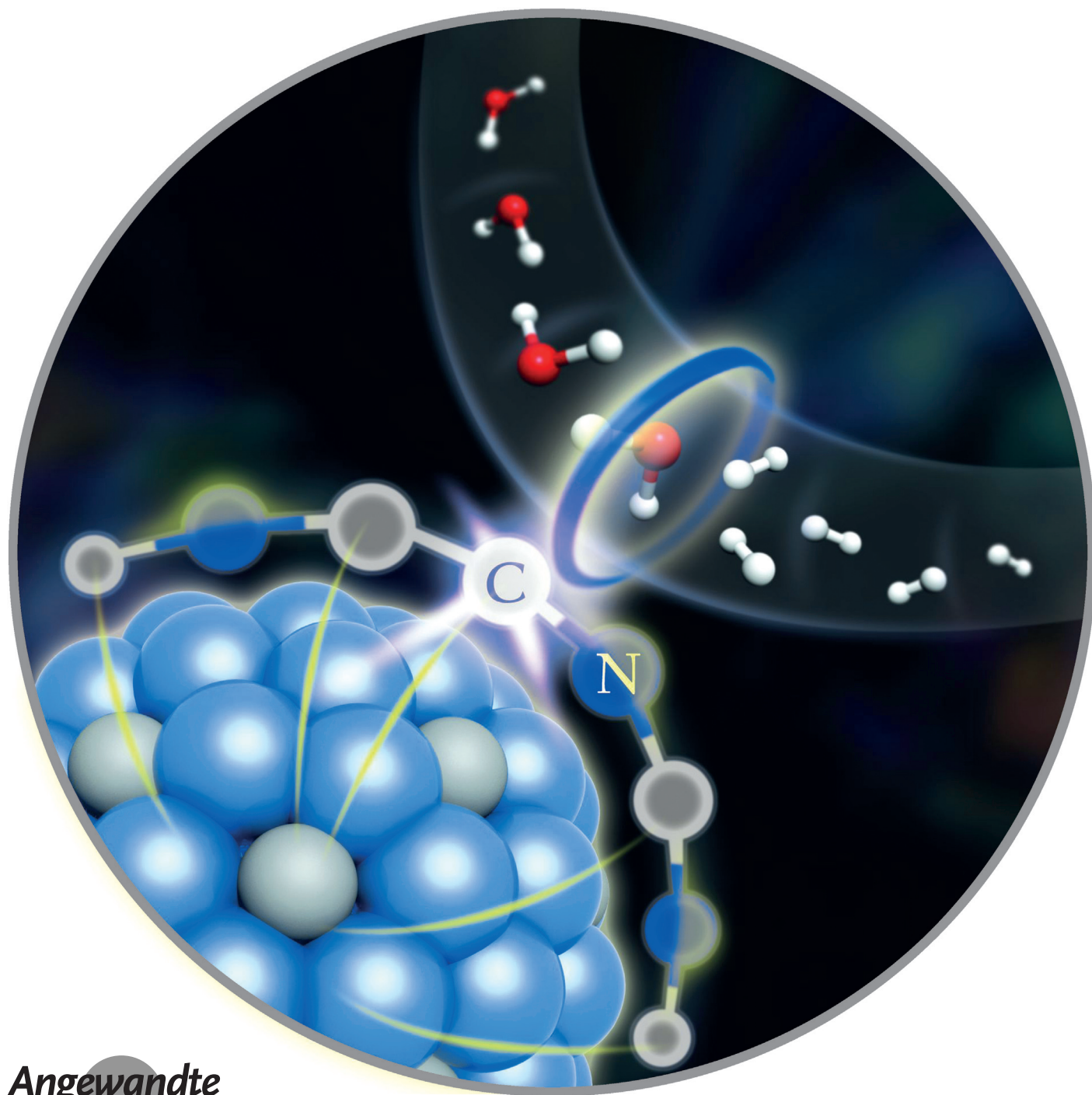


Coupling Mo₂C with Nitrogen-Rich Nanocarbon Leads to Efficient Hydrogen-Evolution Electrocatalytic Sites

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Abstract: In our efforts to obtain electrocatalysts with improved activity for water splitting, meticulous design and synthesis of the active sites of the electrocatalysts and deciphering how exactly they catalyze the reaction are vitally necessary. Herein, we report a one-step facile synthesis of a novel precious-metal-free hydrogen-evolution nanoelectrocatalyst, dubbed $\text{Mo}_2\text{C}@\text{NC}$ that is composed of ultrasmall molybdenum carbide (Mo_2C) nanoparticles embedded within nitrogen-rich carbon (NC) nanolayers. The $\text{Mo}_2\text{C}@\text{NC}$ hybrid nanoelectrocatalyst shows remarkable catalytic activity, has great durability, and gives about 100% Faradaic yield toward the hydrogen-evolution reaction (HER) over a wide pH range (pH 0–14). Theoretical calculations show that the Mo_2C and N dopants in the material synergistically co-activate adjacent C atoms on the carbon nanolayers, creating superactive non-metallic catalytic sites for HER that are more active than those in the constituents.

With an annual production of approximately 500 billion cubic meters, hydrogen (H_2) is one of the most important industrial feedstocks, currently widely used for petroleum refining and ammonia synthesis. This scenario is likely to change further, with hydrogen's potential to serve as a renewable alternative to fossil fuels in the future, and the surge of research on it as a result. However, current industrial production of H_2 primarily involves fossil fuels (e.g., natural gas),^[1] which, needless to say, generate the greenhouse gas CO_2 . Thus, more effort is needed to develop cleaner and sustainable hydrogen-production methods involving renewable energy-coupled electrocatalytic water splitting and photo(electro)chemical water splitting.^[1,2]

At the heart of these efforts, and challenges therein, lies the design and synthesis of the right electrocatalysts for the reactions involved in water splitting. Although Pt-based materials are very active electrocatalysts for the hydrogen-evolution reaction (HER), Pt-free electrocatalysts, based on transition metals such as Mo, W, and Co, are preferable as they are more sustainable due to their low cost and high abundance.^[1,3]

Owing to their similar d-band electronic density-of-state to that of Pt, high electrical conductivity, and optimal hydrogen-adsorption properties, transition-metal carbides, especially molybdenum and tungsten carbides, had long been expected to be effective non-Pt electrocatalysts for HER.^[4] This was realized first in 2012, with the report by the Hu group that commercially available molybdenum carbide microparticles (com- Mo_2C) show good catalytic activity toward HER.^[5] Since then, fine structural optimization of molybdenum carbide catalysts at the nanoscale has been actively pursued, and recent efforts have begun to bear more fruits.^[6–9] However, in all of the molybdenum carbide HER nanocatalysts reported to date, including those containing nanocarbons,^[8,9] the active sites have been considered to be present only on the surfaces of the molybdenum carbides, and the materials' overall catalytic activity has been shown to increase only by increasing the density of these active sites by nanostructuring. Moreover, although some molybdenum carbide/nanocarbon hybrid materials containing dopants have generally been found to have higher catalytic activity,^[6a,8] the effect of dopants and the molybdenum carbide/nanocarbon interface on the materials' catalytic activity remains ambiguous.

Herein, we report a facile, one-step synthetic route that leads to a novel precious-metal-free HER electrocatalyst composed of ultrasmall molybdenum carbide (Mo_2C) nanoparticles embedded within nitrogen-rich carbon (NC) nanolayers (Figure 1A). We also show that the $\text{Mo}_2\text{C}@\text{NC}$ hybrid material exhibits an unprecedented high electrocatalytic activity for HER under acidic, neutral, or basic conditions alike. To the best of our knowledge, this is the first time that a Mo_2C -based material is shown to serve as an efficient HER electrocatalyst over a wide pH range. Theoretical calculations show that the Mo_2C acts as electron donor for the adjacent C atoms in the carbon nanolayers, whereas the N-dopant atoms function as electron acceptor; this synergy between Mo_2C and N dopants is found to yield unprecedented, superactive nonmetallic catalytic sites on the carbon nanolayers that are more active than those in Mo_2C .

The $\text{Mo}_2\text{C}@\text{NC}$ was synthesized by a simple one-step thermal treatment in Ar atmosphere of homogeneously mixed ammonium molybdate and dicyandiamide (Figures 1A and S1; see the Supporting Information, SI, for details). The use of dicyandiamide is crucial in the synthesis of $\text{Mo}_2\text{C}@\text{NC}$ as it undergoes carbonization and helps the deoxygenation of ammonium molybdate, leading to the in situ generation of the nanocarbon species coupled with the Mo_2C nanoparticles. The most optimal pyrolysis temperature and weight ratio (ammonium molybdate/dicyandiamide) were found to be 800 °C and 1:2, respectively, and this condition gave a material that is denoted hereafter as $\text{Mo}_2\text{C}@\text{NC}$, unless indicated otherwise.

The structure and composition of the $\text{Mo}_2\text{C}@\text{NC}$ were studied by powder X-ray diffraction (XRD), Raman, and X-ray photoelectron spectroscopy (XPS; Figure S2). The results showed that $\text{Mo}_2\text{C}@\text{NC}$ was composed of β -phase of Mo_2C and N-rich carbon with N/C atomic ratio of about 1:5. Transmission electron microscopy (TEM) images (Figure 1B,C) showed that $\text{Mo}_2\text{C}@\text{NC}$ consisted of uniformly

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201504376>.

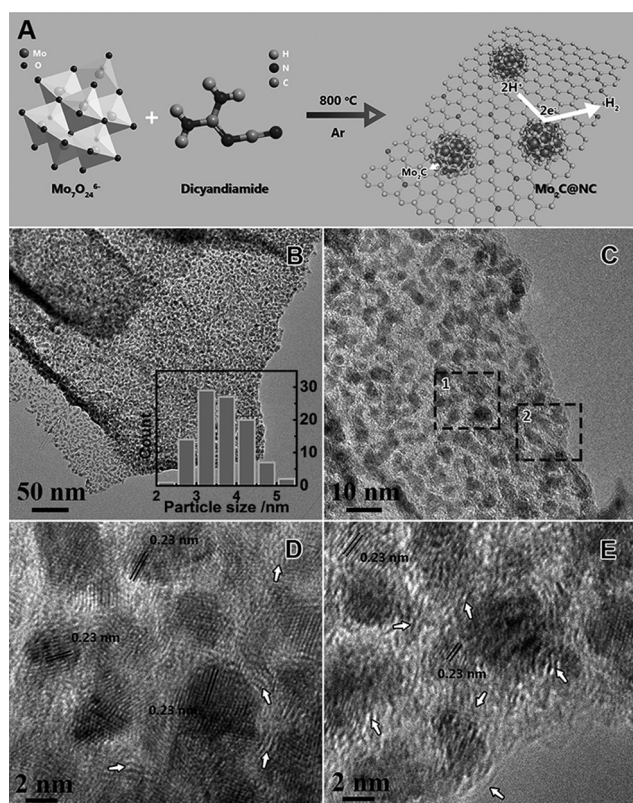


Figure 1. A) Illustration of the synthesis and the structure of $\text{Mo}_2\text{C}@\text{NC}$. B, C) TEM images of $\text{Mo}_2\text{C}@\text{NC}$. Inset in (B) displays particle size distribution of the Mo_2C nanoparticles. D, E) HRTEM images of the areas 1 and 2, respectively, in (C). The distance between the lines is 0.23 nm in all cases.

shaped nanoparticles with an average size of 3.6 nm that are encapsulated within lamellar carbon matrices. Elemental mapping of $\text{Mo}_2\text{C}@\text{NC}$ (Figure S3) revealed that the Mo, N, and C atoms were homogeneously distributed over the entire material, suggesting that the Mo_2C nanocrystals were uniformly distributed within the carbon matrices. High-resolution TEM images (Figure 1D and E) further corroborated that the Mo_2C nanoparticles were wrapped in carbon nanolayers. The observed lattice spacing on carbide nanoparticles was ca. 0.23 nm, which corresponds to the distance between the (101) crystal planes of $\beta\text{-Mo}_2\text{C}$ phase. In addition, some crystalline nanocarbons with 2–4 layers of carbon atoms, with a lattice spacing of ca. 0.34 nm, were seen around the carbide nanoparticles (as indicated with white arrows in Figure 1D and E), although amorphous carbon still dominated the lamellar carbon matrix around the nanoparticles.

The electrocatalytic activity of $\text{Mo}_2\text{C}@\text{NC}$ for HER in acidic (pH 0), neutral (pH 7), or basic (pH 14) media was then evaluated (SI). For comparison, the electrocatalytic activity of commercially available Mo_2C (com- Mo_2C), N-doped carbon (NC), and Pt/C (20 wt %) was also measured by using the same weight of samples in all the cases.

First, the electrocatalytic activity of the materials in acidic media was investigated. As shown in Figure 2A, the N-doped carbon and com- Mo_2C produced a current density of 1 mA cm^{-2} at an overpotential (η) of 360 and 300 mV,

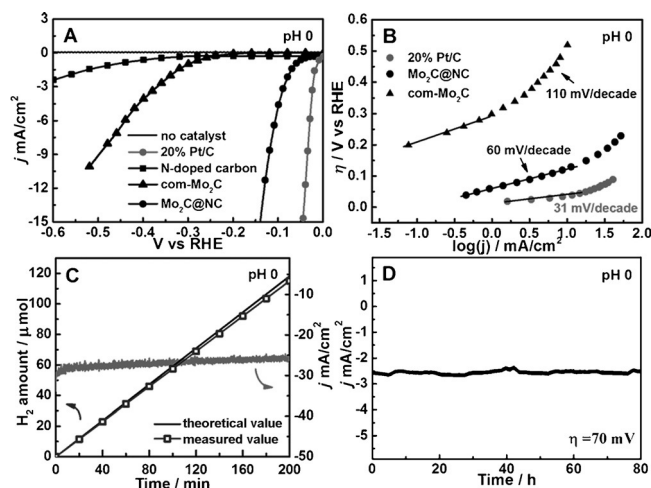


Figure 2. A) Steady-state current density as a function of applied voltage during HER at pH 0 over 20 wt % Pt/C, N-doped carbon, com- Mo_2C , and $\text{Mo}_2\text{C}@\text{NC}$. B) Tafel plots for the HER over 20 wt % Pt/C, com- Mo_2C , and $\text{Mo}_2\text{C}@\text{NC}$. C) Electrochemical efficiency of hydrogen production over $\text{Mo}_2\text{C}@\text{NC}$ at a current density of ca. 25 mA cm^{-2} , measured for 200 min. D) Current density vs. time (i - t) curve of HER over $\text{Mo}_2\text{C}@\text{NC}$ at $\eta = 70 \text{ mV}$ over 80 h-long electrocatalytic reaction.

respectively, whereas $\text{Mo}_2\text{C}@\text{NC}$ gave the same current density at a much lower η of 60 mV. In line with this result, $\text{Mo}_2\text{C}@\text{NC}$ gave a smaller Tafel slope (60 mV/decade) than com- Mo_2C (110 mV/decade; Figure 2B). Moreover, $\text{Mo}_2\text{C}@\text{NC}$ showed a higher exchange current density ($9.6 \times 10^{-2} \text{ mA cm}^{-2}$) than com- Mo_2C ($1.2 \times 10^{-3} \text{ mA cm}^{-2}$). Hence, $\text{Mo}_2\text{C}@\text{NC}$ can be said to be a much better electrocatalyst for HER than either N-doped carbon or com- Mo_2C . Furthermore, $\text{Mo}_2\text{C}@\text{NC}$ afforded a current density of 10 mA cm^{-2} (i.e., the current density expected for a 12.3 % efficient solar water-splitting device) at relatively low η of 124 mV. Thus, the results overall demonstrated that $\text{Mo}_2\text{C}@\text{NC}$ was an excellent water-splitting electrocatalyst. In fact, $\text{Mo}_2\text{C}@\text{NC}$'s catalytic activity is either comparable with or superior to the best Mo_2C -based HER electrocatalysts reported so far (Table S1).

Figure 2C compares the graphs of the amount of H_2 generated from the HER over $\text{Mo}_2\text{C}@\text{NC}$ versus the theoretically possible H_2 that can be evolved from electrochemical HER. $\text{Mo}_2\text{C}@\text{NC}$ clearly shows not only a stable hydrogen-evolution rate but also a rate ($34.5 \mu\text{mol h}^{-1}$) that is very close to the theoretically achievable value. In other words, the result demonstrates that $\text{Mo}_2\text{C}@\text{NC}$ gives about 100 % Faradaic yield and has excellent stability in HER. $\text{Mo}_2\text{C}@\text{NC}$ actually retained its activity and morphology even after 80 h-long electrocatalytic HER (Figures 2D and S4).

Until now most Mo_2C -based HER electrocatalysts have been found to work well only in acidic media.^[5–9] However, many water-alkali and chloro-alkali HER electrolyzers need active and durable catalysts that can operate in basic environment, and many microbial electrolysis cells typically need electrocatalysts that can function well in neutral media.^[10] As shown in Figure 3A and B, our $\text{Mo}_2\text{C}@\text{NC}$ exhibited good electrocatalytic activity toward HER both in

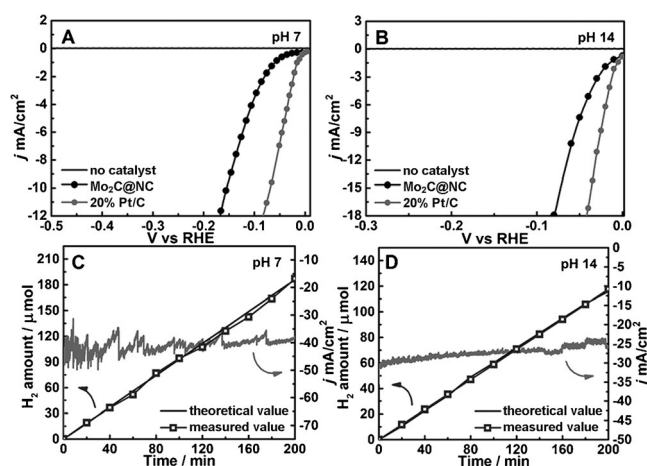


Figure 3. A,B) Steady-state current density as a function of applied voltage at pH 7 and pH 14 over 20 wt% Pt/C and Mo₂C@NC. C,D) Efficiency of hydrogen production over Mo₂C@NC at pH 7 and pH 14. The values of current density are all normalized with the surface area of the GCE.

neutral and basic media, affording a current density of 10 mA cm⁻² at ultrasmall overpotentials of 156 and 60 mV, respectively. It is worth noting that such high catalytic activity in neutral or basic media has never been achieved for Mo₂C-based catalysts before (Table S1), and Mo₂C@NC's activity in neutral and basic media was comparable to those of the best non-Mo₂C-based, noble metal-free HER electrocatalysts (Tables S2 and S3). Additionally, Mo₂C@NC showed excellent stability and about 100% Faradaic yield in both media (Figures 3C,D and S5). Overall these results clearly indicate that the Mo₂C@NC is a highly versatile, efficient HER electrocatalyst for a wide pH range (pH 0–14).

To uncover the interplay between the structures and the catalytic activity of the materials, a series of relevant samples was prepared by varying the weight ratio of the precursors (i.e., ammonium molybdate/dicyandiamide) and the pyrolysis temperature, and their properties were examined (Figure 4). Note that Mo₂C materials form only at or above 800 °C; so, by maintaining the temperature constant (800 °C), but using 1:1 and 1:3 ratios of the precursors, two different materials that were labeled as s-800-1/1 and s-800-1/3, respectively, were synthesized. Additionally, by keeping the ratios of the precursors constant (1:2), but using 900 and 1000 °C, two more materials denoted as s-900-1/2 and s-1000-1/2, respectively, were obtained. The

Mo₂C@NC discussed above, which was made from a 1:2 ratio of precursors at 800 °C, was denoted as s-800-1/2 here for comparison.

Sample s-800-1/1 was found to have Mo₂C microparticles without carbon residue, possibly due to the relatively low dicyandiamide used for its synthesis, whereas s-800-1/3 was found to have N-doped carbon-encapsulated MoC nanoparticles with ca. 3.2 nm in size (Figures S6 and S7). Note that s-800-1/2 contained Mo₂C nanoparticles (≈3.6 nm) embedded within N-doped carbon nanolayers. Thus, the results suggest that the carbon matrices prevent the Mo₂C nanoparticles from coalescence/sintering at high temperatures. The materials' catalytic activity (Figure 4A) was found to decrease in the order of s-800-1/2 > s-800-1/3 > s-800-1/1, indicating that the small-size carbide particles were important for the material's catalytic activity. In view of the fact that both s-800-1/2 and s-800-1/3 had carbon-encapsulated carbide nanoparticles with similar size, the higher catalytic activity of s-800-1/2 might be due to the higher density of N dopants in it (Figure 4B).

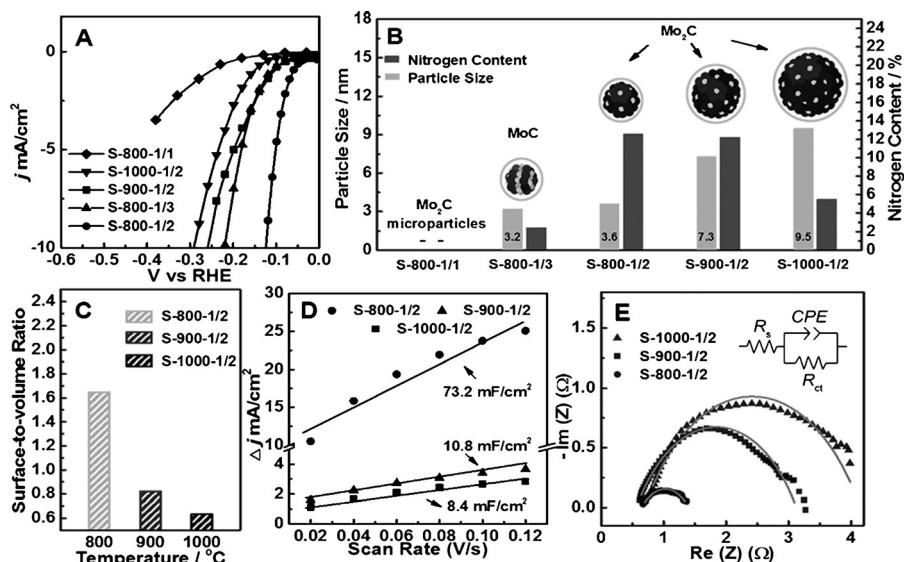


Figure 4. A) Comparison of the catalytic activities of five samples synthesized at different temperatures and ratios of starting materials. B) Comparison of particle size and N/C atomic ratio for the five samples prepared under different conditions. C) The calculated surface-to-volume ratios based on particle sizes of the samples. D) The difference in current density (Δj) between the anodic and cathodic sweeps (Δj) versus scan rate; the slope of the fitting line is used for determination of the double-layer capacitance (C_{dl}). E) Nyquist plots obtained by electrochemical impedance spectroscopy (EIS) for s-800-1/2, s-900-1/2, and s-1000-1/2. The data are fitted to the simplified equivalent circuit shown in the inset, and the fitting results are plotted as solid traces.

On the other hand, the materials s-800-1/2, s-900-1/2, and s-1000-1/2 were all found to have carbon-encapsulated Mo₂C nanoparticles, with increasing particle size and decreasing order of N-dopant density as their pyrolysis temperature was increased (Figures 4B, S8, and S9). These structural variations correlated well with the catalytic activities of the materials, which decreased in the order of 800-1/2 > s-900-1/2 > s-1000-1/2, Figure 4A. Accordingly, the surface-to-volume ratio of

carbon nanoparticles and the electrochemical surface area for the obtained samples (which is $s\text{-}800\text{-}1/2 > s\text{-}900\text{-}1/2 > s\text{-}1000\text{-}1/2$, Figure 4 C and D) were both found to be directly related to the material's catalytic activity. Additionally, electrochemical impedance spectra (Figure 4 E) showed that $s\text{-}800\text{-}1/2$ had a much lower Faradaic impedance than $s\text{-}900\text{-}1/2$ and $s\text{-}1000\text{-}1/2$, indicating that the electron transfer rates in HER was much faster in the presence of $s\text{-}800\text{-}1/2$ than the latter two.

To gain further insight into the high electrocatalytic activity of the $\text{Mo}_2\text{C}@NC$ material, we additionally performed density functional theory (DFT) calculations by constructing the correlative theoretical models (Figure S10 and Tables S4 and S5). It is well known that the adsorption free energy of H ($\Delta G(H^*)$) can serve as a good measure for the activity of a catalytic material for HER, for which a catalyst that gives $\Delta G(H^*) \approx 0$ is considered a good candidate for HER.^[11] Our calculations of the $\Delta G(H^*)$ value on the surfaces of $\text{Mo}_2\text{C}@NC$ are described in Figure 5 and Table S5. For comparison, a similar calculation

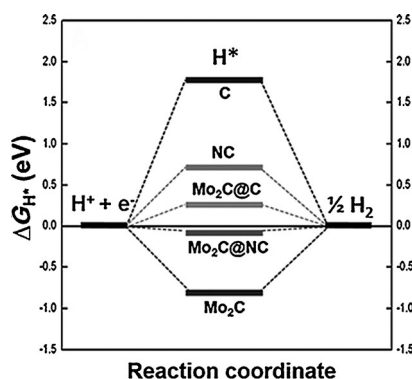


Figure 5. The calculated free-energy diagram of HER at equilibrium potential for five possible structures, namely $\text{Mo}_2\text{C}@NC$, $\text{Mo}_2\text{C}@C$, Mo_2C , C, and NC.

was conducted for carbon-layer-encapsulated Mo_2C nanoparticles ($\text{Mo}_2\text{C}@C$), Mo_2C , carbon layer (C), and N-rich carbon layer (NC). As illustrated in Figure 5, $\text{Mo}_2\text{C}@NC$ gave a much smaller $\Delta G(H^*)$ value than its constituents (i.e., C, NC, and Mo_2C), indicating that the hybrid nanomaterial possessed a higher catalytic activity for HER. This is in good agreement with the experimental results discussed above. Furthermore, $\Delta G(H^*)$ of $\text{Mo}_2\text{C}@NC$ was much smaller than that of $\text{Mo}_2\text{C}@C$, indicating that the N dopants introduced in the carbon nanolayers further enhanced the electrocatalytic performance of the material. In fact, the carbon atoms adjacent to the N dopants were found to be the most electrocatalytically active sites in $\text{Mo}_2\text{C}@NC$ (see SI).

The presence of synergistic effects between the Mo_2C nanoparticles and the N dopants in $\text{Mo}_2\text{C}@NC$ were further explored by comparing the difference in charge density ($\Delta\rho$) between $\text{Mo}_2\text{C}@NC$ and $\text{Mo}_2\text{C}@C$ (Figure S11). An electron-transfer process from Mo_2C to the carbon layer in $\text{Mo}_2\text{C}@C$ was evident from the observed blue color on all of the carbon atoms in the corresponding $\Delta\rho$ plot. However, besides this electron-transfer process, electron transfer from the adjacent C atoms (those shown in yellow) to N atoms was simulta-

neously seen in $\text{Mo}_2\text{C}@NC$. These results revealed the strong electron-withdrawing features of N dopants in the material. This, in turn, could induce a complex electron-transfer process ($\text{Mo}_2\text{C} \rightarrow \text{C} \rightarrow \text{N}$) in $\text{Mo}_2\text{C}@NC$, making the neighboring C atoms to play dual roles both as electron acceptors and electron donors. This result reinforces the presence of the synergy between Mo_2C and N dopants, rendering unprecedented catalytic activity to the C atoms adjacent to N atoms in the carbon layer and making $\text{Mo}_2\text{C}@NC$ a highly efficient HER catalyst.

In conclusion, a precious-metal-free HER electrocatalyst containing ultrasmall molybdenum carbide (Mo_2C) nanoparticles embedded in nitrogen-rich carbon (NC) nanolayers has been synthesized in one step from inexpensive precursors. Theoretical studies have revealed a synergistic effect between Mo_2C and N dopants that yield superactive nonmetallic HER catalytic sites on the carbon nanolayers.

Acknowledgements

X.Z. and W.C. appreciate the financial support from the NSFC (21371070, 21401066, 21103065, and 21373099), Jilin Province Science and Technology Development Project (20150520003JH), and the Ministry of Education of China (20110061120024 and 20130061110020). T.A. gratefully acknowledges financial support by the NSF (NSF CBET-1134289). This work was also supported by the Graduate Innovation Fund of Jilin University (2015010).

Keywords: catalytically active site · composite material · electrocatalysis · molybdenum carbide · water splitting

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10752–10757
Angew. Chem. **2015**, *127*, 10902–10907

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Received: May 13, 2015

Published online: July 23, 2015