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**Three dimensional porous graphene supported NiMo nanoparticles
capsuled by N-doped graphene as acid-stable, earth abundant catalysts for
highly efficient hydrogen evolution**

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[Abstract] The hydrogen evolution reaction in electrochemical water splitting is a potential alternative of producing hydrogen gas without using any fossil fuels. Pt and other noble metals still play a major role of HER catalysts due to the high catalytic activities and stability in acidic electrolytes. However, the scarcity and high cost become main obstacles to widespread use. At present, though several non-noble metal catalytic systems were established, most of these catalysts are degraded very fast in acidic electrolytes accompanied by serious decline of HER performances. Here we report acid-stable, earth-abundant catalysts with high HER activity, which is NiMo nanoparticles covered by N-doped graphene on the surface of three dimensional porous graphene. With the protection of graphene layers, the non-noble catalysts show chemical stability in acidic electrolytes without losing the high hydrogen evolution activity, opening a potential pathway to develop noble metal-free HER catalysts.

[Introduction] The renewable energy has attracted great attentions in recent decades due to the growing threat of CO₂ emission and global warming. Hydrogen, one of the most promising alternatives of traditional fossil fuel, achieves conversion of chemical energy to electricity or heat through fuel cell or combustion. Nowadays, the hydrogen production is mainly dominated by methane reforming which consumes natural gas and is not a sustainable method, emitting by-product gas. Water splitting combined with renewable electrical sources, such as wind power, solar energy, hydro energy, etc., are considered as clean and sustainable ways to produce hydrogen. The hydrogen evolution reaction (HER) is one of the half reactions of water splitting, occurring at cathodes, which has sluggish reaction kinetics and needs more potential than theoretical value. Therefore, a wide range of catalysts are developed in recent decades to lower overpotential and achieve larger current density. Platinum is the best performance catalyst of HER in acid electrolytes. However, the limited worldwide supply and high cost become main obstacles to its widespread use. Though some low price and plentiful non-noble metals exhibit excellent HER activities, the acid-soluble characteristic of these catalysts imposes restrictions on using under acidic conditions. Here we demonstrate a N-doped graphene capsuled NiMo nanoparticles on 3D N-doped graphene (capsuled NPNiMo@3D N-graphene) as HER catalysts and shows high activity and chemical stability in 0.5M H₂SO₄ solution.

[Methods] The synthesis process of NiMoO₄ nanofibers was already reported in details [1]. The dried NiMoO₄ nanofibers were put into a quartz tube furnace and annealed at 500-1000°C for 1h under a mixed atmosphere of H₂/Ar to achieve porous NiMo. After that, the temperature was decreased to 800-900°C for N-doped graphene (N-graphene) growth for 15s on the surface of NiMo using a chemical vapor deposition (CVD) method with mixed gases of pyridine, H₂ and Ar. The weak acid was used to remove the resulting porous NiMo substrates to obtain 3D porous N-graphene. Then, the NiMoO₄ nanofibers were deposited on the surface of 3D N-

graphene under vacuum. After completely drying up, the 2nd CVD process was similarly performed. The graphene layers were grown on the surface of NiMo nanoparticles through the 2nd CVD to achieve the capsuled structures. The morphology and microstructure of this catalyst were characterized by a scanning electron microscope (SEM, JEOL JSM-4300) and transmission electron microscope (JEOL JEM-2100F and JEM-ARM200F). The X-ray diffraction (XRD) was carried out using a RIGAKU SmartLab 9MTP diffractometer with a 9.0 kW rotating anode generator (Cu K α 1 radiation; $\lambda = 1.5406 \text{ \AA}$). Raman spectra was performed using a Renishaw InVia Reflex 532 with an incident wavelength of 532.5nm. The X-ray photoelectron spectroscopy (XPS, AXIS ultra DLD, Shimazu) with Al K α using X-ray monochromator as well as X-ray energy-dispersive spectroscopy (EDS, SDD Type, Detection surface area 30 mm²; Solid angle 0.26 sr) were utilized for chemical analysis.

[Results and Discussion]

The morphology of capsuled NPNiMo@3D N-graphene was investigated by SEM and TEM. The SEM (Figure 1a) suggests that the capsuled NPNiMo@3D N-graphene has a bicontinuous and open porous 3D structure with a pore size less than 1 μm . The NiMo nanoparticles were dispersed uniformly on the surface of 3D N-graphene as shown in Figure 1b. The EDS mapping image indicates the homogeneously distributed nanoparticles on the surface of N-graphene were mainly composed of nickel and molybdenum.

The capsuled NPNiMo@3D N-graphene was used as a working electrode to investigate the HER performance in a three electrode (grassy carbon and silver/silver chloride as a count electrode and reference electrode). For comparisons, the NiMo alloy, pure 3D N-graphene, and 10 wt% Pt/C were also similarly carried out. As shown in Figure 2, the pure 3D porous N-graphene without any NiMo revealed almost no HER activity even with the overpotential of 200 mV. The NiMo alloy uncovered by graphene exhibited a near zero onset overpotential and achieved a current density of 10 mA cm⁻² at only 50 mV. However, the current density decreased rapidly to almost zero after 1000 CV cycles due to the severe dissolution of NiMo in 0.5M H₂SO₄ solution. The capsuled NPNiMo@3D N-graphene showed simultaneously high HER activity and excellent stability. The current density decreased negligibly after 1000 CV cycles, which was beyond the performance of commercial 10 wt% Pt/C. Through the chronoamperometry test, the capsuled NPNiMo@3D N-graphene was kept a current density of about 53 mA cm⁻² under the overpotential of 150 mV for 20 h, exhibiting a long-term stability.

[References]

[1] P. R. Jothi *et al.* *Journal of Power Sources* **277**, 350 (2015).

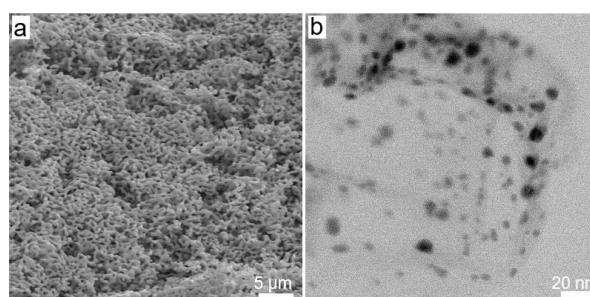


Fig. 1. (a) SEM image; (b) TEM image of capsuled NPNiMo@3D N-graphene.

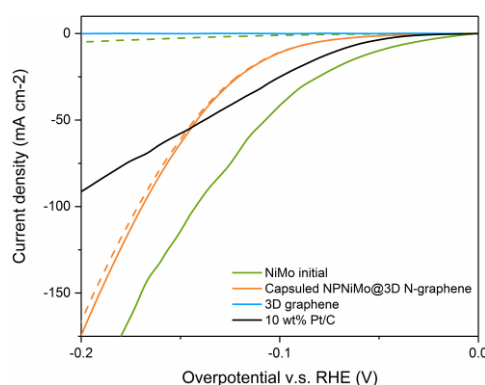


Fig. 2. Polarization curves of the NiMo, capsuled NPNiMo@3D N-graphene, pure 3D N-graphene and 10 wt% Pt/C; the dashed lines mean the performances after 1000 CV cycles.