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The effect of carbon quantum dots on electrocatalytic hydrogen evolution reaction of manganese-nickel phosphide nanosheets

Weiwu Chen,^{a,b} Zhaojun Qin,^{a,c} Brian McElhenny,^b Fanghao Zhang,^{b,d} Shuo Chen,^b Jiming Bao,^{c,d} Zhiming M. Wang,^{*a} Hai-Zhi Song^{*a} and Zhifeng Ren^{*b}

Transition-metal phosphides (TMPs) are good electrocatalysts for hydrogen evolution reaction (HER) due to their high catalytic efficiency and low cost. Carbon quantum dots (CQDs) deposited on top of TMPs could make them even better for HER by increasing the surface area and the number of active sites. Here we report a method to synthesize CQDs-modified manganese-nickel phosphide (CQDs/Mn_xNi_{5-x}P₄) for efficient and stable HER activity using inexpensive raw materials. In 0.5 M H₂SO₄, CQDs/Mn_xNi_{5-x}P₄ requires a low overpotential of only 31 mV to achieve a current density of 10 mA cm⁻², as well as having a low Tafel slope of 41.0 mV dec⁻¹, a large exchange current density of 1.753 mA cm⁻², and good stability, making it better than most reported transition-metal-based catalysts. Moreover, CQDs/Mn_xNi_{5-x}P₄ also displays high activity and stability in alkaline solution, revealing that the ancillary role played by CQDs could be beneficial in both acidic and alkaline conditions. Based on our results, we believe that CQDs have great potential to be applied to other materials with various morphologies and structures for designing high-performance HER catalysts.

Introduction

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With the growing concerns of energy scarcity and environmental degradation, the exploration of clean and renewable energy resources has become increasingly more pivotal.^{1, 2} Being a zero-carbon carrier, hydrogen (H₂) that can be produced from either water or fossil fuels is considered to be an ideal clean-energy candidate.³⁻⁵ Electrochemical water splitting can result in H₂ exhibiting better purity with higher efficiency than that produced from fossil fuels. However, less than 5% of the hydrogen used has been produced from the electrochemical hydrogen evolution reaction (HER), while that produced from fossil fuels has accounted for 95%.⁶⁻⁸ To realize a green recycling system with reduced fossil-fuel dependence, the development of electrocatalytic water splitting for hydrogen production has great significance.

Electrocatalysts, as the core parts of an advanced water electrolyzer, determine its activity, kinetics, and stability.⁹⁻¹¹ Thus, the major challenge for widespread electrochemical hydrogen generation involves the search for state-of-the-art electrocatalysts.¹² Pt and Pt-based compounds are regarded as pioneering HER catalysts, but their high cost and scarcity greatly limit their application in industrial production.¹³⁻¹⁵ Transitionmetal phosphide (TMP) compounds demonstrate impressive catalytic efficiency and are inexpensive due to the abundance of transition metals in the Earth's crust.¹⁶⁻¹⁸ Wang *et al.* reported an electrocatalyst based on CoP_2 nanoparticles grown on reduced graphene oxide sheets, requiring an overpotential of 88 mV to achieve a current density of 10 mA cm⁻².¹⁹ However, the catalytic performance of TMPs remains inferior to that of Pt and Pt-based materials.

For pursuing efficient HER electrocatalysis, morphology control and suitable structural design to achieve a large special surface area catalyst and broaden the catalytically active facet on its surface are usually effective.^{20, 21} In terms of a larger surface area, the key for a great electrocatalyst is to discover a material that exhibits excellent catalytic properties, including good electrical conductivity, high corrosion tolerance, and suitable free energy of hydrogen adsorption.²²⁻²⁴ In general, two aspects have great influence on the improvement of electrocatalytic performance, catalytically intrinsic activity and active sites.²⁵ Many efforts have been devoted to achieving each of these aspects by employing several strategies for TMPs, such as hierarchical structure, heterometal doping, and surface modification.²⁶⁻²⁸ For example, Cr doped FeNi-P nanoparticles and N doped CoP nanoarrays have been reported, and the HER performance of these two TMPs shows significant improvement after the Cr or N doping.^{29, 30} Elemental doping alone, however, is not enough to make the performance of the TMPs exceed that of Pt and Pt-based materials. Besides, substrates are needed to support TMP materials. Thus, searching a material containing TMPs as an effective catalyst without substrate and better performance than Pt-based materials is the focus of this study. Carbon quantum dots (CQDs) have attracted significant attention as inexpensive and nontoxic nanocarbon materials

^a. Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China. Email: zhmwang@uestc.edu.cn, hzsong1296@ 163.com

^b Department of Physics and TcSUH, University of Houston, Houston, TX 77204, USA. Email: zren@uh.edu

^c Department of Electrical and Computer Engineering, University of Houston, Houston, TX 77204, USA.

^d Department of Chemistry, University of Houston, Houston, TX 77204, USA

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that exhibit rapid electron transfer and high stability, which gives them great potential for pH-universal catalysis.³¹⁻³³ Abundant functional groups, such as –OH and –COOH, exist on the surfaces of CQDs, providing many beneficial active sites and enabling CQDs to be an excellent auxiliary material for electroactive catalysis.³⁴⁻³⁶ In particular, the natural merits of small OD nanoparticles (less than 10 nm) allow flexibility in anchoring CQDs to different structures.^{37, 38} However, most research thus far has focused on employing CQDs to enhance the photocatalytic properties of different composites, rather than being applied in electrocatalysts, let alone to form excellent HER catalysts by combining them with three-dimensional transition-metal nanomaterials.

Here we report a universal method to achieve manganesedoped nickel-phosphide nanosheets modified by carbon quantum dots without substrate, designated as CQDs/Mn_xNi₅₋ _xP₄, which not only requires only quite inexpensive raw materials, but also exhibits robust properties for HER in both acidic and alkaline conditions. Different amounts of CQDs are attached on the surfaces of Mn_xNi_{5-x}P₄ nanosheets to adjust the activity for HER by controlling the concentration of the CQD solution used in the synthesis process. We find that when CQDs are uniformly distributed on the surfaces without any agglomerations, they boost the catalytic efficiency and stability of Mn_xNi_{5-x}P₄. In 0.5 M H₂SO₄, the catalyst requires an overpotential of only 31 mV to achieve a current density of 10 mA cm⁻², which is as good as that of the noble Pt catalyst (33 mV required to achieve 10 mA cm⁻²). It is found that CQDs can turn a good HER catalyst into an excellent one that outperforms

most other reported catalysts. Thus, we believe there tis great potential for CQDs to be beneficially applied to other structures.

Results and discussion

The Ni₅P₄ and Mn_xNi_{5-x}P₄ nanosheets were synthesized by onestep chemical vapor deposition to phosphatize the Ni foam following the previously reported procedure.³⁹⁻⁴¹ The CQD solutions were prepared via electrochemical stripping from two graphite rods according to the previous reports.^{42, 43} Mn_xNi_{5-x}P₄ nanosheets were immersed in 0.5, 1, 1.5, and 2 mg mL⁻¹ CQDs solutions to obtain Mn_xNi_{5-x}P₄ nanosheets with different CQD contents after annealing, labeled as 1-CQDs/Mn_xNi_{5-x}P₄, 2-CQDs/Mn_xNi_{5-x}P₄, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄, respectively. The typical X-ray diffraction (XRD) patterns (Fig. 1a) show that all of the as-prepared samples are based on Ni₅P₄ with all their peaks indexed to the Ni₅P₄ standard pattern (PDF#18-0883). It is worth noting that the peaks of Mn-doped Ni_5P_4 shift to smaller 2 θ angles compared to Ni_5P_4 (inset, Fig. 1a), illustrating that the replacement by Mn, which has a larger radius than Ni, induces the expansion of the crystal lattice.44,45 Moreover, no XRD peaks of metallic Ni are observed in any samples, suggesting that the Ni foam has been completely converted to Ni₅P₄.

X-ray photoelectron spectroscopy (XPS) (Fig. 1b-d) and energy-dispersive X-ray spectrum (EDS) analysis (Fig. 1e) were then used to investigate the elemental surface composition of



Figure 1. Phase characterization of the samples. (a) XRD patterns of Ni foam, Ni_5P_4 , $Mn_xNi_{5-x}P_4$, and 3-CQDs/ $Mn_xNi_{5-x}P_4$. High-resolution XPS spectra of (b) Mn 2p, (c) Ni 2p, and (d) P 2p. (e) EDS pattern of 3-CQDs/ $Mn_xNi_{5-x}P_4$. (f) TG analysis of the asprepared samples.

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Figure 2. SEM images of (a, b) Ni_5P_4 , (c, d) $Mn_xNi_{5-x}P_4$, (e, f) 3-CQDs/Mn_x $Ni_{5-x}P_4$, and (g, h) 4-CQDs/Mn_x $Ni_{5-x}P_4$ at different magnifications. (i) TEM image of 3-CQDs/Mn_x $Ni_{5-x}P_4$.

the 3-CQDs/Mn_xNi_{5-x}P₄ sample. The Mn 2p spectrum for 3-CQDs/Mn_xNi_{5-x}P₄ (Fig. 1b) exhibits two peaks at 642.3 and 654.2 eV, which are assigned to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively, proving the existence of elemental Mn.⁴⁶ The XPS spectrum of Ni 2p for 3-CQDs/Mn_xNi_{5-x}P₄ (Fig. 2c) is fitted with two spin-orbit doublets at binding energies (BEs) of 855.0 and 872.7 eV, assigned to the Ni 2p_{3/2} and Ni 2p_{1/2} of Ni₅P₄, respectively, and the peak at BE of 130.2 eV in the P 2p spectrum (Fig. 2d) is consistent with the P 2p from Ni₅P₄.⁴⁷ The XPS peaks originating from the Ni and P for 3-CQDs/Mn_xNi_5-xP_4 clearly shift toward lower energy levels compared with those for Ni₅P₄, which is consistent with the XRD results and indicates that a stronger electron structure results from Mn substitution.^{48, 49} The atomic ratio of Mn, Ni, and P from XPS is 0.4:4.4:4.0 for 3-CQDs/Mn_xNi₅₋ _xP₄, which is similar to the result from the EDS measurement (0.4:4.8:4.0). Additionally, a carbon signal is evident in the EDS pattern (Fig. 2e), which suggests that CQDs exist on the surface of the sample. The Raman spectra of 1-CQDs/Mn_xNi_{5-x}P₄, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄ shown in Fig. S1a exhibit the typical G-band (1598 cm⁻¹) and D-band (1367 cm⁻¹) of carbon materials, confirming the existence of CQDs in these

compounds.⁵⁰ Furthermore, thermogravimetric (TG) analysis (Fig. 1f) was conducted to verify the CQD content with flowing oxygen. The weight decrease is due to the reaction of CQDs with oxygen. It shows that the weight ratios of the CQDs are 2.17%, 3.62%, 4.17%, and 5.58% for 1-CQDs/Mn_xNi_{5-x}P₄, 2-CQDs/Mn_xNi_{5-x}P₄, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄, respectively.

Scanning electron microscopy (SEM) images (Fig. 2a-h) show that the Ni₅P₄, Mn_xNi_{5-x}P₄, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄ samples are all covered with nanosheet arrays separated by adequate spaces, which offers the HER catalysts a large surface area and good accessibility. The SEM images of Ni₅P₄ (Fig. 2a-b) and Mn_xNi_{5-x}P₄ (Fig. 2c-d) reveal that the nanosheets of both materials are quite smooth and thin, which indicates that Mn doping has little effect on the nanosheet morphology. For 3-CQDs/Mn_xNi_{5-x}P₄ (Fig. 2e-f), there is no definite evidence of CQDs in the SEM images, but the surfaces of its nanosheets are rougher than those of Ni₅P₄ and Mn_xNi_{5-x}P₄, which allows speculation about the existence of CQDs. As shown in Fig. 2g and h, small particles appear on the nanosheet surfaces of 4-CQDs/Mn_xNi_{5-x}P₄, indicating that there are many CQDs, such that some of them converge to form clusters.

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Figure 3. Electrocatalytic performance of different catalysts in 0.5 M H_2SO_4 . (a) Polarization curves, (b) overpotentials at current densities of 10 and 100 mA cm⁻², and (c) Tafel plots of the as-prepared samples and Pt wire. (d) Chronopotentiometry curves of 3-CQDs/Mn_xNi_{5-x}P₄ at different current densities. (e) Capacitive current *vs.* scan rate curves of the as-prepared samples. (f) Nyquist plots of different electrocatalysts.

Transmission electron microscopy (TEM) was used to further determine the characteristics and distribution of CQDs on the nanosheets. The TEM image of 3-CQDs/Mn_xNi_{5-x}P₄ (Fig. 2i) shows that CQDs are densely and uniformly distributed on the surface of the nanosheet and it is apparent that clusters would form easily with the addition of more CQDs, consistent with the results from the SEM (Fig. 2e-f) and elemental mapping (Fig. S2) images of 3-CQDs/Mn_xNi_{5-x}P₄. As shown in the inset of Fig. 2i, the CQDs are about 5 nm in diameter and have a lattice space of 0.322 nm, which corresponds to the (002) crystallographic planes of graphite.⁵¹ The TEM images of the 1-CQDs/Mn_xNi_{5-x}P₄ and 2-CQDs/Mn_xNi_{5-x}P₄ nanosheet surfaces (Fig. S3) show that the CQDs are unevenly distributed and sparser than on those of 3-CQDs/Mn_xNi_{5-x}P₄.

The HER activity of the prepared samples was evaluated in 0.5 M H₂SO₄ by a three-electrode electrochemical station with a graphite foil serving as the counter electrode. Fig. 3a shows the HER polarization curves, illustrating the effects of Mn doping and CQDs modification on the catalytic activity of the materials. 3-CQDs/Mn_xNi_{5-x}P₄ requires overpotentials of only 31 and 101 mV to achieve current densities of 10 and 100 mA cm⁻², respectively, which is clearly less than those required by Ni₅P₄ (94 and 180 mV), Mn_xNi_{5-x}P₄ (74 and 157 mV), and 3-CQDs/Ni₅P₄ (63 and 126 mV) to achieve the same current densities (Fig. 3b). The performance of the samples containing Mn and those containing CQDs is better than that of the samples without Mn and without CQDs, respectively. Apparently, Mn doping promotes the catalytic performance of Ni₅P₄, while modification by CQDs further enhances the electrocatalytic activity, making

it comparable to the state-of-the-art Pt. Compared with other recently reported catalysts summarized in Table S1, 3-CQDs/Mn_xNi_{5-x}P₄ requires the lowest overpotential at the current density of 10 mA cm⁻², indicating its excellent electrocatalytic performance.

The Tafel slope (Fig. 3c) of 3-CQDs/Mn_xNi_{5-x}P₄ is 41.0 mV dec⁻ ¹, lower than that of Ni foam (102.9 mV dec⁻¹), Ni₅P₄ (83.4 mV dec⁻¹), Mn_xNi_{5-x}P₄ (76.7 mV dec⁻¹), and 3-CQDs/Ni₅P₄ (58.7 mV dec⁻¹), and near that of Pt (34.2 mV dec⁻¹). The small Tafel slope for $3-CQDs/Mn_xNi_{5-x}P_4$ indicates that the HER process is determined by the Volmer-Heyrovsky mechanism.52 The exchange current density (j_0) , which is calculated by extrapolating the horizontal intercept in the Tafel plots, is about 1.753 mA cm⁻² for 3-CQDs/Mn_xNi_{5-x}P₄, superior to that of the other transition-metal-based catalysts in Table S1. The turnover frequency (TOF) was also calculated to evaluate the intrinsic catalytic activity according to the previous reports (details are provided in the Supporting Information).^{29, 53} The TOF at an overpotential of 100 mV for 3-CQDs/Mn_xNi_{5-x}P₄ is 0.067 s⁻¹, higher than the 0.021 s⁻¹ for Ni₅P₄, the 0.029 s⁻¹ for Mn_xNi_{5-x}P₄, and the 0.035 s⁻¹ for CQDs/Ni₅P₄. The small Tafel slope, large j₀, and high TOF indicate the fast electron transfer rate and excellent catalytic kinetics of 3-CQDs/Mn_xNi_{5-x}P₄, which are of great benefit to its HER activity.54, 55

As an essential aspect of a catalyst's HER performance, the long-term durability of the 3-CQDs/ $Mn_xNi_{5-x}P_4$ was assessed by continuous current chronopotentiometry and cyclic voltammetry (CV) scanning. As displayed in Fig. 3d, galvanostatic measurements of the 3-CQDs/ $Mn_xNi_{5-x}P_4$ catalyst

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Figure 4. Electrocatalytic performance of the catalysts with different amounts of CQDs in 0.5 M H₂SO₄. (a) Polarization curves, (b) Tafel plots, (c) capacitive current *vs.* scan rate curves, and (d) Nyquist plots of different electrocatalysts.

at different current densities of 10, 100, and 500 mA cm⁻² show only a slight decay in potential over 72 h of constant hydrogen evolution. After 3000 cycles, the polarization curve of 3-CQDs/Mn_xNi_{5-x}P₄ shows negligible change compared with that of the initial case (Fig. S4). Furthermore, Raman (Fig. S1b), XRD and XPS (Fig. S5), and EDS (Fig. S6) measurements were again employed after the long-term testing. The Raman, XRD, and XPS peaks before and after testing do not exhibit notable shifts, and the ratios before and after testing from XPS and EDS are similar, verifying the good stability of 3-CQDs/Mn_xNi_{5-x}P₄.

It is always informative to normalize the catalytic effect by the electrochemical effective surface area (ECSA), which is responsible for an electrocatalyst's intrinsic catalytic property. The ECSA is proportional to the electrochemical double-layer capacitance (C_{dl}), which can be evaluated by the CV scanning. The slope of the fitted line by Δj vs. scan rate is two times that of C_{dl} , where Δj is the difference between the positive and negative current values in the CV curves (Fig. S7). As shown in Fig. 3e, the C_{dl} of 3-CQDs/Mn_xNi_{5-x}P₄ is 89.7 mF cm⁻², which is noticeably larger than that of Ni_5P_4 (35.4 mF cm⁻²), $Mn_xNi_{5-x}P_4$ (40.9 mF cm⁻²), and 3-CQDs/Ni₅P₄ (78.4 mF cm⁻²). As shown in Fig. S8, 3-CQDs/Mn_xNi_{5-x}P₄ exhibits a larger Brunauer-Emmett-Teller (BET) surface area than Mn_xNi_{5-x}P₄, which is consistent with the results from ECSA testing. The larger ECSA could provide more active sites, which would enhance the absorption of water molecules and the catalytic reaction rate. Moreover, electrochemical impedance spectroscopy (EIS) was conducted to investigate the interface behavior and electrical conductivity of 3-CQDs/Mn_xNi_{5-x}P₄. The Nyquist plots (Fig. 3f) show that the charge-transfer resistance (R_{ct}) of 3-CQDs/Mn_xNi_{5-x}P₄ is only 1.5 Ω , much smaller than the 21.0 Ω of Ni₅P₄, the 10.1 Ω of Mn_xNi₅₋ $_{x}P_{4}$, and the 4.8 Ω of 3-CQDs/Ni₅P₄. This indicates a more efficient charger exchange during the HER process, which could contribute to the excellent electrode kinetics. Accordingly, we can speculate that while Mn doping has a small impact on the specific surface area of the material, it can effectively reduce the charge-transfer resistance during the HER process. It is believed that the compound-metal phosphide shows the reinforced charge exchange between two metal atoms, which yields two electron donors to enhance the proton discharge.^{56,} ⁵⁷ Furthermore, the modification by CQDs leads to the increased surface area and reduction of the impedance, thus boosting the catalytic activity of Ni₅P₄. Fig. 4a shows the effect of CQDs concentration on the catalytic performance (polarization curves of 1-CQDs/Mn_xNi_{5-x}P₄, 2-CQDs/Mn_xNi_{5-x}P₄, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄, together with 3-CQDs/Ni foam for comparison). Even modified by CQDs, Ni foam still exhibits inferior HER performance. On the other hand, $Mn_xNi_{5-x}P_4$ samples modified by CQDs exhibit improved catalytic activity, suggesting that CQDs could be an excellent auxiliary material for HER catalysis. For 1-CQDs/Mn_xNi_5-xP_4, 2-CQDs/Mn_xNi_5-xP_4, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄, the overpotentials needed to yield a current density of 10 mA cm⁻² are 63, 52, 31, and 54 mV, respectively, with respective Tafel slopes (Fig. 4b) of 71.4, 53.8, 41, and 60.9 mV dec⁻¹. Both the overpotential and the Tafel slope decrease as the surface coverage by the CQDs

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Figure 5. Electrocatalytic performance of different catalysts in 1 M KOH. (a) Polarization curves, (b) overpotentials at current densities of 10 and 100 mA cm⁻², and (c) Tafel plots of the samples and (d) chronopotentiometry curves of 3-CQDs/Mn_xNi_{5-x}P₄ at different current densities for HER. (e) Polarization curves of the samples and (f) chronopotentiometry curves of 3-CQDs/Mn_xNi_{5-x}P₄ at different current densities for OER.

increases, until uniform saturation of the catalyst surface is reached $(3-CQDs/Mn_xNi_{5-x}P_4)$. With higher concentration, the CQDs begin to aggregate into clusters and they completely cover the surface of $Mn_xNi_{5-x}P_4$, thus affecting the overall catalytic activity of the electrode. As shown in Fig. 4c-d, the ECSA values for 1-CQDs/MnxNi5-xP4, 2-CQDs/MnxNi5-xP4, 3-CQDs/Mn_xNi_{5-x}P₄, and 4-CQDs/Mn_xNi_{5-x}P₄ are 50.6, 74.0, 89.7, and 66.7 mF cm⁻², respectively, corresponding to their respective CV curves shown in Fig. S9, and their R_{ct} values are 7.5, 2.9, 1.5, and 3.9 Ω , respectively. The increasing ECSA and decreasing R_{ct} that accompany the increasing amount of CQDs up to a certain point verify that CQDs can provide many beneficial active sites and accelerate the reaction kinetics. Clustering of the CQDs, however, adversely affects the effective surface area and the charger-exchange resistance of the electrocatalyst, resulting in reduced catalytic activity.

Since 3-CQDs/Mn_xNi_{5-x}P₄ exhibits the most desirable HER electrocatalytic activity in the acidic condition, its behavior in an alkaline solution was further investigated. Fig. 5a shows the polarization curves of Ni₅P₄, Mn_xNi_{5-x}P₄, 1-CQDs/Mn_xNi_{5-x}P₄, and 3-CQDs/Mn_xNi_{5-x}P₄ in 1 M KOH. The 3-CQDs/Mn_xNi_{5-x}P₄ sample exhibits the best performance with an overpotential of 56 mV needed to drive a current density of 10 mA cm⁻², lower than that of Ni₅P₄ (126 mV), Mn_xNi_{5-x}P₄ (99 mV), and 1-CQDs/Mn_xNi_{5-x}P₄ (83 mV) (Fig. 5b), and comparable to the reported transitionmetal-based catalysts (Table S2). As shown in Fig. 5c, 3-CQDs/Mn_xNi_{5-x}P₄ also exhibits a smaller Tafel slope value (50.0 mV dec⁻¹) compared with the 85.4 mV dec⁻¹ of Ni₅P₄, the 75.6 mV dec⁻¹ of Mn_xNi_{5-x}P₄, and the 67.9 mV dec⁻¹ of 1-CQDs/Mn_xNi_{5-x}P₄, indicating its better reaction rate in the

alkaline condition. Moreover, the potential changes only negligibly after 72 h of chronoamperometric testing under different current densities (Fig. 5d), which illustrates its good long-term durability and further indicates that the CQDsmodified electrocatalyst has good stability in both acid and base media. Meanwhile, the required overpotentials and the Tafel slopes of 3-CQDs/Mn_xNi_{5-x}P₄ in 0.5 M H₂SO₄ and 1 M KOH are significantly lower than those of their unmodified counterparts, revealing that the ancillary role of CQDs can be applied to both acidic and alkaline conditions. Furthermore, the OER performance of the as-prepared electrodes was evaluated in 1 M KOH (Fig. 5e). The 3-CQDs/Mn_xNi_{5-x}P₄ sample needs an overpotentials of 229 and 361 mV to achieve current densities of 10 and 100 mA cm⁻², respectively, which is comparable with the previous reports,^{58, 59} which shows 3-CQDs/Mn_xNi_{5-x}P₄ is a promising catalyst with good stability shown in Fig. 5f.

Conclusions

We have utilized a facile mothed to fabricate self-standing three-dimensional $Mn_xNi_{5-x}P_4$ nanosheets with different amounts of surface coverage by CQDs for efficient hydrogen evolution in water splitting by electrolysis. Greater amounts of CQDs, up to a certain point, lead to a larger effective surface area and lower charge-transfer resistance, which provide more active sites and faster reaction kinetics, respectively, thus boosting the catalytic activity of $Mn_xNi_{5-x}P_4$. Both the overpotential and the Tafel slope decrease as the amount of CQDs on the nanosheet surfaces increases, until the CQDs reach uniform surface saturation (3-CQDs/Mn_xNi_{5-x}P_4). The 3-

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CQDs/Mn_xNi_{5-x}P₄ catalyst requires the lowest overpotentials of 31 and 56 mV to achieve a current density of 10 mA cm⁻² in acidic and alkaline solutions, respectively, with good stability over 72 h in both acid and base. Additionally, the same catalyst requires overpotentials of only 229 and 361 mV to achieve current densities of 10 and 100 mA cm⁻² for oxygen evolution in an alkaline solution, as well as exhibiting good stability in base. In light of the efficient improvement in both HER and OER electrocatalytic performance, it is believed that CQDs could be combined with other two- or three-dimensional materials to achieve very good electrochemical catalysts in both acidic and alkaline conditions.

Experimental

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Synthesis of Ni_5P_4 and $Mn_xNi_{5\text{-}x}P_4$ nanosheets

An aqueous solution of manganese acetate was used as the Mn precursor solution. The dry Ni foam bonded with the Mn precursor was placed at the middle of a tube furnace and red phosphorous powder was placed at the upstream, with a continuous argon flow used for the synthesis. The $Mn_xNi_{5-x}P_4$ nanosheets were grown at 500 °C for 1 h and were then cooled down naturally under argon atmosphere. The Ni_5P_4 nanosheets were prepared by the same method, but without Mn precursor. **Preparation of CQDs/Mn_xNi_5-xP4** nanosheets

Two graphite rods were used as the two electrodes, deionized water was used as the electrolyte, and the bias was set as 25 V. After the graphite rods were corroded for several days, a brown CQD solution was obtained and then adjusted into concentrations of 0.5, 1, 1.5, and 2 mg mL⁻¹. $Mn_xNi_{5-x}P_4$ nanosheets were immersed in the different solutions to obtain $Mn_xNi_{5-x}P_4$ nanosheets with different CQD contents after annealing. The samples prepared by 0.5, 1, 1.5, and 2 mg mL⁻¹ CQDs / $Mn_xNi_{5-x}P_4$, 3-CQDs/ $Mn_xNi_{5-x}P_4$, and 4-CQDs/ $Mn_xNi_{5-x}P_4$, respectively. For comparison, 3-CQDs/Ni foam and 3-CQDs/ Ni_5P_4 samples were also prepared by the same method, but with Ni foam and Ni_5P_4 nanosheet substrates, respectively.

Further experimental details regarding materials, characterization, and electrochemical measurements are provided in the Supporting Information.

Conflicts of interest

There are no conflicts to declare.

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