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Facile synthesis of various highly dispersive CoP nanocrystal embedded carbon matrices as efficient electrocatalysts for the hydrogen evolution reaction[†]

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In order to promote the hydrogen evolution reaction (HER) catalytic efficiency of cobalt phosphide (CoP) and then construct efficient HER catalysts, a facile procedure has been adopted to prepare tiny CoP nanoparticle (NP) embedded carbon matrices without using any extreme conditions and harmful organic reagents or surfactants. Meanwhile, in order to explore the influence of structures of carbon matrices on preventing the free growth of CoP NPs and enhancing the HER catalytic efficiency of the CoP-carbon catalysts, imporous reduced graphene oxide (RGO), macroporous carbon (MPC), mesoporous carbon vesicles (MCVs) and ordered mesoporous carbon (OMC) were used for preparing CoP-carbon HER catalysts. SEM and TEM measurements show that size-controlled CoP NPs indeed grew more uniformly on the OMC frameworks than those on MCVs, MPC and RGO. As expected, the HER is catalyzed more efficiently on CoP-OMC accompanied by a small onset potential of -77.74 mV vs. RHE, a low Tafel slope of 56.67 mV dec⁻¹, a small over-potential value of 112.18 mV at 10 mA cm⁻², and the outstanding long-term stability. These results show that CoP-OMC inherently exhibits better HER catalytic activity than other CoP-based catalysts in acidic electrolytes. Such excellent performances are attributed to the synergistic effect of the highly catalytic sites provided by the uniformly dispersed and size-controlled CoP NPs embedded on OMC, excellent proton transport efficiency, and improved electron transport with a high electron transfer rate. Our results provide useful information that the mesoporous conductive matrices could be applied to greatly improve the HER catalytic efficiency of various HER catalytically active centers.

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Introduction

Hydrogen, a clean energy carrier, being the cleanest of all fuels, has long been expected to play a pivotal role in our energy landscapes by mitigating (if not completely eliminating) our reliance on fossil fuels. However, molecular hydrogen does not exist naturally on earth. Although molecular hydrogen could be obtained from water (the most abundant and renewable hydrogen source) by the water-splitting reaction, it is inherently quite difficult. The production of molecular hydrogen by the electrochemical reduction of water is an important component of several developing clean-energy technologies. Similarly, it is also necessary to use efficient hydrogen evolution reaction (HER) electrocatalysts to increase the reaction rate and lower the over-potential of water electrolysis. As expected, platinum group metals are the most efficient catalysts for the HER, capable of driving significant currents close to the thermodynamic potential.^{1,2} However, noble metals are unsuitable for large scale hydrogen production because of their scarcity and high cost. It is therefore important to explore efficient alternatives made entirely of earth-abundant elements to noble metals for the HER. Abundant nickel-based alloys are often used commercially as HER catalysts functioning in alkaline electrolytes.3,4 Unfortunately, these HER catalysts cannot work under the strongly acidic conditions involved in the proton-exchange membrane (PEM) technique and thus lack compatibility with PEM-based electrolysis units.5 The development of acid-stable non-noble-metal HER catalysts is still necessary and huge progress has been made in the past years. Molybdenum-based compounds have received great success for catalyzing the HER in acidic electrolytes such as MoS2,6 MoSe2,7 Mo₂C,⁸ etc. However, there still remains a big challenge to improve their catalytic efficiency to meet the requirements of practical application.9,10 Still one can see from these reported results that the identification of novel high-performance HER catalysts based on non-precious materials is very attractive.

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It is well-known that the hydrodesulfurization (HDS) and HER work in the same way in that they both rely on the reversible binding of catalysts and hydrogen, with hydrogen dissociation to yield H₂S in HDS and with protons bound to catalysts to promote hydrogen formation in the HER. It is thus deduced that catalysts for HDS may be active for the HER. More recently, transitionmetal phosphides (TMPs) have been an important class of compounds with metalloid characteristics and are being intensively studied for the application as catalysts for the HDS reaction.11,12 Particularly, vast recent research has indeed proven MoP,¹³ Ni₂P,¹⁴ FeP,^{15,16} CoP^{17,18} and Cu₃P¹⁹ to be efficient hydrogen-evolving catalysts due to their attractive hydrogen transfer properties. When used as non-noble metal HER catalysts, they really show enhanced catalytic efficiency in acidic electrolytes. However, the catalytic activity of these catalysts still has not reached the level of Pt-based catalysts limited by the density and reactivity of active sites. Furthermore, poor electron and proton transport efficiency, low surface area, and instability under operating conditions are common pitfalls of these HER electrocatalysts.^{20,21} Generally, the exposed edges are affected by the morphologies and structures of catalysts. Hence, designing TMP-based HER electrocatalysts with more edge sites and better electron and proton transport activity is one effective strategy to enhance their HER catalytic activity. In this regard, forming highly dispersed TMP nanoparticles (NPs) with the controllable sizes (i.e., edge rich) on conducting matrices is an ideal protocol to further enhance the HER catalytic efficiency of catalysts.²²

The use of conductive carbon as a support material can not only improve the conductivity of the hybrid catalyst but also increase the dispersion of the active phases so that the catalyst phases offer more active sites and prevent the rapid decrease of activity sites as far as possible.23,24 Since they were synthesized for the first time, vast publications have paid intensive attention on the electrochemical applications of ordered mesoporous carbon (OMC),25 onion-like mesoporous carbon vesicles (MCVs)26 and macroporous carbon (MPC).27 Meanwhile, the research results also demonstrated that the particular porous structures and unique properties of these porous carbon materials really make them very attractive materials for designing electrochemically catalytic platforms with abundant and accessible edge sites. Additionally, density functional theory calculations have theoretically indicated that the TMP surface, which has exposed metal and phosphorus sites, exhibits an ensemble effect, whereby the proton-acceptor and hydride-acceptor centers are both present to facilitate the catalysis of the HER.28 As far as we are aware, there was no attention given to the study of the electrocatalytic application of OMC, MCV and MPC materials with different pore characteristics for loading of TMP NPs and catalyzing the HER. Thus, we wish to regard the CoP as an example and structure the catalysts of CoP NPs supported on porous carbon matrices. Meanwhile, we also expect to refrain CoP NPs from growing freely in the preparation process in the presence of carbon matrices and then acquire more electrochemical active sites with more excellent charge transfer efficiency compared with the pure ones.

Herein, we present our recent efforts in developing nanohybrids that consist of porous carbon materials (MPC, MCV and



Scheme 1 Illustration of the preparation procedures for the free CoP NPs, CoP–RGO, CoP–MCV, CoP–MPC and CoP–OMC samples.

OMC) decorated with CoP nanocrystals (denoted as CoP-carbon) by the low-temperature phosphorization of the corresponding Co₃O₄-carbon precursors. Moreover, in order to prove the capital importance of porous structures of carbon matrices in improving the catalytic ability of HER catalytic centers, reduced graphene oxide (RGO) nanosheets, without characteristic porous structures, have also been used as matrices for comparison. Wideangle X-ray diffraction (XRD), nitrogen adsorption-desorption isotherms, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectroscopy, X-ray photoelectron spectroscopy (XPS), FT-IR spectra, etc. were primarily used for analyzing the structures, morphologies and composition of as-prepared catalysts. Furthermore, the HER catalytic activities were tested by using the cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. Scheme 1 schematically shows the entire procedures for preparing CoP-carbon catalysts.

Experimental

Reagents and apparatus

Reagents and apparatus used in this paper are described in the ESI.†

Synthesis of the Co₃O₄-carbon and free Co₃O₄ NP samples

The Co_3O_4 -carbon hybrids were synthesized using a hydrothermal method. In a typical synthesis, the as-prepared carbon matrices (40 mg) were added into 48 mL ethanol and 2 mL water, respectively. After the mixture was sonicated for several minutes, 1.2 mL of 0.6 M Co(OAc)₂ aqueous solution and 1 mL

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of NH₄OH were added under stirring at room temperature. Then the suspension was kept at 80 °C and stirred for 20 h. After that, the mixture was transferred to an 80 mL Teflon-lined autoclave and maintained at 150 °C for 3 h. Finally, the asprepared products were collected by centrifugation and washed with ethanol and deionized water. Free Co_3O_4 NPs were prepared using the same method without using any carbon matrix.

Synthesis of the CoP-carbon and free CoP NP samples

20 mg of the Co_3O_4 -OMC hybrid and 100 mg of sodium hypophosphite were mixed together and grind to a fine powder by using a mortar. Then, the mixture was calcined at 300 °C for 2 h with a heating speed of 2 °C min⁻¹. The obtained product was washed with deionized water and dried at 80 °C overnight. The same procedure was used to prepare free CoP NPs, CoP-RGO, CoP-MCV and CoP-MPC samples.

Preparation of working electrodes

A rotating disk electrode (RDE, d = 5 mm) was used for all electrochemical experiments. Prior to be modified, it was polished carefully with 1.00, 0.30 and 0.05 mm alumina powders and then cleaned with HNO₃ (1 : 1), ethanol and deionized water, respectively. Catalyst ink was prepared by mixing 5 mg of the as-prepared catalyst powders with 1 mL of Nafion solution (0.1 wt%) within 45 min of ultrasonication. Then 11.1 µL of catalyst ink (containing 55.5 µg of catalysts) was dropped onto a cleanly washed GCE (loading ~0.285 mg cm⁻²) and dried under an infrared lamp before electrochemical experiments.

Electrochemical measurements

Electrochemical measurements were performed in a standard three-compartment cell at 25 °C. The modified RDE, Pt wire and Ag/AgCl (in saturated KCl solution) electrodes acted as the working, counter and reference electrodes, respectively. The electrolyte used was 0.5 M H₂SO₄ aqueous solution. The CV and LSV tests were carried out by using a Par 2273 Potentiostats Electrochemistry Workstation. All potentials appeared in this paper are referred to the reversible hydrogen electrode (the potentials recorded and referred to the Ag/AgCl electrode in each experiment were calculated by using the formula $E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059 \text{pH} + 0.198 \text{ V}$, where $E_{\rm RHE}$ is the potential *vs.* the reversible hydrogen electrode (RHE), $E_{\rm Ag/AgCl}$ is the potential *vs.* the Ag/AgCl electrode, and pH is the pH value of the electrolyte).²³ All current densities are the ratios of currents and geometric areas of working electrodes.

Results and discussion

Fig. 1A–D show the schematic diagrams of the resulting carbon matrices. Meanwhile, the corresponding SEM and TEM images of these carbon materials are also shown in Fig. 1E–L. Fig. 1E and I show typical SEM and TEM images of RGO sheets, it is clear that RGO exhibits a representative laminated nanosheet structure. But MCV consists of irregular spheres containing the particle sizes in the range of 100–300 nm (Fig. 1F). The detailed

structures of MCV spheres are further shown in the TEM image (Fig. 1J). One can see that MCV spheres show multilayer vesicle mesostructures and the distances between two layers vary from several nanometers to 25 nm, indicating the good structural ordering of MCVs. The SEM image of OMC (Fig. 1G) demonstrates that OMC is made up of carbon nanorods. The typical TEM images viewed from [1, 0, 0] (Fig. 1K) and [0, 0, 1] (inset of Fig. 1K) directions for OMC provide direct visualization of the morphology and internal mesostructure of OMC, demonstrating that OMC exhibits highly ordered 2D-hexagonal arrays of carbon nanorods and well-developed mesopores between adjacent carbon nanorods. The textural structure of the pristine MPC is seen as a well-defined interconnected macroporous nanostructure (Fig. 1H), meanwhile, the pores of MPC were closely packed and well-interconnected with an average size of about 100 nm (Fig. 1L).

The surface areas of RGO, MPC, MCV and OMC are determined by N₂ adsorption-desorption isotherms. The N₂ physisorption isotherms of four samples all exhibit type IV shapes. As shown in Fig. 1M-P, the remarkable hysteresis loops of MCV, MPC and OMC indicate their porous nature. As recorded in Table S1,[†] OMC has a BET specific surface area and a pore volume of 905 $m^2 \: g^{-1}$ and 1.58 $cm^3 \: g^{-1},$ respectively, which are larger than those of RGO (113 $m^2 g^{-1}$ and 0.31 $cm^3 g^{-1}$), MCVs (559 m² g⁻¹ and 1.15 cm³ g⁻¹), and MPC (449 m² g⁻¹ and $0.92 \text{ cm}^3 \text{ g}^{-1}$). Additionally, the pore sizes of four carbon matrices were obtained from desorption branches of their isotherms by the Barrett-Joyner-Halenda method. One can see that RGO has a pore size distribution mainly from 20 to 160 nm (inset of Fig. 1M). However, MCVs and OMC contain the mean pore size distributions of 6.7 (insets of Fig. 1N) and 4.8 nm (inset of Fig. 1O), respectively, suggesting that the abundant mesoporous structures are well-displayed for OMC and MCVs. Distinctively, for MPC, the relatively large pore structures of about 100 nm in size have been observed as the predominant units (inset of Fig. 1P). These pore size distribution results together with the SEM and TEM characterization results have verified the structural characteristics of several carbon matrices in detail.

The XRD analysis was performed to characterize the structures of carbon matrices, Co3O4-carbon nanohybrids and CoPcarbon nanocomposites. As shown in Fig. 2A, the diffraction peak located at about 11.8° indicates the crystalline structure of GO (curve a). The broad peak located at about 25° in the XRD pattern corresponds to the (002) reflection of RGO (curve b). Interestingly, the diffraction peak at 11.8° disappears for RGO, suggesting that GO was thoroughly reduced by ethanol in the preparation process. Broad peaks at about 25° also appear in the XRD patterns of MPC (curve c), MCVs (curve d) and OMC (curve e) matrices. In contrast, as shown in Fig. 2B, the free Co₃O₄ NPs (curve a), Co₃O₄-RGO (curve b), Co₃O₄-MPC (curve c), Co₃O₄-MCV (curve d) and Co₃O₄-OMC (curve e) samples all show six additional peaks at about 31° , 37° , 45° , 56° , 59° and 65°, which are indexed to the (220), (311), (400), (422), (511) and (440) planes of Co₃O₄ nanocrystals (JCPDS 42-1467), respectively.29 Finally, after the phosphorization procedure, only the diffraction peaks of the CoP phase are observed at 32°, 36°, 46°,



Fig. 1 The schematic diagrams of the RGO (A), MCV (B), OMC (C) and MPC (D) matrices. SEM images of the RGO (E), MCV (F), OMC (G), and MPC (H) matrices. TEM images of the RGO (I), MCV (J), OMC (K), and MPC (L) matrices. Nitrogen adsorption–desorption isotherms of the RGO (M), MCV (N), OMC (O), and MPC (P) matrices, inset: the corresponding pore size distribution curves.

48°, 52°, and 57° for the free CoP NPs (curve a), CoP–RGO (curve b), CoP–MPC (curve c), CoP–MCV (curve d) and CoP–OMC (curve e) samples (Fig. 2C), which are indexed to the (011), (111), (112), (211), (103) and (301) planes of CoP nanocrystals (JCPDS-29-0497), respectively.³⁰ These observations suggested the successful chemical conversion of Co₃O₄ NPs into CoP NPs in the phosphorization procedure.

Fig. S1A[†] shows the general morphologies of free CoP NPs, it can be observed that the free CoP NPs have grown freely in solution during the preparation process. Meanwhile, the asprepared free CoP NPs would aggregate into large particles with irregular morphology. Surprisingly, the particle size distribution continues from 20 to a few hundred nanometers (Fig. S1B†). Fig. 3A–D show the general morphologies of CoP–RGO, CoP–MPC, CoP–MCV and CoP–OMC by the typical SEM images. CoP nanocrystals deposited on the surface of the RGO matrix are well dispersed (Fig. 3A) and the particle size distribution is narrower compared with that for the free CoP NPs. Meanwhile, the corresponding TEM image (Fig. 3E) and histograms of particle size distribution (Fig. 3I) for CoP–RGO show an average diameter of 7.58 nm (the particle size distribution is mainly from 5 to 11 nm). Especially, when the same preparation



Fig. 2 (A) Typical XRD patterns of carbon matrices: GO (a), RGO (b), MPC (c), MCV (d), and OMC (e). (B) Typical XRD patterns of the Co_3O_4 based materials: free Co_3O_4 NPs (a), Co_3O_4 -RGO (b), Co_3O_4 -MPC (c), Co_3O_4 -MCV (d), and Co_3O_4 -OMC (e). (C) Typical XRD patterns of the CoP-based materials: free CoP NPs (a), CoP-RGO (b), CoP-MPC (c), CoP-MCV (d), and CoP-OMC (e).

procedures were repeated with the use of porous carbon matrices, the CoP nanocrystals were homogeneously dispersed on the surface of these porous carbon matrices (Fig. 3B–D). Concomitantly, the average diameter of CoP nanocrystals dispersed on MPC is 6.2 nm (Fig. 3F and S2†); meanwhile, the particle size distribution is mainly from 4 to 9 nm (Fig. 3J),

which clearly prove that the macroporous structures of MPC indeed contribute to the uniform dispersion of CoP nanocrystals. Thankfully, the presence of abundant mesoporous structures in MCVs will further limit the free growth of CoP nanocrystals (the recorded average diameter is about 5.99 nm) as shown in the TEM image (Fig. 3G) and histograms of particle size distribution of CoP-MCV (Fig. 3K). At the same time, the CoP-MCV also shows more narrow particle size distribution (mainly from 4 to 8 nm), indicating that carbon matrices containing abundant mesoporous structures could mediate the in situ growth of CoP nanocrystals with a highly uniform dispersion. Most of all, as shown in Fig. 3H, OMC containing the most mesoporous structures and largest BET superficial area really contributes to the minimum average particle size of 5.21 nm for CoP-OMC (meanwhile, as shown in Fig. 3L, CoP-OMC also shows the most narrow size distribution only from 3 to 7 nm), which once again demonstrates the capital importance of mesoporous structures in improving the dispersion of catalytic centres. Finally, the HR-TEM image taken for one such CoP nanocrystals reveals lattice fringes with a 'd' spacing of 0.19 and 0.28 nm, which correspond to the (211) and



Fig. 3 SEM images of the CoP-RGO (A), CoP-MPC (B), CoP-MCV (C), and CoP-OMC (D) samples. TEM images of the CoP-RGO (E), CoP-MPC (F), CoP-MCV (G), and CoP-OMC (H) samples. Inset of H corresponds to the HR-TEM image of the CoP-OMC sample. The histograms of the particle size distributions for the CoP-RGO (I), CoP-MPC (J), CoP-MCV (K), and CoP-OMC (L) samples.

(011) planes of CoP nanocrystals (inset of Fig. 3H). All of these results strongly support the formation of CoP–OMC nanocrystals from Co_3O_4 –OMC by the low-temperature phosphidation reaction. Fig. S3 and S4† show the evolution process of nanocrystals in the preparation procedures. The typical EDX spectra of these CoP–carbon samples were also recorded (Fig. S6†), which suggest the atomic ratios (cobalt : phosphorus) of about 1 : 1 for four samples. It is clear that the C, O, Co and P elements were all detected in the EDX spectra of four CoP–carbon samples and their contents are also accurately recorded in Table S2.† One can see that the mass percentages of CoP nanocrystals are all between 35 and 38 wt% for all samples.

As shown in Fig. S7,† the FT-IR spectra of RGO, MPC, MCV and OMC matrices show broad bands at around 3500–3300, 1740, 1575, 1225 and 1065 cm⁻¹ ascribed to the vibrations of –OH, C=O, C=C, C–O–C and C–O on the surfaces of carbon matrices.²³ Meanwhile, the FT-IR spectra of those Co₃O₄–carbon samples (Fig. S8A†) indicate that the Co₃O₄ nanocrystals are successfully formed. On the other hand, after the thorough phosphorization procedure, those characteristic peaks of the CoP nanocrystals appear in all CoP-based samples (Fig. S8B†). These results once again demonstrate that the Co₃O₄ nanocrystals have been thoroughly translated to CoP nanocrystals.

To further elucidate the chemical composition of Co_3O_4 –OMC and CoP–OMC hybrids, XPS measurements were carried out. The XPS spectra of Co_3O_4 –OMC indicate that the Co_3O_4 nanocrystals are successfully formed on OMC (Fig. S9†). The XPS survey spectrum of CoP–OMC (Fig. 4A) shows the characteristic peaks of C 1s, O 1s, Co 3s, Co 3p, Co 2p, P 2s and P 2p, indicating the existence of the P element in CoP–OMC. At the same time, the peak intensity of the O 1s spectrum for the CoP–OMC sample weakens obviously compared with that for Co_3O_4 –OMC (Fig. S9D†), which indicates that most O elements have been replaced by P elements in CoP–OMC. Fig. 4B shows the high resolution Co 2p XPS spectrum of CoP–OMC, the Co $2p_{3/2}$ region shows two peaks at 781.2 and 779.0 eV, and the Co $2p_{1/2}$ region shows one peak at 794.4 eV. Meanwhile, the high-resolution P 2p region shows two peaks at 130.5 and 129.8 eV



Fig. 4 XPS survey spectrum of CoP–OMC (A). Deconvoluted high resolution XPS spectra of Co 2p (B) and P 2p (C).

reflecting the binding energy of P $2p_{1/2}$ and P $2p_{3/2}$, respectively, along with one peak at 134.0 eV. The peaks at 779.0 and 129.8 eV are close to the binding energies for Co and P in CoP nanocrystals, but the peaks at 781.2 and 134.0 eV can be attributed to oxidized Co and P species. When compared with the binding energy of Co metal (778.1 to 778.2 eV), the Co 2p binding energy of 779.0 eV exhibits a positive shift; while, the P 2p binding energy of 129.8 eV exhibits a negative shift from that of elemental P (130.2 eV).³¹ The XPS analysis results suggest that the cobalt element in CoP has a partial positive charge while the phosphorus has a partial negative charge, demonstrating transfer of electron density from Co to P. The surfaces of CoP-OMC feature pendant base P (δ^-) moieties in close proximity to the metal center Co (δ^+), so the CoP-OMC composite is active towards the HER.

To demonstrate the electrochemical performance of free CoP NPs, CoP-RGO, CoP-MCV, CoP-MPC and CoP-OMC, LSV tests were first performed. As shown in Fig. 5A, polarization curves of all CoP-based catalysts were obtained in 0.5 M H₂SO₄ solution with a scan rate of 2 mV s^{-1} . For comparison, the commercial Pt-C catalyst (20 wt%) was also examined. One can see that the Pt-C catalyst shows a small onset potential (E_{onset}) of -24.58 mV, affording a current density (*j*) of 10 mA cm⁻² just at a small over-potential (η) of 44.46 mV. While the free CoP NPs show an E_{onset} value of -167.40 mV. In sharp contrast, the CoP-RGO, COP-MPC, COP-MCV and COP-OMC only show small Eonset values of -118.9, -105.3, -95.6 and -77.7 mV, respectively. These results undoubtedly highlight the importance of carbon matrices for enhancing the HER catalytic activity of CoP phases. Furthermore, the more negative potential indeed leads to a rapid rise of cathodic currents for all samples. However, the CoP–OMC catalyst affords a *j* value of 10 mA cm⁻² at a smaller η value of 112.18 mV compared with the CoP-RGO (156.87 mV), CoP-MPC (141.73 mV), CoP-MCV (134.34 mV) and free CoP NPs (212.29 mV) as shown in Fig. 5B. These η values compare favorably with the behavior of most previously reported nonnoble metal HER catalysts (Table 1), suggesting the superior catalytic activity of CoP-OMC over other four CoP-based catalysts. In addition, to verify the origin of the superior catalytic activity of CoP-OMC, the typical polarization curves for the free COP NPs, OMC matrix, Co₃O₄-OMC and CoP-OMC are also recorded in Fig. S10.[†] It is clear that both the Co₃O₄-OMC and the OMC matrix show terrific HER catalytic efficiency compared with the free CoP NPs and CoP-OMC. Such excellent performances for CoP-OMC may be attributed to the synergistic effect of the OMC matrix and the highly dispersive CoP NPs.

To understand the detailed underlying mechanism of HER activity, Tafel plots based on polarization curves of CoP, CoP–RGO, CoP–MPC, CoP–MCV, CoP–OMC and commercial Pt–C catalysts are acquired, as shown in Fig. 5C. The linear regions of Tafel plots were fit to the Tafel equation ($\eta = b \log j + a$, where j is the current density and b is the Tafel slope) to obtain slope b.³² Tafel slopes of 32.95, 56.67, 63.10, 69.83, 70.22 and 88.27 mV dec⁻¹ were obtained for the commercial Pt–C, CoP–OMC, CoP–MCV, CoP–MPC, CoP–RGO and free CoP NPs, respectively. According to previous reports, in general, three principal steps can be involved in a HER, as usually noted by the



Fig. 5 (A) LSV curves of the CoP NPs, CoP–RGO, CoP–MPC, CoP–MCV, CoP–OMC, and commercial Pt–C catalysts in 0.5 M H_2SO_4 with a scan rate of 2 mV s⁻¹, respectively. (B) Enlargement of the shadow region in (A). (C) Tafel plots of the free CoP NPs, CoP–RGO, CoP–MPC, CoP–MCV, CoP–OMC, and Pt–C catalysts, respectively. (D) Nyquist plots of electrochemical impedance spectra of the free CoP NPs, CoP–RGO, CoP–RGO, CoP–MPC, CoP–MPC, CoP–MPC, CoP–MCV, CoP–OMC, and Pt–C catalysts recorded at –200 mV vs. RHE. CV curves of CoP–OMC (E) and free CoP NPs (F) at different potential scanning rates. (G) Linear fitting of Δj of CoP-based samples ($\Delta j = j_a - j_c$) vs. scan rates at a given potential (+0.26 V vs. RHE).

Table 1	Comparison of HER	performance in acid	dic electrolytes for	CoP-based cataly	sts with other HER	electrocatalysts
			2			2

	Current density	η at 10 mA	Exchange current	
Catalyst	$(j, mA cm^{-2})$	cm^{-2} (mV)	density (mA cm $^{-2}$)	Ref.
Free CoP NPs	10	212.29	0.039	This work
CoP-RGO	10	156.89	0.057	
CoP-MPC	10	141.73	0.074	
CoP-MCV	10	134.34	0.091	
CoP-OMC	10	112.18	0.161	
CoP/CNT	10	122	0.13	29
MoS ₂ /RGO	10	150	_	34
Mo ₂ C/CNT	10	152	0.014	35
Ni ₂ P NPs	10	116	0.033	36
FeP nanosheets	10	240	_	16
Co-NRCNTs	10	260	0.01	37

Volmer, Heyrovsky, and Tafel steps. If the Volmer step associated with proton absorption is rate-determining, a slope of 120 mV dec⁻¹ should be obtained, while Heyrovsky and Tafel steps should give 40 and 30 dec^{-1} , respectively. Accordingly, the HER mechanism of our hybrid catalysts all follows the Volmer-Heyrovsky reaction where electrochemical desorption is the ratedetermining step. The low Tafel slope values of our CoP-carbon hybrid catalysts are attributed to the strong electronic coupling between nanoscale tiny CoP NPs and carbon matrix surfaces. Especially, the smallest Tafel slope value of the CoP-OMC catalyst is advantageous for practical catalytic application, since it leads to a rapid increase of the HER rate with over-potential.33 The exchange current densities (j_0) of the commercial Pt-C $(0.58 \text{ mA cm}^{-2})$, CoP-OMC $(0.16 \text{ mA cm}^{-2})$, CoP-MCV $(0.09 \text{ mA cm}^{-2})$, CoP-MPC $(0.08 \text{ mA cm}^{-2})$, CoP-RGO (0.06 mA) cm^{-2}) and free CoP NPs (0.04 mA cm^{-2}) were also calculated by applying the extrapolation method to the Tafel plots (Fig. S11[†]). In detail, CoP–OMC yields a j_0 value of 0.16 mA cm⁻², which is larger than those of most previous reports (Table 1),^{29,34-37} suggesting the superior HER catalytic activity and confirming the enrichment effect of the OMC matrix.

Additionally, we used electrochemical impedance spectroscopy (EIS) to investigate the electrode kinetics under the catalytic HER operating conditions. Nyquist plots and data fittings to a simplified Randles circuit (Fig. 5D) reveal that the charge transfer resistance (R_{ct}) value of CoP–OMC (57 Ω) is much lower than those of CoP-MCV (83 Ω), CoP-MPC (94 Ω), CoP-RGO (140 Ω) and free CoP NPs (352 Ω). The calculated results reveal that the coupling of carbon matrices to the less-conductive CoP NPs indeed brings about enhanced electron transport abilities of CoP-carbon hybrids.9,30 Especially, the CoP-OMC with the maximum mesoporous structures indeed displays the best electron transport ability. Further experiments with free CoP NPs (Fig. S12A[†]) show that the proton transport process might be insufficient for free CoP NPs, as evidenced by a significant current increase with the scan rates increasing from 2 to 40 mV s^{-1} . While CoP-OMC shows a very similar catalytic current under similar testing conditions (Fig. S12B⁺), which is probably due to its abundant open-framework structures that allow efficient charge and reactant transport in the catalytic process.³⁸

We also estimated the relative differences in electrochemically active surface areas of different CoP-based samples using a simple CV method. The current response in the potential window used for CV (0.23 to 0.33 V vs. RHE) at different scan rates (20 to 180 mV s^{-1}) should be only due to the charging of the double-layer (Fig. 5E and F, and S13[†]). The double-layer capacitances (C_{dl}) of all samples were extracted by plotting the $\Delta j = j_{\rm a} - j_{\rm c}$ at a given potential (0.26 V vs. RHE) against the CV scan rates (Fig. 5G).³⁹ It is clear that the calculated C_{dl} values increase in the order of free CoP NPs $(2.57 \text{ mF cm}^{-2}) <$ CoP-RGO (5.23 mF cm⁻²) < CoP-MPC (9.43 mF cm⁻²) < CoP-MCV (11.17 mF cm⁻²) < CoP-OMC (22.72 mF cm⁻²). The $C_{\rm dl}$ values were directly proportional to the electrochemically active surface area,19,40 thus indicating that CoP-OMC has a much higher surface roughness than other four CoP-based samples which certainly contributes to the improved catalytic performances. To further understand the intrinsic catalytic properties of the as-synthesized CoP-based catalysts, we studied their turnover frequency (TOF) values which describe the average activity of each HER active site. Following the procedures reported before, ^{32,41,42} the number of active sites and corresponding TOF values at -200 mV for the free CoP NPs and CoP–OMC samples have been measured. The number of active sites and the corresponding TOF value recorded at $-200 \text{ mV} \nu s$. RHE for free CoP NPs (0.59×10^{16} and 1.7 s^{-1}) are much smaller than those for CoP–OMC (6.11×10^{16} and 2.7 s^{-1}). Meanwhile, the TOF value of CoP–OMC is much more excellent than some other catalysts reported before^{39,43,44} and is comparable to the TOF values reported for other highly active catalysts.^{18,32,45,46}

Durability is a key factor in evaluating the catalyst performance. To evaluate the durability, the free CoP NPs and CoP-OMC catalyst were cycled continuously for 2000 cycles in 0.5 M H_2SO_4 (Fig. 6A). One can see that only a slight activity loss was observed at the end of the cycling for CoP-OMC (about 6.7% loss at -0.25 V vs. RHE after 2000 cycles), demonstrating that CoP-OMC has superior stability in a longterm electrochemical process. Conversely, a drastic degradation of current density was observed for the free CoP NPs (about 34.8% loss at -0.25 V vs. RHE after 2000 cycles). Continuous HER at a static over-potential of 150 mV vs. RHE was also conducted to further demonstrate the stability (Fig. 6B). It is clear that the chronoamperometric electrolysis provides evidence of the excellent stability of CoP-OMC at -150 mV vs. RHE, meanwhile no performance degradation was observed after electrolysis for more than 30 h. To further understand the different durability behaviors of CoP-OMC and free CoP NPs, morphological evolutions of the two catalysts have been investigated by SEM. After the durability test,



Fig. 6 (A) Polarization curves for CoP–OMC and free CoP NPs in 0.5 M H_2SO_4 solution with a scan rate of 2 mV s⁻¹ before (solid line) and after 2000 cycles (dot line) at a scan rate of 100 mV s⁻¹ between 0 and -0.30 V vs. RHE. (B) Time dependence of the current density for CoP–OMC at a static over-potential of 150 mV for 30 hours. SEM images of the CoP–OMC (C) and free CoP NPs (D) samples after the accelerated durability test.

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no obvious aggregation is observed for the tiny CoP nanocrystals on CoP-OMC surfaces (Fig. 6C). For example, the original porous structure of the OMC matrix and the particle size of the CoP-OMC are still very well preserved after the durability test. Unfortunately, the morphological change of the free CoP NPs is easy to observe using the SEM image due to the severe aggregation of the CoP NPs (Fig. 6D). It is clear that the mesoporous OMC matrix significantly inhibits the aggregation of CoP NPs and the tiny CoP nanocrystals are tightly inlaid inside the carbon skeletons. Thus, the abundant CoP NPs embedded in the skeletons of OMC will keep a consistent state in a long-term electrochemical process thus leading to the superior stability of CoP-OMC. However, for the free CoP NP sample, most CoP NPs will seriously aggregate because of the absence of the OMC matrix. Meanwhile, the states of CoP NPs will invariably change to the worse direction, which will predicatively lead to the decrease of exposed active sites and cause the decrease of the catalytic current.

The generated gas was analyzed by gas chromatography (GC) analysis. The generated hydrogen was measured quantitatively using a calibrated pressure sensor to monitor the changes in pressure in the cathode compartment of an H-type electrolytic cell. Potentiostatic cathodic electrolysis was performed by maintaining a CoP–OMC modified glassy carbon plate at an over-potential of -0.20 V *vs.* the RHE for 7000 seconds. To calculate the Faradaic efficiency (FE) of the electrocatalytic hydrogen evolution process, we compared the amount of experimentally quantified hydrogen with the theoretically calculated hydrogen (assuming 100% FE). The agreement between both the theoretically and experimentally measured values suggests an FE of close to 100% (Fig. 7).

Fig. 8 shows a comparison between the surface area, R_{ct} and $C_{\rm dl}$ area along with the $E_{\rm onset}$, Tafel slope, j_0 and η at 10 mA cm⁻² of five catalysts. Experimental results demonstrate that the HER catalytic efficiency increases in the order of free CoP NPs < CoP-RGO < CoP-MPC < CoP-MCV < CoP-OMC. Meanwhile, the electron transport abilities and real electrochemical active areas of these as-prepared catalysts also follow the same order. One can see that the excellent HER catalytic activity results from not only the intrinsic properties of CoP crystals, but also from the carbon substrates containing special structures. Especially, the use of porous carbon matrices such as MPC, MCV and OMC can hugely promote the catalytic efficiency of CoP nanocrystals. On the other hand, the existence of abundant mesopores in the carbon skeletons (MCV and OMC) really results in a larger electrochemical active area, smaller diameter size of CoP nanocrystals, and more excellent HER catalytic efficiency for the CoP-MCV and CoP-OMC samples compared with those for the macroporous CoP-MPC and imporous CoP-RGO nanocomposites. Therefore, we can draw the conclusion that the especially better HER catalytic efficiency of the as-prepared CoP-OMC catalyst compared with other catalysts is based on its larger surface area, more abundant mesoporous nanostructures, and more excellent electron and proton transport rates. (1) The large surface area and small crystallite size bring about a higher number of exposed active sites which will promote the electrochemical



Fig. 7 Amount of theoretically calculated (black) and experimentally measured (red) hydrogen *versus* time of CoP–OMC under a static over-potential of 200 mV *vs.* RHE.

reduction of H^+ ions and desorption of H atoms in the HER. (2) It is crucial to enhance the proton/electron transport rate in the electrode and at the electrode/electrolyte interface. Experimentally, the abundant mesoporous structures and the continuous frameworks of the OMC matrix indeed provide excellent reactant transport efficiency and high electron transfer rate for the as-prepared CoP-OMC catalyst due to the short transport pathways for electrons and reactant. More importantly, the mesoporous nanostructures of OMC are capable of making the penetration of electrolytes into the whole electrode matrix facilely and further reduce the diffusion resistance, and therefore overcome the primary kinetic limits of electrochemical processes. (3) As the mesoporous OMC matrix significantly inhibits the aggregation of CoP NPs and the tiny CoP nanocrystals that are tightly inlaid inside the carbon skeletons, the CoP-OMC catalyst has superior stability in a long-term electrochemical process. Therefore, the rational design and fabrication of mesoporous electric nanostructures as matrices is imperative for the high performance HER electrocatalysts.



Fig. 8 Correlative effects of BET surface area, R_{ct} and C_{dl} at the onset potentials, the over-potentials needed to attain a current density of 10 mA cm⁻², the Tafel plots, and the j_0 of the free CoP NPs, CoP-RGO, CoP-MPC, CoP-MCV, and CoP-OMC samples.

Conclusions

In conclusion, we have designed novel materials of tiny CoP nanocrystal embedded carbon matrices (RGO, MPC, MCV and OMC) as the efficient non-precious-metal HER catalysts. SEM, TEM, XRD, XPS and FT-IR measurements reveal that the CoPcarbon materials have been successfully prepared. It can be seen that the carbon matrices especially those containing lots of mesoporous structures significantly inhibit the aggregation of CoP nanocrystals in the preparation procedure. In acids, the HER is catalyzed more easily and efficiently on the porous CoP-MPC, CoP-MCV and CoP-OMC catalysts than that on the imporous CoP-RGO and free CoP NPs. More importantly, the CoP-OMC inherently exhibited better HER catalytic and superior stability in a long-term electrochemical process compared with other four samples. These results all illustrate that the use of a carbon matrix with a large surface area, abundant mesoporous nanostructures, and excellent electron transport rate can effectively enhance the catalytic performances of the as-prepared HER electrocatalysts. Furthermore, the idea of designing catalysts by using conductive supporting materials with abundant mesoporous structures and large surface areas could be applied to construct more catalytic materials as a general strategy for improving the catalytic activity of various catalysts.

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