Electronic Supplementary Information (ESI)

In situ Growth of Ni-Fe Alloy on Graphene-like MoS_2 for Catalysis of Hydrazine Oxidation

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Experimental Section

Materials

Graphene sheets (95%) were purchased from Nanjing XFNano Materials Tech Co., Ltd, China. molybdenum disulfide (99%) was purchased from aladdin-reagent Co. Ltd. Unless otherwise stated, all chemicals were used as received without further purification. De-ionized water (18.2 MΩ) was used throughout the experiments.

Instruments

Transmission electron microscopy (TEM) images were performed on Tecnai G2 F30 electron microscope operating at 100 kV. XRD data was obtained by a XPERT-PRO X-ray diffractometer using Cu K α radiation. Atomic force microscope (AFM) images were obtained by a Agilent 5500 SPM systems with taping mode. Scanning electron microscopy (SEM) images were performed on JSM-6701F. Raman spectra were obtained by inVia Reinishaw confocal spectroscopy with 514 nm laser excited. To study the electrocatalytic characteristics of Ni-Fe/MoS_2 hybrid, a conventional three-electrode system was used at 50℃ throughout this work. A GC electrode (3 mm in diameter) served as the working electrode, a platinum wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The electrolyte was 0.1 M hydrazine hydrate/0.015 M NaOH which had been purged with N_2 for 10min prior to the experiment. CV scans were recorded using CHI660C Electrochemical analyzer (CHI Instrument Corp. Shanghai).

The details of graphene-like MoS_2 preparation

According to the literature[1]: 30 mg of MoS_2 powder was added to 25 mL flasks. 10 mL of

ethanol/water with EtOH volume of 45% was added as dispersion solvent. The sealed flask was sonicated for 8 h, and then the dispersion was centrifuged at 3000 rpm for 20 mins to remove aggregates. The supernatant was collected and the concentration of MoS_2 in 45% ethanol/water was estimated to be 0.02mg mL^{-1}. The prepared dispersion of graphene-like MoS_2 was centrifuged to 0.2mg ml^{-1}, and then 10 uL of this MoS_2 suspension was dropwise added to a GC electrode (3 mm in diameter) which was served as the working electrode.

The details of DC electroplating

An electrochemical cell with a two-electrode configuration was used for the experiments. A copper plate (50mm×10mm×1mm)was used as the cathode and a glass carbon electrode (3mm) which loaded the materials used as anode. The two electrodes were placed into a cell using $NiSO_4 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ as plating solution at 50℃. After plating 5 seconds, the electrode was washed with deionized water and then dired.

Nickel iron DC electroplating formula

Nickel(II) sulfate 250g/l
Iron(II) sulfate 25.6g/l
Boric acid 40g/l
Sodium chloride 25g/l
Saccharim 2g/l
Sodium citrate 14.7g/l
Ascorbic acid 0.5g/l
2-Butyne-1,4-diol 0.6g/l
Sodium dodecylbenzenesulphonate 0.05g/l

Table S1

The compositions of the Ni-Fe alloy catalysts derived from inductively coupled plasma spectra (ICP)

The concentration of Nickel(II) sulfate (g/L)	The quality of Iron(II) sulfate (g/L)	The compositions of the most active catalysts
250	0	$Ni_{100}Fe_0$
250	20	$Ni_{90}Fe_{10}$
250	30	$Ni_{80}Fe_{20}$
250	40	$Ni_{70}Fe_{30}$
250	60	$Ni_{60}Fe_{40}$
0	100	Ni_0Fe_{100}

HRTEM

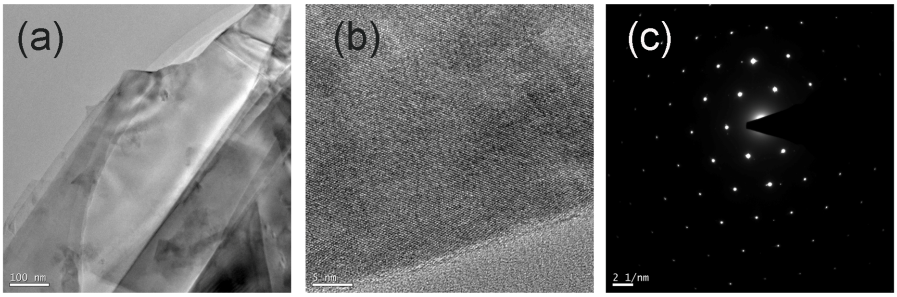


Fig. S1 (a) HRTEM image of the graphene like MoS_2. Scale bar is 100 nm; (b) HRTEM image of the graphene like MoS_2. Scale bar is 5 nm; (c) The SAED pattern of the graphene like MoS_2.

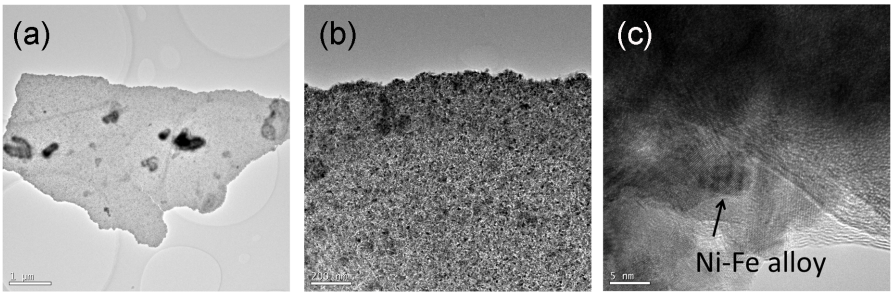


Fig. S2 (a) HRTEM image of the Ni-Fe/MoS_2. Scale bar is 1 um; (b) HRTEM image of the Ni-Fe/MoS_2 hybrid. Scale bar is 200 nm; (c) HRTEM image of the Ni-Fe/MoS_2 hybrid. Scale bar is 5 nm.

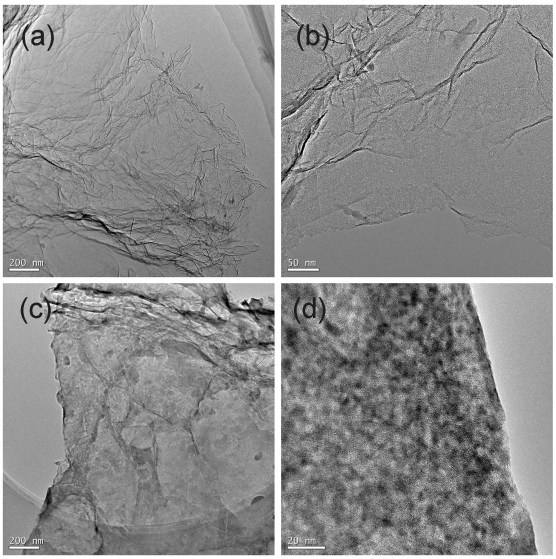


Fig. S3 (a) HRTEM image of graphene. Scale bar is 200 nm; (b) HRTEM image of graphene. Scale bar is 50 nm; (c) HRTEM image of the Ni-Fe/graphene. Scale bar is 200 nm; (d) HRTEM image of the Ni-Fe/graphene. Scale bar is 20 nm.

AFM

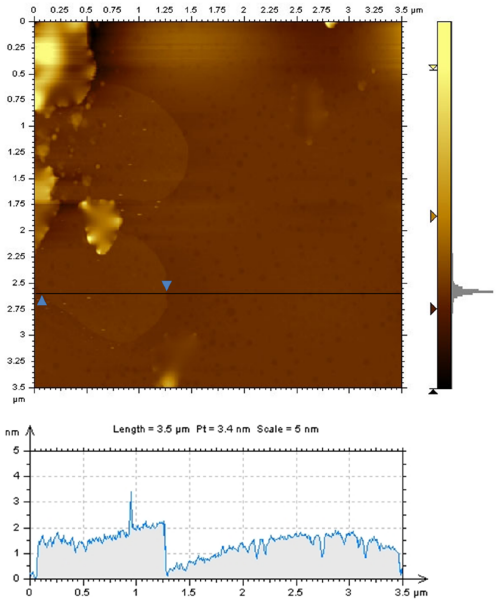


Fig. S4 AFM image of the graphene-like MoS_2.

Raman

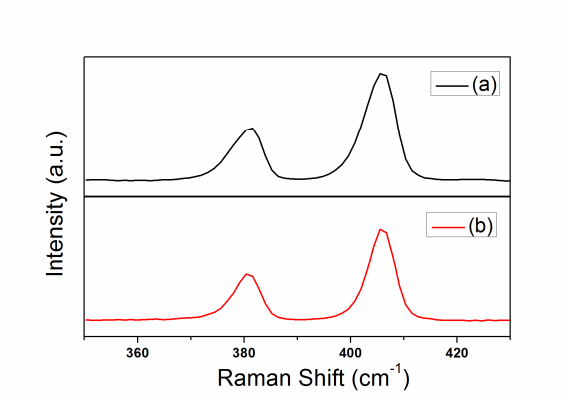


Fig. S5 Raman spectra of (a) MoS_2; (b) the $Ni_{80}Fe_{20}/MoS_2$.

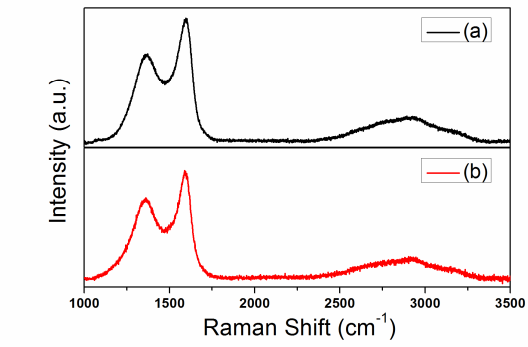


Fig. S6 Raman spectra of (a) graphene; (b) the $Ni_{80}Fe_{20}$/graphene.

Cyclic voltammetry

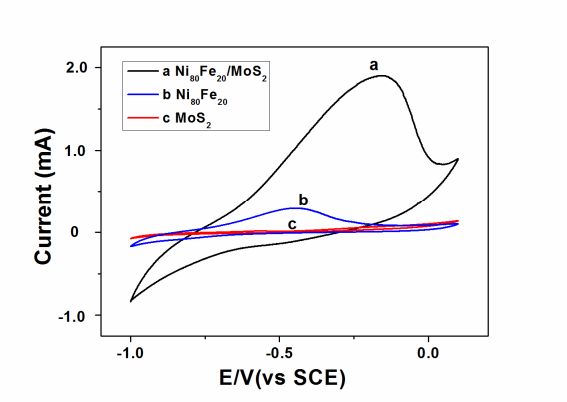


Fig. S7 Cyclic voltammetry measurements of (a) the $Ni_{80}Fe_{20}/MoS_2$ hybrid; (b) the $Ni_{80}Fe_{20}$ hybrid; (c) the graphene-like MoS_2 at a scan rate of 100 mV s^{-1}.

Chronoamperometric measurement

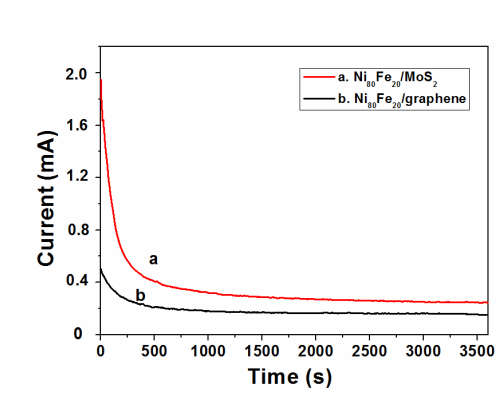
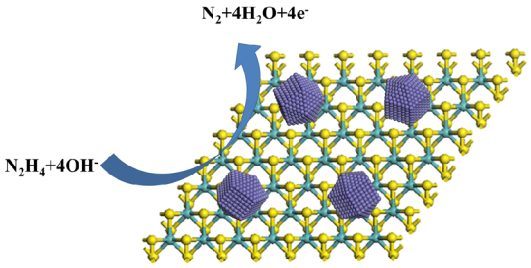


Fig. S8 Chronoamperometric measurement in 0.025 M NaOH and 0.1 M hydrazine hydrate at -0.4 V. (a) the $Ni_{80}Fe_{20}/MoS_2$ hybrid; (b) the $Ni_{80}Fe_{20}$/graphene hybrid.



Scheme S1 Schematic illustration of the mechanism for the Ni-Fe/MoS_2 hybrid have superior electrocatalytic activity for hydrazine electrooxidation is proposed.

The mechanism for the Ni-Fe/MoS_2 hybrid have superior electrocatalytic activity for hydrazine electrooxidation is proposed. The catalytic activity of MoS_2 originated from the sulfur

edges while the graphene-like MoS_2 have more active edges than bulk MoS_2. The two N atoms of N_2H_4 could coordinate with Ni-Fe alloy nanoparticles to form N(ad), and the edges of the nanosized MoS_2 crystallites also could promote the dissociation of N_2H_4 and adsorbed hydrogen atom at the catalytic edge site, thereby accelerate the production of H_2O. [2-4]

From another perspective, graphene-like MoS_2 as prepared is a n-type semiconductor.[5-6] Consequently, electron is prefered to transfer in it. Moreover, electron can be acted as a strong oxidating reagent. In contrary, graphene prefered to transfer p-type carriers,[7] which is not helpful for the oxidation.

This feature indicated that a notable synergistic effects of Ni-Fe alloy and graphene-like MoS_2 would be contribute to enhance the catalytic activity.

References:

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