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Enabling Colloidal Synthesis of Edge-Oriented MoS_2 with Expanded Interlayer Spacing for Enhanced HER Catalysis

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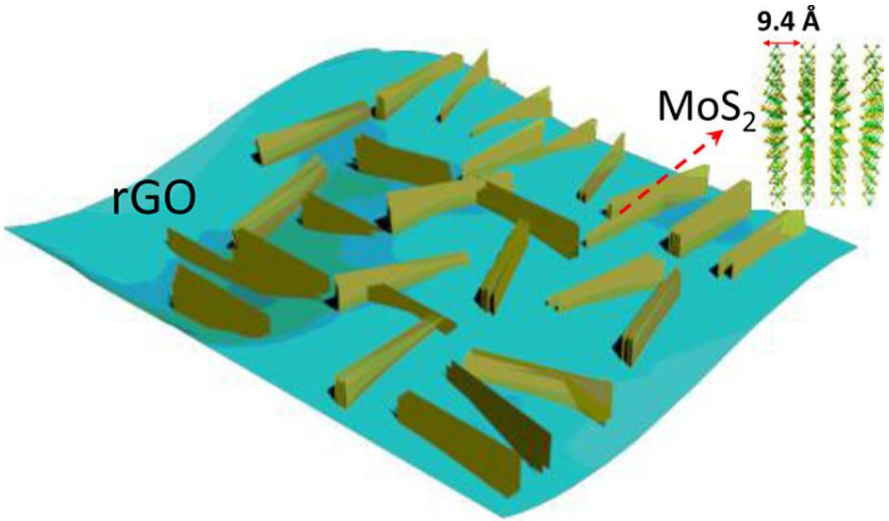

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Introduction :

- Increasing catalytic activity of non-Pt nanomaterials (e.g., oxides, chalcogenides, organic−inorganic complex, and so forth.) toward electrochemical hydrogen evolution reaction (HER) represents a challenging but promising research direction because of the importance of hydrogen production in clean energy applications.
- In this direction, nanostructured MoS2 has been actively explored as an inexpensive catalyst to promote HER in recent years.
- Previous work has highlighted the importance of the intrinsic structural parameters including crystalline phase, edge site density/orientation and interlayer spacing on determining HER catalytic activity of MoS2 nanostructures.

  For example, highly conducting 1T-phase MoS2 sheets (metallic octahedral structure) exhibit improved HER catalytic activity compared to the semiconducting 2H-phase MoS2 sheets (semiconducting trigonal prismatic structure) because both edges and basal surfaces in 1T MoS2 are catalytically active whereas only the edges of 2H MoS2 are active.
- However, the significant instability of the 1T MoS2 prevents its wide use in HER applications. As for the structurally stable 2H MoS2, HER activity can be enhanced by either exposing high density of active MoS2 edges or expanding the interlayer spacing of MoS2 nanostructures.

- It is even more promising to fabricate nanostructured MoS_2 that can simultaneously exhibit both high-density edges and expanded interlayer spacing, which can synergistically improve HER activity of the MoS_2.

Previous reports :

- Wang et al. reported an approach relying on rapid sulfurization of thin ALD Mo films with hot S vapor, which produces MoS_2 nanostructures with well-aligned edge-oriented (EO) geometry, which is favorable for pulling electrons from underneath support electrode (due to the high inlayer conductivity) to the active edge sites to promote HER.
- In addition, intercalation of lithium in the EO MoS_2 can expand the van der Waals gaps to further increase its HER performance in terms of enhanced current density and reduced Tafel slope.
- Only a few successful examples have been reported for the synthesis of EO & IE MoS_2 with normal interlayer spacing (i.e., ∼6.2 Å) through gas-phase sulfurization of thin Mo and Mo oxide films. The solid−vapor phase synthesis is costly, difficult to scale up.

In this Paper :

Selectively promoted heterogeneous nucleation/growth of MoS2 on graphene monolayer sheets. The MoS2 nanosheets were edge oriented (EO) with expanded interlayer spacing (∼9.4 Å) supported on reduced graphene oxide (rGO) sheets and successfully synthesized through colloidal chemistry, showing the promise in low-cost and large-scale production.

Synthesis of EO & IE MoS2 :

3 mg of GO nanosheets was dispersed in 6 mL of DMF with assistance of ultrasonication for 0.5 h.
To this dispersion was added 10 mg of (NH4)2MoS4, which was dissolved with assistance of magnetic stirring for 20 min under ambient condition.
The DMF dispersion containing both GO and (NH4)2MoS4 was transferred to a 10 mL reaction vessel that was sealed and placed in a microwave reactor . The dispersion was then quickly heated to an appropriate temperature (e.g., 200, 220, 240, and 260 °C) in a period of ∼10 s and the temperature was maintained for 2 h to complete the reaction.
The products were then collected via centrifugation followed by washing with DI water and ethanol and then dried in an oven.

Results and discussions :

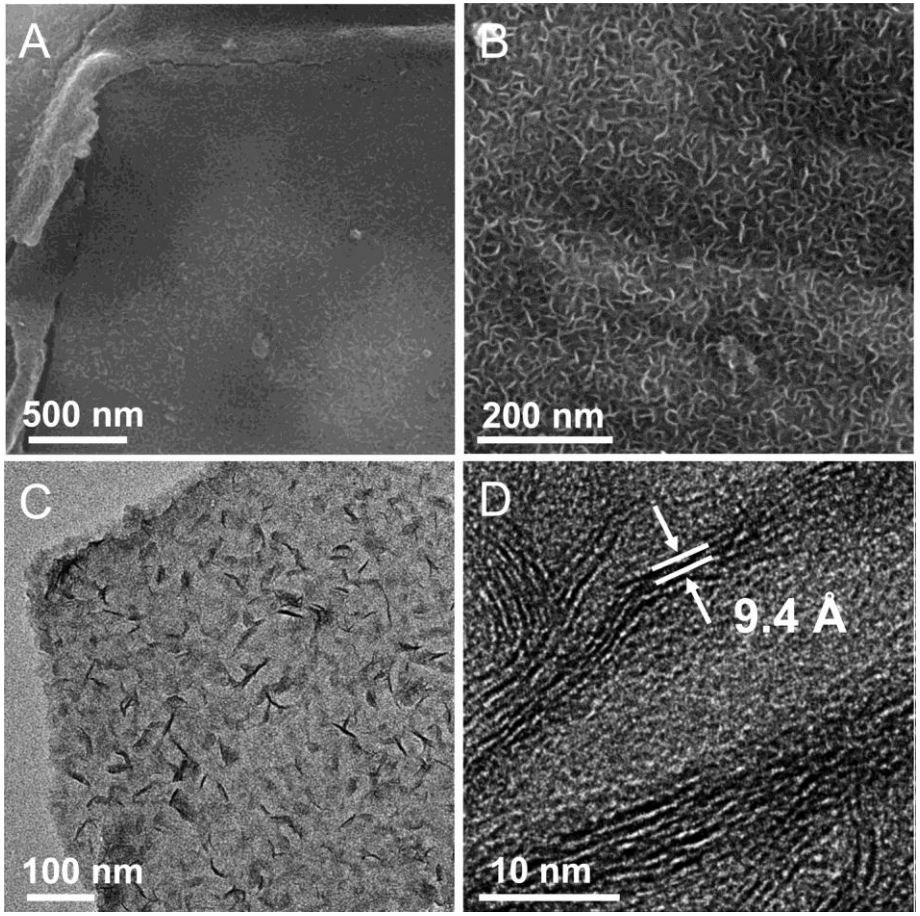

Figure 1. (A,B) SEM and (C) TEM images of EO&IE MoS2/rGO sample synthesized from a reaction at 260 °C for 2 h. (D) HRTEM image of several EO&IE MoS2 nanosheets on a rGO nanosheet, highlighting the layered structure and exposed edges in the MoS2 nanosheets.

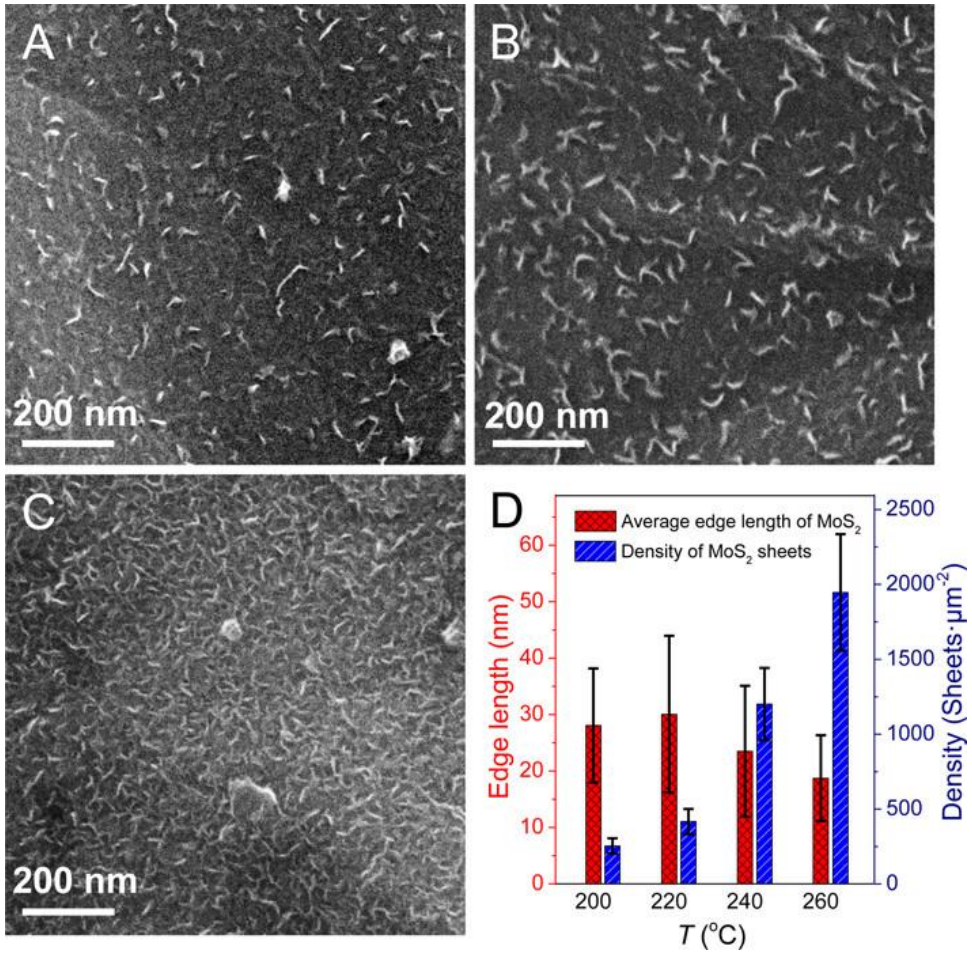

Figure 2. SEM images of EO&IE MoS2/rGO synthesized from reactions at different temperatures: (A) 200 °C, (B) 220 °C, and (C) 240 °C. The reaction time was 2 h. (D) Statistic analysis of the number of MoS2 nanosheets on 1 μm2 rGO surface (blue columns) and the average edge length of one MoS2 nanosheet (red columns).

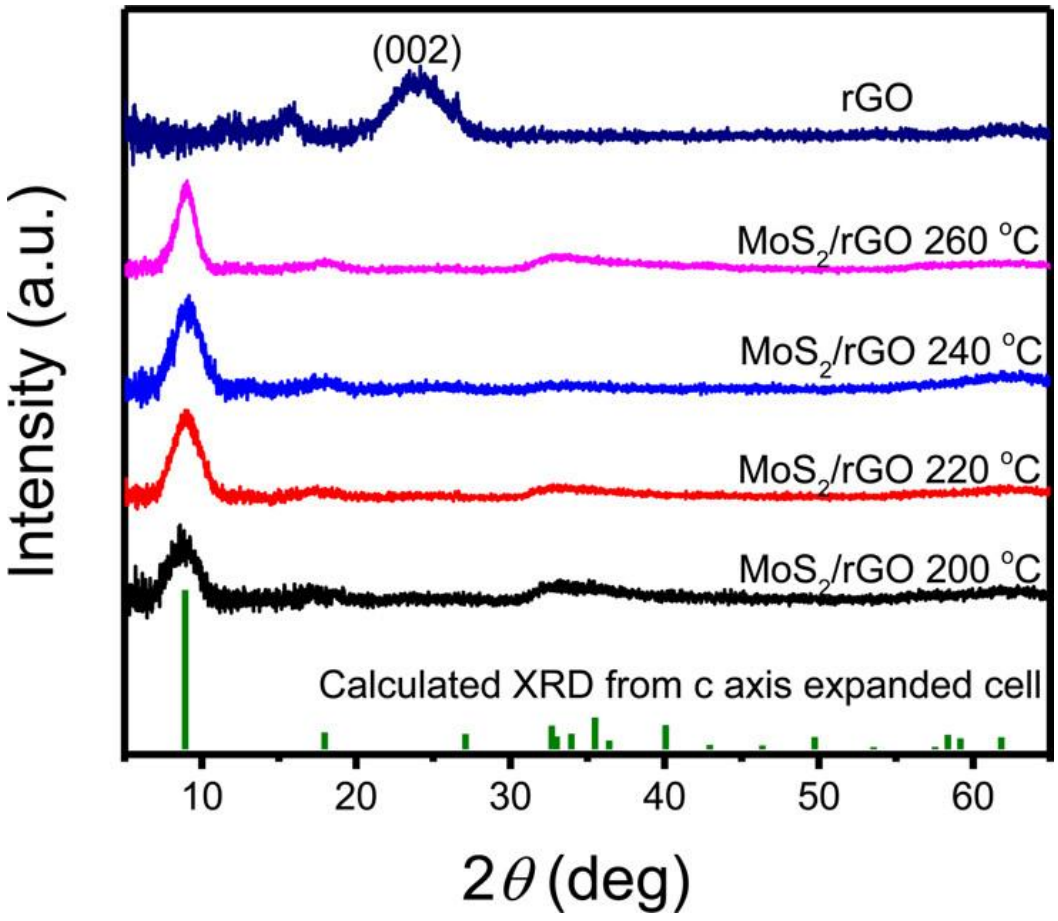

Figure 3. X-ray diffraction patterns of EO&IE MoS2/rGO synthesized from reactions at different temperatures. The calculated pattern a MoS2 lattice with expansion along the c-axis is plotted for reference (green curve).

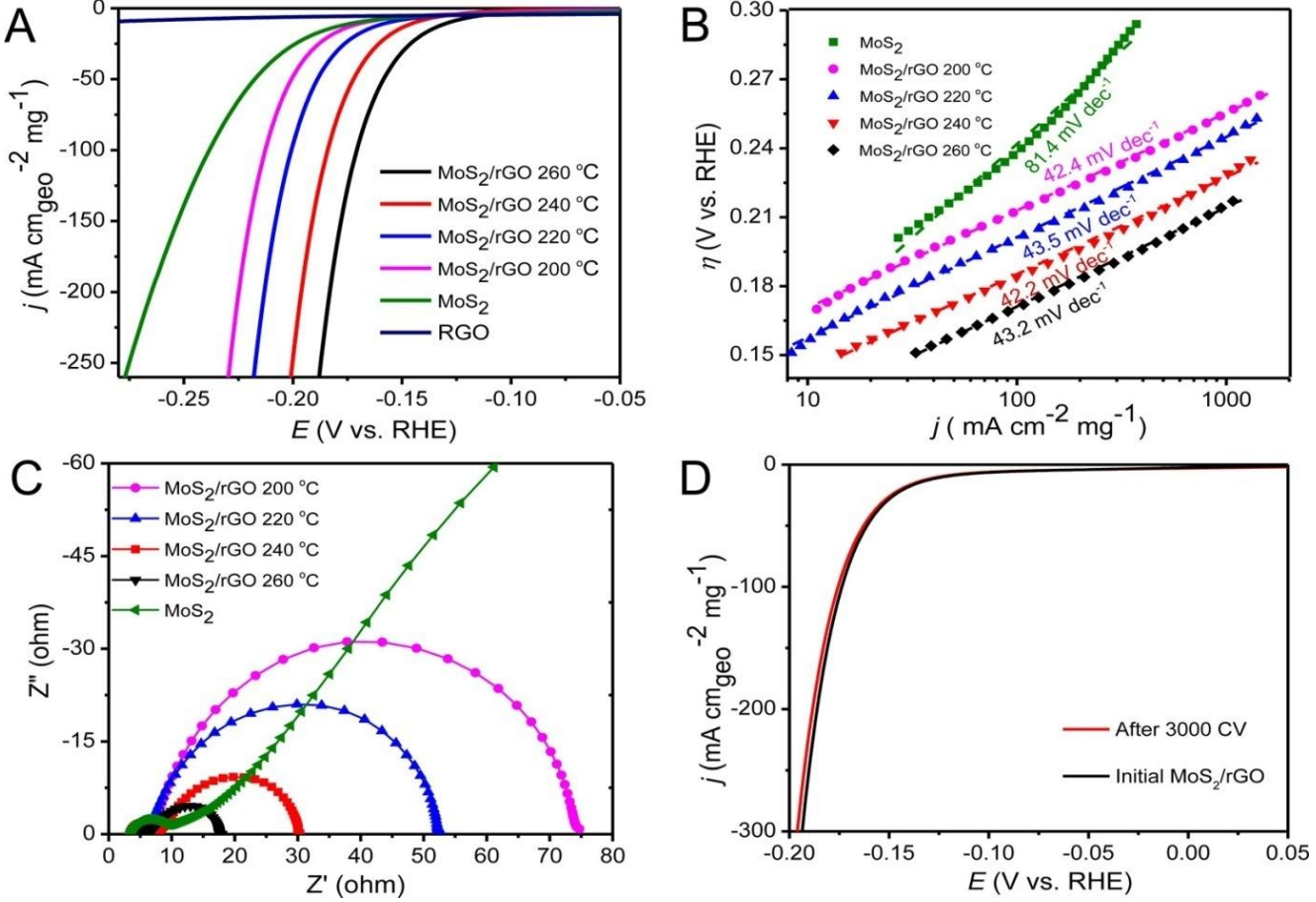

Figure 4. (A) Normalized polarization curves for HER on modified glassy carbon electrodes comprising EO&IE MoS2/rGO catalysts synthesized at different temperatures, IE MoS2 microflowers and rGO sheets synthesized at 220 °C. The potential sweep rate was 5 mV s−1.

(B) Tafel plots and (C) Nyquist plots of the corresponding catalysts of (A). (D) Comparison of polarization curves of the EO&IE MoS2/rGO sample synthesized at 260 °C before (black) and after (red curve) 3000 potential cycles between −0.3 and 0.3 V versus RHE at a sweep rate of 200 mV s−1.

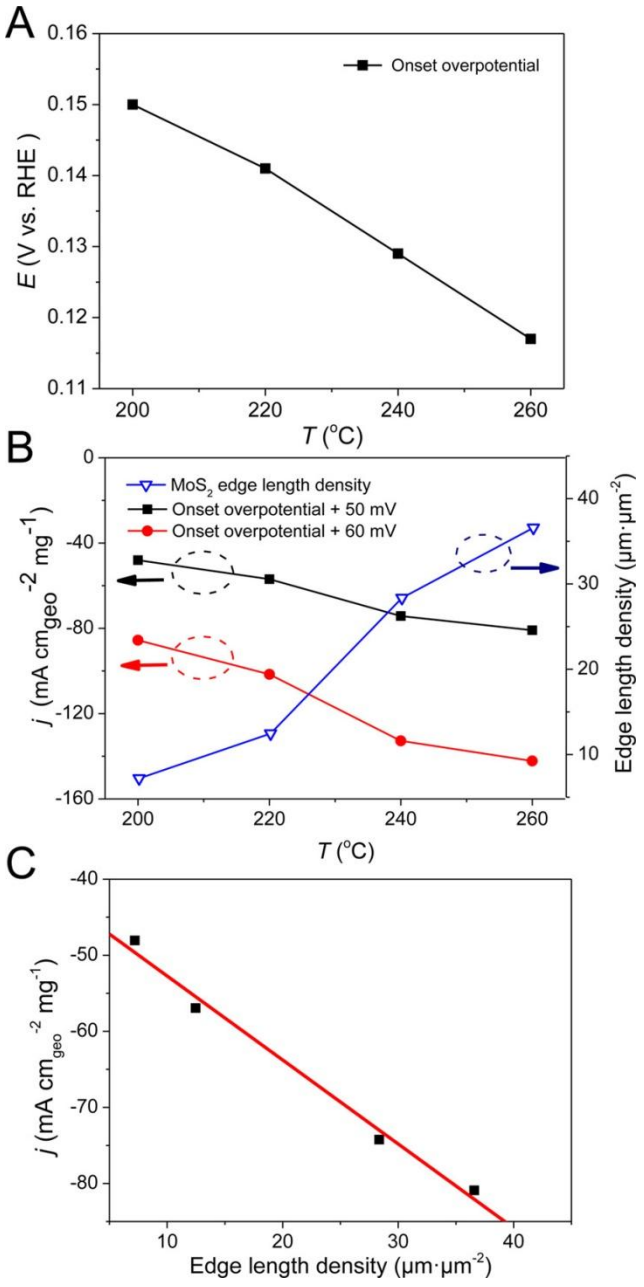

Figure 5. (A) Onset overpotentials required to initiate HER for EO&IE MoS2/rGO synthesized at different temperatures. (B) Current density at the same offset overpotential for different EO&IE MoS2/rGO catalysts. The MoS2 edge length density (i.e., total MoS2 edge length with unit of μm on 1 μm2 rGO surface) of different catalysts are also plotted for comparison. (C) The linear relationship between current density and the MoS2 edge length density for the EO&IE MoS2/rGO catalysts.

Summary :

- By taking advantage of unique heterogeneous nucleation and growth processes of MoS2 on GO sheets and the unique reaction kinetics in the microwave solvothermal reaction, MoS2 nanosheets with expanded interlayer spacing of 9.4 Å have been successfully grown on rGO sheets to show EO geometry that effectively exposes catalytically active MoS2 edges toward electrolyte.

- The edge-oriented and interlayer-expanded (EO&IE) MoS2/rGO exhibited significantly improved catalytic activity toward hydrogen evolution reaction (HER) in terms of larger current density, lower Tafel slope, and lower charge transfer resistance compared to the corresponding interlayer-expanded MoS2 sheets without edge-oriented geometry.

- These understandings shed light on rational design of high-performance HER catalysts that can be achieved by controlling nucleation and growth kinetics of colloidal chemistry.