



Ultrathin MoS₂ nanosheets growing within an *in-situ*-formed template as efficient electrocatalysts for hydrogen evolution



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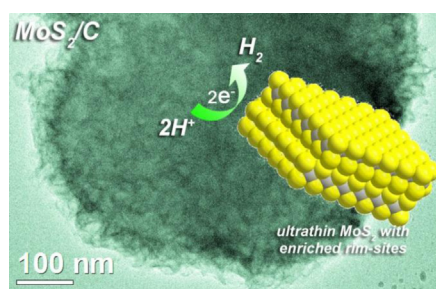
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HIGHLIGHTS

- The space-confined growth by polysaccharides is used to fabricate ultrathin MoS₂.
- Superior electrochemical HER performances are presented on MoS₂/C nanocatalysts.
- The remarkable performance results from the promoted active-sites and conductivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 August 2014

Received in revised form

6 November 2014

Accepted 9 November 2014

Available online 10 November 2014

Keywords:

Hydrogen evolution

Molybdenum sulfide

Nanosheets

Active sites

Conductivity

ABSTRACT

The space-confined growth by *in-situ* formed polysaccharides during hydrothermal process is successfully employed to fabricate ultrathin MoS₂ nanosheets, which further evolve to MoS₂/C evenly integrating nanosheets (2–4 nm) with conducting carbon after carbonization. The MoS₂/C exhibits an excellent activity for hydrogen evolution reaction (HER) with a small onset overpotential of ~80 mV and a high current density of 88 mA cm⁻² at η = 200 mV, which is associated with the enriched rim-sites on ultrathin MoS₂ and the improved conductivity by carbon matrix. This work demonstrates that the ultrathin MoS₂ nanosheets within carbon, possessing synergistically-enhanced activity and conductivity for HER, are feasible through the space-confined growth based on polysaccharide matrix, and this would open up new opportunities for exploiting highly efficient electrocatalysts.

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1. Introduction

Hydrogen has been pursued as one of the most promising energy carriers in future [1]. The production of hydrogen from water using renewable energy in the form of electricity has been

proposed as a practical way for a sustainable hydrogen production [2,3]. Although precious metals, e.g., platinum, show high efficiency in the electrochemical hydrogen evolution reaction (HER), their scarcity and high cost severely inhibit the further applications [3,4]. Advanced catalysts with element-abundance, economic-cost and stability are desired for HER to scale-up such clean-energy technologies [3–5].

Inspired by the previous discoveries in the hydrogenation and dehydrogenation of petroleum chemicals, several nanocatalysts of

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metal non-oxides, e.g., MoS₂ [6], Mo₂C [7,8], WS₂ [9], WC [10], Ni₂P [11], CoP [12] etc., have been recently explored for electrochemical HER. Among them, nanosized MoS₂, traditionally used in hydrodesulfurization (HDS) [13], is promising due to its low cost, high chemical stability, defined nanostructures, and excellent electrocatalytic properties [14]. The most active sites of MoS₂ are demonstrated to be the (010) and (100) planes exposing unsaturated Mo- and S-edges, rather than the inert (002) basal plane [6]. Increasing the number of exposed MoS₂ edges is crucial to improve the electrocatalytic efficiency, which has been verified by engineering nanostructured MoS₂ to preferentially expose edge-sites in a highly ordered double-gyroid nanoporous network [15]. Moreover, the “rim-edge” model proposed in HDS reactions reveals that the rim-sites, referring to the edges of top and bottom S–Mo–S slabs, are more active for (de)hydrogenation than the edge-sites associated with the sandwiched S–Mo–S [16], indicating the further improved HER activity on ultrathin MoS₂ nanosheets with enriched rim-sites (Fig. 1a). Recently, the ultrathin MoS₂ obtained via top-down strategies, mainly chemical and electrochemical exfoliation, have presented the superior performance for HER [17–19]. Unfortunately, they are limited by the complicated manipulation expelling O₂ and water. Bottom-up methods restricting the growth along [001] direction are desired due to the convenience for achieving ultrathin MoS₂ and the further regulation on structural features, e.g. disorder or defect sites [14,20,21]. The confinement of MoS₂ within conducting matrix would lead to the facile control on crystal growth, and load active nanosheets on conducting substrates or supports to overcome the poor bulk conductivity of MoS₂ [3]. For this purpose, carbon nanotubes [22], graphite [23], graphene [24] and mesoporous carbon [25] have been introduced. However such as-formed substrates are inhibited by the high cost, the messy synthesis, and particularly the lack of strong chemical interaction with Mo precursors, which is vital for the defined growth of MoS₂.

Herein, we propose a new route to confine MoS₂ growth within an *in-situ* formed polysaccharide matrix from glucose condensation during hydrothermal processes, and after the following

carbonization, MoS₂/C nanocomposites evenly integrating ultrathin MoS₂ nanosheets (2–4 nm) with conducting carbon are successfully harvested (Fig. 1b). The polysaccharide matrix with abundant hydroxyl and glucosidic groups possesses the enhanced chemical interactions with Mo precursors, which would benefit the space-confined growth of MoS₂ towards ultrathin nanosheets [26]. As been expected, the as-prepared MoS₂/C exhibits an excellent HER activity characterized by higher current densities and lower onset overpotentials than the conventional MoS₂. In particular, the MoS₂/C with a suitable MoS₂ content of 14.8% shows a small onset overpotential (η_{onset}) of ~80 mV, a high current density of 88 mA cm⁻² at $\eta = 200$ mV, which are ascribed to the abundant rim-sites on ultrathin MoS₂ nanosheets and the improved conductivity by carbon. Owing to the effective space-confined growth, the synergic enhancement of both activity and conductivity, and the facile synthesis using renewable resource of glucose, this work would open up new opportunities for developing efficient, economic and stable electrocatalysts.

2. Experimental details

2.1. Materials

Glucose (C₆H₁₂O₆), ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, AHM), thiourea (CS(NH₂)₂), sodium metavanadate (NaVO₃), and sublimed sulphur were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). And Nafion solution (5 wt% in lower aliphatic alcohols and water) was purchased from Sigma–Aldrich.

2.2. Synthesis of MoS₂/C nanospheres

0.80 g of glucose with a varied amount of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, AHM) and thiourea (CS(NH₂)₂) was dissolved in 15.0 mL of distilled water (referring to the feeding ratios in Table S1), and then the solution was turned to a Teflon-lined stainless-steel autoclave. After hydrothermal

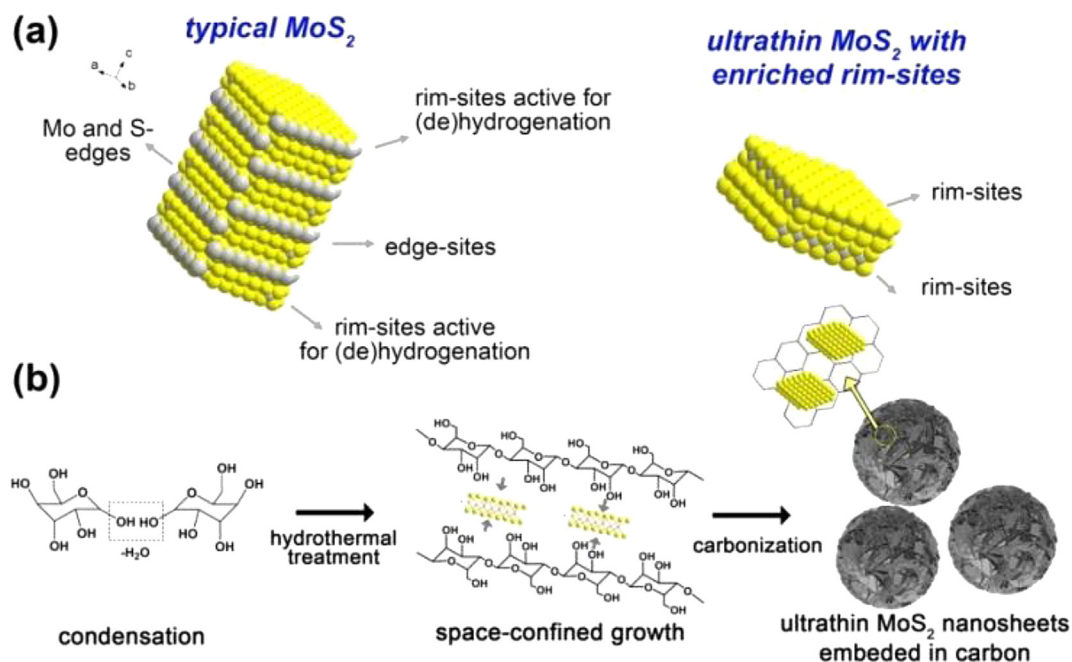


Fig. 1. Schematic illustration for (a) active sites replying on the different thickness of MoS₂, and (b) fabrication of MoS₂/C employing *in-situ* formed polysaccharides as a template to confine MoS₂ growth.

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