 were completely converted into MoO2. At the same time, Cu ions were reduced to metallic Cu nanoparticles. In order to remove metallic Cu, the resultant sample was subsequently etched with FeCl3 solution. Finally, the MoP@PC-CNTs was obtained after phosphidation, where (NH4)2HPO4 was used as a phosphorus source.
Interestingly, the in situ generated MoP nanocrystals as seeds were encapsulated into P-doped porous carbon matrix as peel, further forming pomegranate-like MoP@PC nanospheres. The representative scanning electron microscopy (SEM) images of NENU-5-CNTs in Fig. S1a, b show that the NENU-5 nanospheres with a size of about 300 nm and smooth surface were in situ coated on the CNTs backbone. From Fig. S1c, the transmission electron microscopy (TEM) image reveals that the uniformly distributed NENU-5 nanospheres are closely intertwined with CNTs. Simultaneously, it is clearly observed that CNTs stretch out from the surface of a NENU-5 crystal, further stringing other NENU-5 crystals together, which is beneficial to improve the connection among crystals. As displayed in Fig. S1d, the powder X-ray diffraction (PXRD) spectra of NENU-5-CNTs matches well with the simulated crystals. As displayed in Fig. S1c, the transmission electron microscopy (TEM) image reveals that the uniformly distributed NENU-5 nanospheres are closely intertwined with CNTs.

As exhibited in Fig. 2b and c, the interpenetration is also confirmed by the clear observation of CNTs penetrating throughout the nanospheres and connecting with the adjacent ones. This unique structure would be expected to form a connected conductive network and provide abundant active interfaces and robust conjugation between MoP@PC and CNTs [32,50]. Plentiful of nanoparticles (dark spots) encapsulated in a carbon shell were probed. However, it was found that a small part of MoP nanoparticles is outside the carbon shell after carbonization and phosphidation processes. This may be attributed to the following reason: in the synthetic process, a very small amount of H3PMo12O40 may be adsorbed on the surface of CNTs, which were not encapsulated by NENU crystals. The high-resolution (HR) TEM in the inset of Fig. 2b demonstrates well-defined lattice fringes of 0.21 and 0.34 nm, which match with the (010) facet of hexagonal MoP and (002) plane of graphitic carbon, respectively, reconfirming that these dark nanoparticles should be MoP nanocrystals. The elemental mapping images in Fig. 2d–g shows the existence of C, Mo, and P elements in the MoP@PC-CNTs composite and the CNTs backbone is decorated with MoP@PC. Also, it is found that the elemental distribution profiles of P and Mo are very similar, implying that MoP nanoparticles was successfully fabricated and partial P atoms were also doped into carbon matrix. Therefore, the above results unambiguously prove that a pomegranate-like nanospherical morphology with MoP nanocrystals as seeds and P-doped carbon layers as shell was formed, and coated on the CNTs backbone. From Fig. 2h, the PXRD shows the characteristic peaks at 27.91, 32.03, 43.01, 57.19, 64.74, 67.54, and 74.08°, indexed to (001), (100), (110), (111), (102), and (201) planes of hexagonal MoP (JCPDS, No. 65–6487), respectively. No other peaks are detected except for the weak (002) diffraction peak of graphitic carbon located at 26°, which may stem from the loading of MoP with high density. The surface area of MoP@PC-CNTs is 355 m² g⁻¹ calculated by Brunauer-Emmett-Teller analysis, which favors the exposure of more active sites. The corresponding pore size distribution is mainly centered at 3.7 nm (Fig. 2i), which can provide effective channels to promote mass transfer and numerous accessible catalytic sites toward HER [23,24,27].

As a comparison, MoO2@PC-CNTs and MoP@PC were achieved and characterized in detail. As seen from Fig. S2, the morphology of MoO2@PC-CNTs is similar to that of MoP@PC-CNTs; whereas the MoP@PC hybrid exhibits an octahedral or slightly truncated octahedral morphology. In this regard, it can verify that the existence of CNTs has a significant influence on the morphologies of the resultant samples, further affecting their electrocatalytic properties for HER. To further support the attribution of MoP species in MoP@PC-CNTs, the PXRD pattern also validates the successful synthesis of MoO2@PC-CNTs and MoP@PC.

X-ray photoelectron spectroscopy (XPS) was further employed to identify the chemical state and composition in the MoP@PC-CNTs hybrid. From Fig. 3a, the survey spectrum demonstrates the coexistence of C, P, Mo, and O elements. As observed from Fig. 3b, the high-resolution C1s XPS can be fitted to four peaks at 284.7, 285.2, 286.5 and 290.4 eV, assignable to C–C/C–C, C–P, C–O, and O–C–O, respectively [45]. In terms of P 2p (Fig. 3c), the binding energies are related to 129.6 eV for P 2p1/2 and 130.5 eV for P 2p3/2, signifying the formation of MoP [23,27]. Additionally, the rest of two peaks are presented at 132.8 eV accompanied with P–C and 133.9 eV, assigned to P–O, respectively [10]. Fig. 3d shows the high-resolution scan Mo 3d electrons, which could be fitted into three doublets. Among them, the doublet (228.4/231.5 eV) can be assigned to Mo species in MoP@PC-CNTs, which are regarded as the active sites for HER [24,28]. The additional two doublets located at 229.2/232.2 eV (Mo4+) and 232.25/236.1 eV (Mo6+) are ascribed to MoO2 and MoO3, which is related to the high surface energy of MoP, as previously reported [10,23,48]. For comparison, MoO2@PC-CNTs and MoP@PC were also investigated by XPS, demonstrated in Fig. S4–5, respectively. It can be seen that these results are similar to those for MoP@PC-CNTs. The corresponding atomic percent of various catalysts are described in Table S1.

To assess the electrocatalytic performance of these materials towards the HER, a standard three-electrode system was carried out in 0.5 M H2SO4 solution. As a comparison, CNTs, MoO2@PC-CNTs, MoP@PC, and 20% Pt–C were also examined. Fig. 4a displays the polarization curves of different samples without IR compensation. As observed, commercial 20% Pt–C shows outstanding HER activity; however, CNTs and MoO2@PC-CNTs indicate relatively poor catalytic performance for the HER. In sharp contrast, MoP@PC-CNTs possesses a low onset potential (−75 mV) as compared to that of MoP@PC (−104 mV). Moreover, the current density rises rapidly as applied potential becomes more negative. Impressively, the MoP@PC-CNTs requires an overpotential of approximate 220 mV to derive the current density of 10 mA cm⁻², which outperforms that of MoP@PC (282 mV).

To further understand the HER mechanism, the Tafel slopes of as-prepared electrocatalysts were analyzed by extrapolating the corresponding polarization curves based on Tafel equation (\(\eta = b \log (i) + a\), where \(b\) is the Tafel slope), demonstrated in Fig. 4b. Strikingly, the MoP@PC-CNTs has the smallest Tafel slope of
55.9 mV dec⁻¹ than those of MoP@PC (61.1 mV dec⁻¹), MoO₂@PC-CNTs (260.7 mV dec⁻¹), and CNTs (238.2 mV dec⁻¹); but it is still inferior to that of commercial 20% Pt-C (30 mV dec⁻¹) [27,45,46]. This results imply the favorable HER kinetics via a Volmer-Heyrovsky mechanism with the rate-limiting step of the electrochemical desorption [31,45]. It is worth mentioning that the value of Tafel slope for MoP@PC-CNTs is comparable to or obviously lower than those of recently reported MoP-based nanomaterials for HER (Table S2) [23,24,27,28]. As per our best knowledge, such a small Tafel slope accompanying with a remarkably low onset overpotential has rarely been reported for MoP-based electrocatalysts, strongly supporting the prominent HER activity of MoP@PC-CNTs.

Stability is a critical parameter for the practical application of electrocatalysts for HER. From Fig. 4d, the current-time chronoamperometric response of MoP@PC-CNTs presents a much slower decay rate and 90.1% of the initial current could be still maintained for at least 10 h. Meanwhile, continuous CV sweeps were tested from –200 to 200 mV at a scan rate of 100 mV s⁻¹. The inset of Fig. 4d exhibits negligible change after 1000 cycles. All the results highlight that the as-synthesized MoP@PC-CNTs composite...
exhibits not only high-efficiency HER activity but also good durability in acidic solution.

In consideration of the mentioned results, the excellent electrochemical performance of MoP@PC-CNTs for the HER can be assigned to the special constitutions and structural superiority. (i) As is well known, MoP nanoparticles possess excellent electrocatalytic activity for HER due to its Pt-like electronic structure [28,29]. Equally important, the dopant of P could regulate the electronic structure of carbon, which contribute to the improvement of catalytic performance for HER [10,45]. (ii)
pomegranate-like structure affords accessible and rich active sites [14]. Likewise, the carbon layer can provide powerful protection for highly active MoP nanoparticles; the mesopores are beneficial to the significant mass transfer and the effective exposure of catalytic sites toward the HER [23,24,48]. (iii) The interconnected network formed by outstretched CNTs enhances the electron transportation and provides effective long-range conductivity. Just as importantly, the functional integration of P-doped carbon nanospheres and CNTs can reduce electrochemical impedance and improve the long-term stability [31,32,50].

To examine the effect of CNTs content on the HER activity, MoP@PC-CNTs with different loadings of CNTs (5 and 15 mg) were as-synthesized through the same method. From the aspect of the onset overpotential and Tafel slope toward the HER (Fig. 5), the MoP@PC-CNTs (10 mg) composite manifests the optimum combination of MoP@PC and CNTs, which can be further proven by the SEM and TEM images (Fig. S7). Namely, due to the lower amount of CNTs in MoP@PC-CNTs (5 mg), the corresponding electrical conductivity was inferior to that of MoP@PC-CNTs (10 mg). Whereas, in the case of MoP@PC-CNTs (15 mg), the content of MoP as the catalytic sites was dramatically decreased with the increase of the amount of CNTs. Consequently, the result reveals that, although the content of CNTs has significant influence on the electrocatalytic activity toward the HER, they are not the only determinant for enhanced catalytic performance. In other words, it can be reasonably presumed that a perfect balance between conductivity and active sites is desired for achieving the optimal electrochemical performance for the HER.

4. Conclusions

In summary, utilizing POMOFs-CNTs composite as precursor, the pomegranate-like MoP@PC coupled with carbon nanotubes hybrid has been synthesized through a facile carbonization followed by phosphidation process for the first time. Amazingly, owing to the pore confinement effect of MOFs, MoP nanoparticles can be effectively encapsulated in the porous carbon matrix as seeds. As well, the carbon shell stemming from the organic ligands as peel can both protect from surface oxidation and agglomeration of MoP nanoparticles and function as an electron highway. Moreover, the incorporation of CNTs contributes to the enhancement of long-range conductivity. Taking advantage of the rationally designed components and unique nanostructural advantage, the composite exhibits remarkably enhanced catalytic activity and excellent stability toward the HER. As a result, this work can provide more opportunities to develop competitive alternatives to Pt-based nanomaterials for various applications such as hydrogen evolution, oxygen evolution, and battery applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2018.06.058.

References


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