

Facile Synthesis of Hollow Carbon Microspheres Embedded with Molybdenum Carbide Nanoparticles as an Efficient Electrocatalyst for Hydrogen Generation

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Electronic Supplementary Information

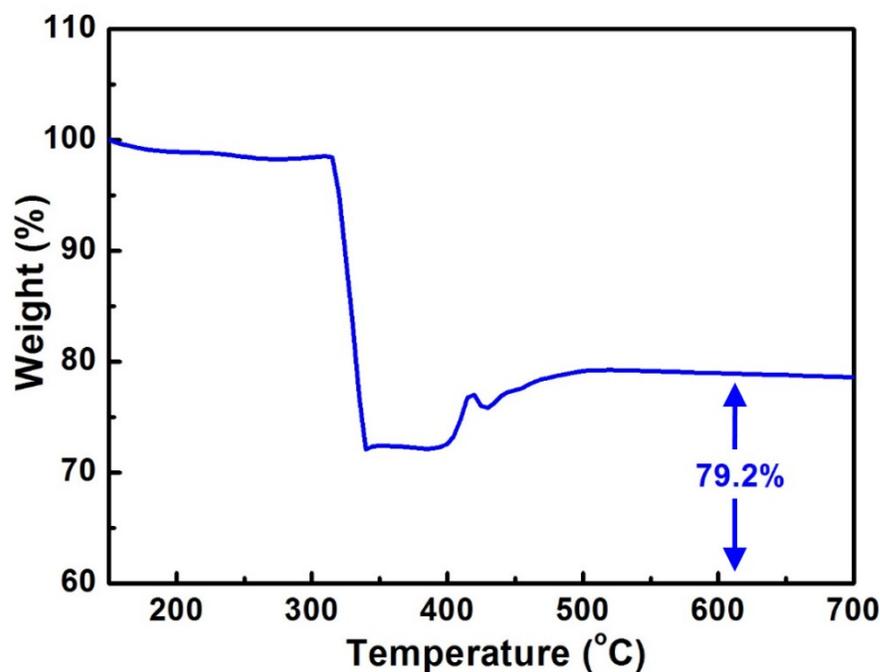


Figure S1. TGA curve of Mo₂C/HCMs in O₂ atmosphere with heating rate of 10 °C min⁻¹.

Computation 1.

At 700 °C, all Mo₂C nanoparticles were oxidized to MoO₃ during the TGA measurement in oxygen atmosphere, and all carbon was removed. The weight percent of Mo₂C in Mo₂C/HCMs is computed according to the follow equation:

$$\frac{2 * w_{Mo_2C}}{M_{Mo_2C}} = \frac{w_{remain}}{M_{MoO_3}}$$

Where w_{Mo_2C} is the weight percent of Mo₂C, M_{Mo_2C} is the molecular weight of Mo₂C, w_{remain} is the weight of MoO₃ suggested by the TGA curve, M_{MoO_3} is the molecular weight of MoO₃. According to the TGA curve, w_{remain} is 79.2%, and then w_{Mo_2C} is computed to be 56.1%.

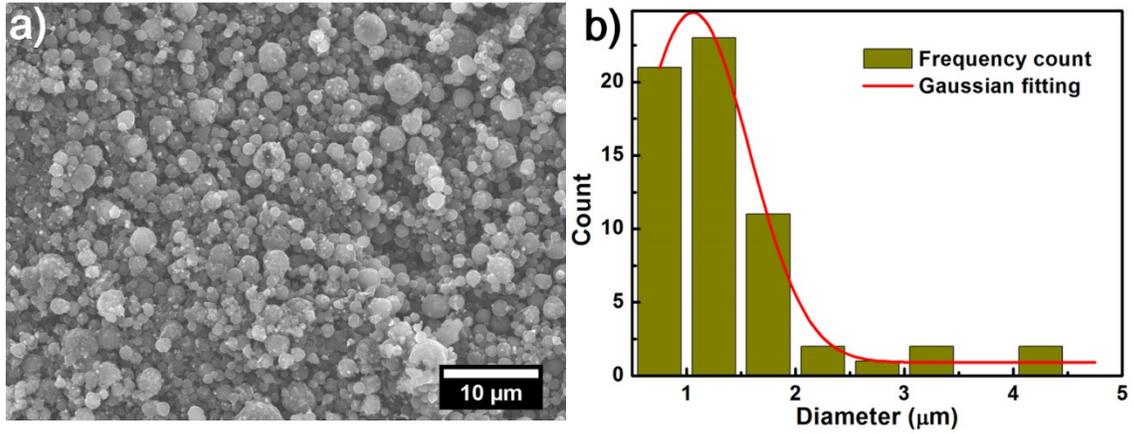


Figure S2. (a) A typical low magnification SEM image of the Mo₂C/HCMs. (b) Diameter distribution of hollow carbon microspheres (HCMs) in the Mo₂C/HCMs.

Table S1. Key performance of representative Mo₂C nanostructures.

| Catalyst | Substrate | Mass density (mg cm ⁻²) | η_{10} (mV) | η_{20} (mV) | Tafel slope (mV/dec) | Electrolyte |
|---|------------------------------|-------------------------------------|------------------------------------|------------------|----------------------|---|
| Mo ₂ C nanoparticles supported on Vulcan carbon black ¹ | GCE | 0.6 | 180 | 210 | 82 | 0.5 M H ₂ SO ₄ |
| Commercial Mo ₂ C particles ² | carbon-paste electrodes | 1.4 | 210 | 225 | 56 | 0.5 M H ₂ SO ₄ |
| Mo ₂ C/CNT Mo ₂ C/XC-72R ³ | carbon paper | 2 | 140(η_8) 200(η_8) | | 55.2 59.4 | 0.1 M HClO ₄ |
| Mo ₂ C nanowires Mo ₂ C nanosheets ⁴ | GCE | 0.357 | 200 225 | 220 260 | 55.8 64.5 | 0.5 M H ₂ SO ₄ |
| Mo ₁ Soy-RGO ⁵ | carbon paper | 0.47 | 177 | -- | 66.4 | 0.1 M HClO ₄ |
| 3D hierarchical porous Mo ₂ C framework ⁶ | GCE | 0.28 | 97 | 125 | 60 | 0.5 M H ₂ SO ₄ |
| Mesoporous m Mo ₂ C nano-octahedrons ⁷ | glassy carbon disk electrode | 0.8 | 142 | 160 | 53 | 0.5 M H ₂ SO ₄ |
| Mo ₂ C-WC Composite Nanowires ⁸ | GCE | 1.28 | 130 | 150 | 52 | 0.5 M H ₂ SO ₄ |
| Mo ₂ C/HCMs | GCE | 0.285 | 179 265 | 203 346 | 83.9 143.4 | 0.5 M H ₂ SO ₄ 1 M KOH |

Electrochemical surface area.

Electrochemical capacitance was measured to evaluate the effective surface area of various catalysts.^{9, 10} Cyclic voltammetry (CV) experiments were performed at various scan rates (60, 80, 100, 120, 140, 160 and 180 mV s^{-1}) in 0.1-0.2 V vs. RHE at pH 7. The cyclic voltammograms of the $\text{Mo}_2\text{C}/\text{HCMs}$ are plotted in Figures S3a and that of the $\text{Mo}_2\text{C}/\text{XC-72R}$ in Figure S3b. The capacitance current density ($\Delta J = J_a - J_c$ at 0.15 V vs. RHE) was plotted against the scan rate and the specific capacitance is estimated by plotting the ΔJ , being 17.2 mF cm^{-2} for the $\text{Mo}_2\text{C}/\text{HCMs}$ and 1.4 mF cm^{-2} for the $\text{Mo}_2\text{C}/\text{XC-72R}$ (Figure 4b). As the specific capacitance is proportional to the surface area and the conductivity of the materials, a much larger specific capacitance of the $\text{Mo}_2\text{C}/\text{HCMs}$ than that of the $\text{Mo}_2\text{C}/\text{XC-72R}$, indicates the high exposure of effective active sites for the $\text{Mo}_2\text{C}/\text{HCMs}$, which is responsible for the excellent HER activity.

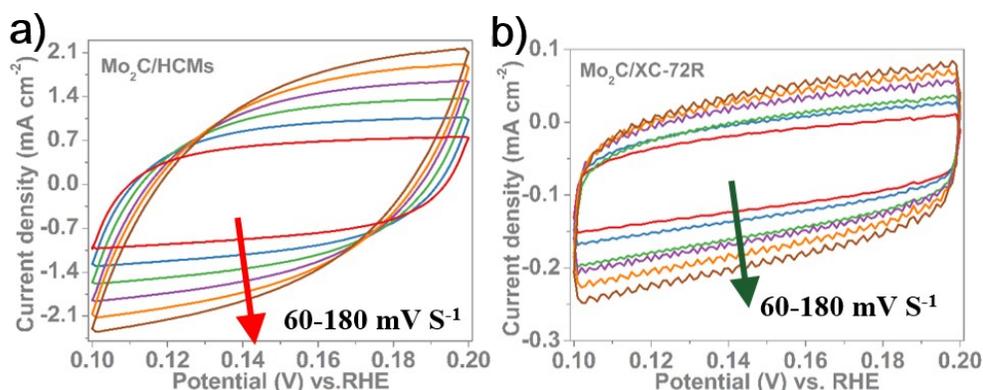


Figure S3. (a,b) Cyclic voltammetry curves of $\text{Mo}_2\text{C}/\text{HCMs}$ and $\text{Mo}_2\text{C}/\text{XC-72R}$ in the region of 0.1-0.2 V vs. RHE, respectively. (c) The differences in current density variation ($\Delta J = J_a - J_c$) at an overpotential of 0.15 V plotted against scan rate fitted to a linear regression enables the estimation of the specific capacitance.

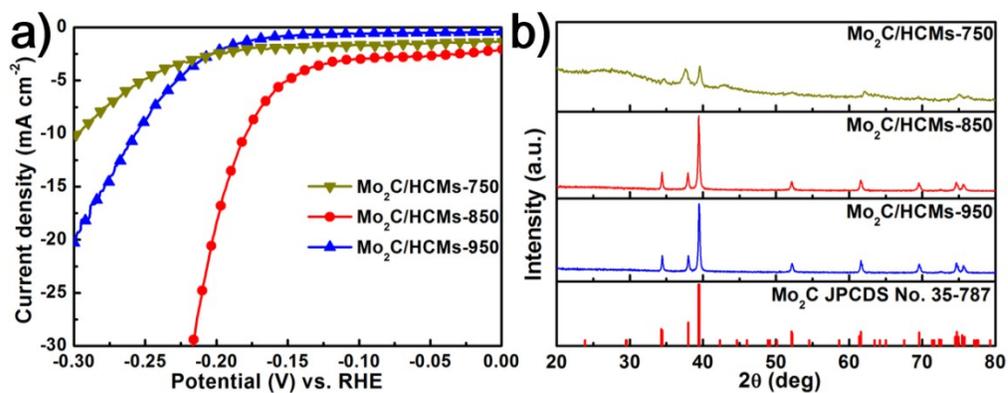


Figure S4. Polarization curves and corresponding XRD patterns of Mo₂C/PCMs-750, Mo₂C/PCMs-850 and Mo₂C/PCMs-950.

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