

1. Synthesis of Electrocatalyst

1.1 Synthesis of NC Electrocatalyst

Aniline (0.1 g) and 10 mL of 1 M HCl solution with ultrasonic for 30 mins for complete dispersion. Then mixture was transferred to 100 mL of a three-neck flask under stirring in an ice water bath. Then slowly added the ammonium sulfate (0.246 g) to the above reaction mixture under stirring in an ice water bath for 8 h and continued stirring at room temperature for 16 h. After the reaction, the green mixture was centrifuged several times, and dried for 12 h in a 60 °C blow-wind drying chamber. The sample was placed in a tube furnace and heated up to 900 °C in a nitrogen-protected atmosphere for 2 h with a heating rate of 2 C min⁻¹, and finally, the NC catalyst was obtained.

1.2 Synthesis of NC/Mo₂C and NC-TiO₂ Electrocatalyst

Aniline (0.1 g) and 10 mL of 1 M HCl solution with ultrasonic for 30 mins for complete dispersion. Then mixture was transferred to 100 mL of a three-neck flask under stirring in an ice water bath. Then slowly added the phosphomolybdic acid (0.1 g) and ammonium sulfate (0.246 g) to the above reaction mixture under stirring in an ice water bath for 8 h and continued stirring at room temperature for 16 h. After the reaction, the green mixture was centrifuged several times for unreacted particles was removed, and dried for 12 h in a 60 °C blow-wind drying chamber. The sample was placed in a tube furnace and heated up to 900 °C in a nitrogen-protected atmosphere for 2 h with a heating rate of 2 C min⁻¹, and finally, the NC catalyst was obtained. Calcination have mostly influenced the effect of the reaction by changing the morphology and properties of the nanocomposites. The metals are commonly stable upto 1000 °C so there is a possible of degradation of M-O ligands and exhibits the ununiform morphology at this temperature. Therefore, here the calcination was carried out at 900 °C for the good activity and to control the agglomeration of the NC/Mo₂C@TiO₂. For the comparison studies, the NC/Mo₂C@TiO₂ was calcinated at 800°C and 1000°C termed as NC/Mo₂C@TiO₂-800 and NC/Mo₂C@TiO₂-1000. Furthermore, the optimization studies were carried out with different ratio of phosphomolybdic acid (i.e. 0.05g and 0.2g) denoted as NC/Mo₂C@TiO₂-0.05 and NC/Mo₂C@TiO₂-0.2 to differentiate the morphology and electrocatalytic performances of 0.1g of phosphomolybdic acid in the NC/Mo₂C@TiO₂. As the same synthesis method following to prepared the NC/TiO₂ catalyst this reaction without adding Mo catalyst carryout.

2. Physical characterization techniques

The morphology of the prepared samples was characterized using a field emission scanning electron microscope (FESEM) (JSM-7610F, Japan). The elemental composition of the prepared materials was analysis by energy-dispersive X-ray spectroscopy (EDS) (JSM-7610F, Japan). Structural characteristics of the catalysts were obtained by Bruker D8 advance (Germany) diffractometer using nickel filter Cu-K α radiation operated at 40 kV and 40 mA. The average wavelength of the radiation was 1.5425 Å. Diffractograms were taken between $2\theta = 20^\circ$ - 80° using a step size of 0.033° [2θ] at a scan rate of 6° [2θ] min^{-1} . The high-resolution transmission electron microscope (TEM) was performed on a JEM-2100 Plus (Japan) field-emission transmission electron microscope with an accelerating voltage of 200 kV. Raman spectroscopic measurements were carried out using a dispersive Raman microscope (Bruker D8 advance, UK) with an excitation wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) of the catalyst samples were recorded using an AXIS ULTRA (UK) electron spectrometer with monochromatic Al K α source (5.5 mA, 15 kV).

3.4 Electrochemical performance test

3.4.1 Working electrode preparation

3.1.1 Preparation method of catalyst coated electrode:

A piece of nickel foam NF (1 cm \times 3 cm) was washed with 2 M hydrochloric acid for 10 minutes, and then washed with deionized water/ethanol mixture. Prior to perform the electrochemical test, 2 mg of catalyst was dispersed in 5 mL containing 30 μL of 5 wt% Nafion and 400 μL ethanol sonication for 30 min. The slurry coated into nickel foam substrate using drop cast method. Finally coated the NF dry at 60°C for 6 hours after drying electrode tested for electrochemical performance.

3.4.2 Electrochemical test system

The electrochemical measurements, namely linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of the catalyst were carried out on a Shanghai Chenhua CHI760D electrochemical workstation using a standard three-electrode system. Among them, the saturated calomel electrode (SCE) is the reference electrode, the platinum is the counter electrode, and the nickel foam coated with the catalyst is used as the working electrode. All test results are converted to reversible electrodes by the following formula. All test results were calculated to a reversible hydrogen electrode (RHE)

by using the following formula: $E \text{ (V vs. RHE)} = E \text{ (V vs. SCE)} + 0.0592 * \text{pH} + E \text{ (SCE)}$. LSV curves were evaluated at $-1.6 \sim -1.0 \text{ V}$ with a scan rate of 5 mV s^{-1} . The catalysts coating NF electrodes can be used as a working electrode. The EIS spectra of the catalysts were obtained at -0.3 V vs. RHE and the frequency range varied from 0.01 to 10 kHz with an A_c amplitude of 5 mV .

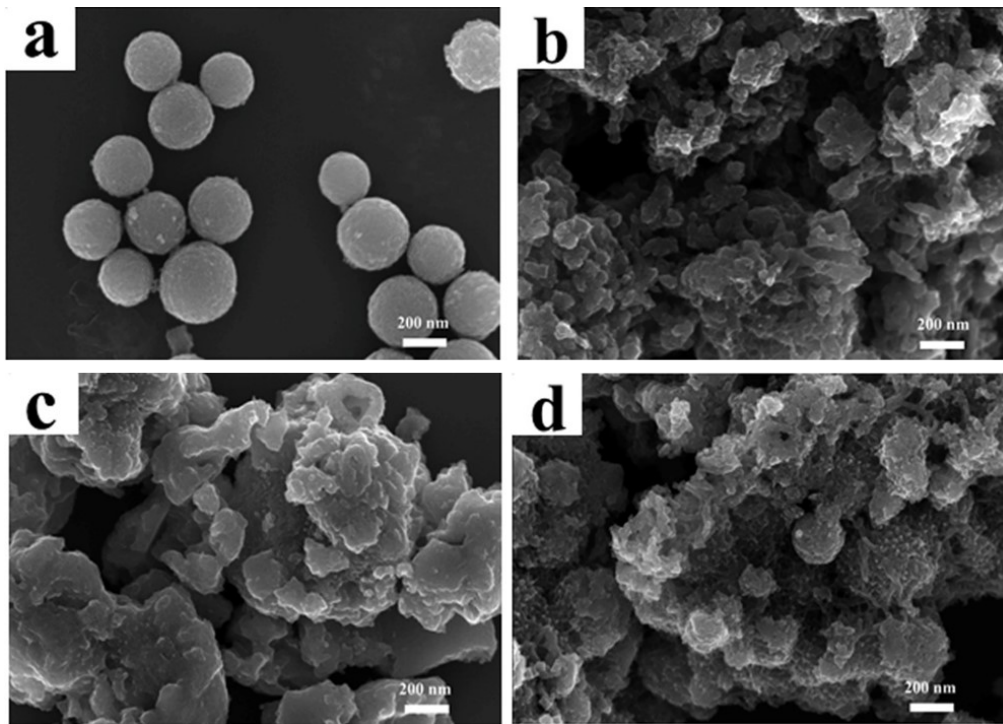


Fig.S1. FESEM images of TiO₂ (a), NC (b), NC@Mo₂C (c), NC@TiO₂ (d).

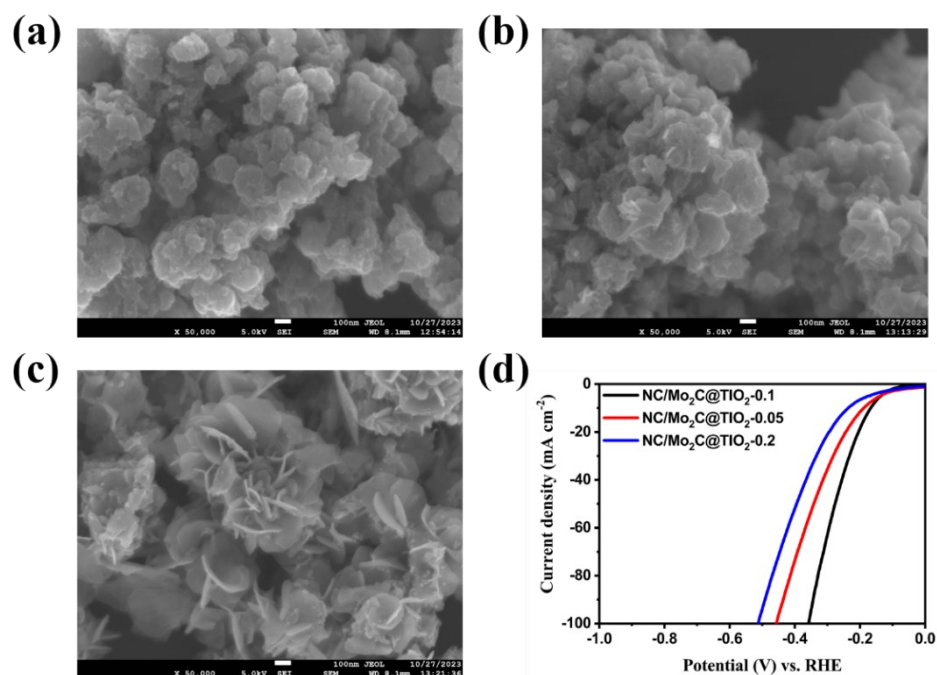


Fig.S2. SEM images of NC/TiO₂@Mo₂C-0.05 (a), NC/TiO₂@Mo₂C-0.1 (b) and NC/TiO₂@Mo₂C-0.2 (c). LSV curves of materials obtained by different dosage of phosphomolybdic acid (d)

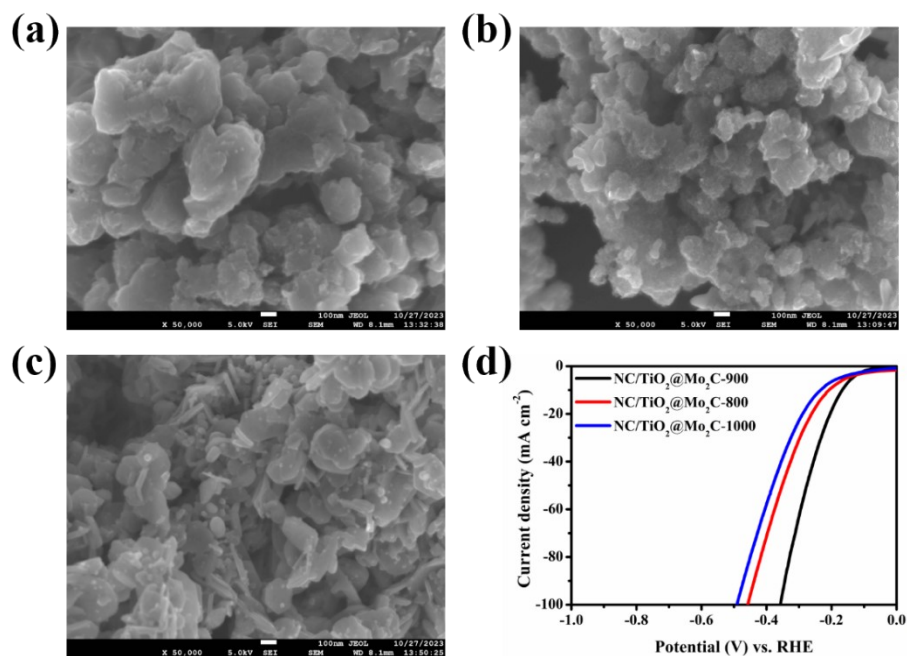


Fig.S3. SEM images of NC/TiO₂@Mo₂C-800 (a), NC/TiO₂@Mo₂C-900 (b) and NC/TiO₂@Mo₂C-1000 (c). LSV curves of materials obtained at different calcination temperatures (d).

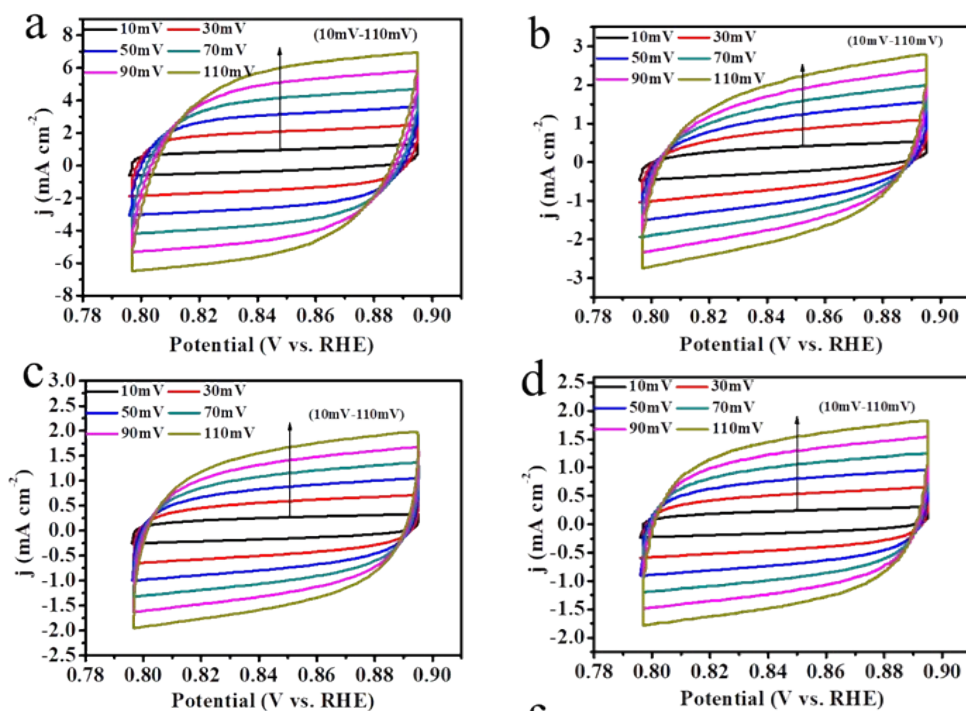


Fig. S4. Cyclic voltammograms (CV) of NC/Mo₂C@TiO₂ (a), NC@Mo₂C (b) and NC@TiO₂ (c), NC (d) in 1M KOH in the non-Faradaic potential range of 0.79 V to 0.89 V at scan rates of 10, 30, 50, 70, 90 and 110 mV s⁻¹, respectively.