INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–8

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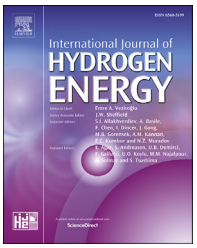

Versatile synthesis of molybdenum sulfide from confined spaces for efficient hydrogen evolution

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ARTICLE INFO

Article history:
Received 28 July 2017
Received in revised form
13 September 2017
Accepted 19 September 2017
Available online xxx

Keywords:
Molybdenum sulfide
Confined growth
Hydrogen evolution reaction
Disulfide unit
Filler crystallite

ABSTRACT

(Quasi-)Amorphous molybdenum sulfide (MoS_x) materials with disulfide (S_2^{2-}) units have superior catalytic activities for hydrogen evolution reaction. However, the structures of the materials are less investigated and diversified. Herein, we first develop a new ethanol-thermal method to prepare MoS_x and further apply versatile confined growth treatment with low-cost filler crystallites to efficiently modify its structure and consequent performance. Expectedly, because the material is quasi-amorphous and very deformable, its morphology varies dramatically from granules to foam-like material with specific surface area increases from 22.53 m^2/g to 76.24 m^2/g under the restriction of confined spaces. Importantly, the amount of S_2^{2-} units which are responsible for the distinction of MoS_x increases as well. By virtue of the confined growth, the catalytic performance of the original material on hydrogen evolution is improved significantly. The over-potential required to obtain 10 mA cm^{-2} current decreases remarkably from 278 mV to 209 mV and the Tafel slope decreases from 160 mV/decade to 72 mV/decade after confined growth. Therefore, we have proposed an effective method to synthesize and promote the catalytic performance of MoS_x.

Introduction

Molybdenum sulfide materials have been recognized as promising non-precious hydrogen evolution reaction (HER) catalysts that are theoretically comparable to platinum. Among molybdenum sulfide catalysts, (quasi-)amorphous molybdenum sulfide (MoS_x) [1–6] exhibits superior activity to its high crystalline counterpart partially due to the boosting number of exposed active sites from the original inert basal plane [7–9] and the unique disulfide (S_2^{2-}) units [9–12] in MoS_x which are confirmed to be effective active sites for hydrogen evolution. Here, MoS_x is used to describe molybdenum sulfide materials which have slight or no crystallinity and also have characteristic S_2^{2-} units. By far, MoS_x materials are prepared by electrodeposition [13,14], photochemical reduction [15], thermolysis [11,16,17], and wet-chemical/hydro-thermal [3,18–21] methods. However, possibly due to the (quasi-)amorphous property, the structures of the materials are pretty simple and not enriched. Since structures of materials are critical to their performances, it is of good necessity to diversify the structures of the promising MoS_x materials.

In nature, the controllable formation of bio-minerals via amorphous materials in confined space is a principle utilized by organisms to produce tissues with sophisticated internal shapes and morphologies [22,23]. Thanks to the amorphous status without much anisotropy or preferred pattern, the precursors or final bio-minerals can be precisely molded into

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https://doi.org/10.1016/j.ijhydene.2017.09.106

enormous shapes easily. The complex amorphous bio-silica structure in diatom [24] and the aragonite tablets restricted by organic frames in the nacreous layer of mollusk shell [25] are typical examples of the principle. Though confined environments in templates have also been extensively used to prepare crystalline molybdenum disulfide (MoS_2) materials, the anisotropy of the crystalline materials may impede the continuous replication and full utilization of the confined spaces in sophisticated templates as implied by the poor spatial replication quality or non-continuous states of the final products [26–28]. However, researchers have replicated confined spaces in delicate biogenic and artificial structures successfully by virtue of deformable amorphous calcium carbonate which can penetrate deeply to form intimate contacts [29,30]. Now that the MoS_x materials also only have limited anisotropy and are highly deformable, intuitively, it is

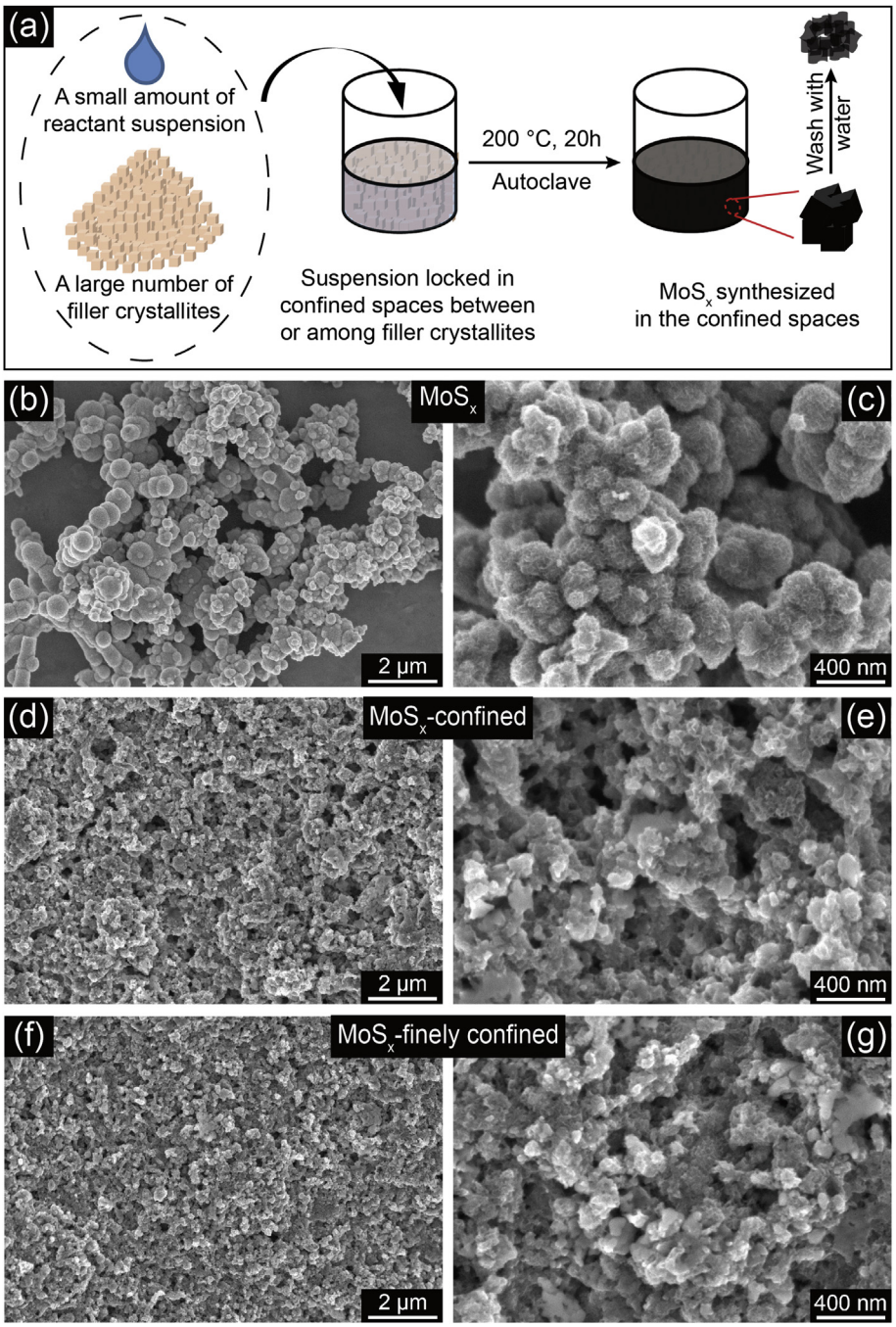

Fig. 1 – Morphologies of molybdenum sulfide (MoS_x) materials: (a) Schematic representation of the confined growth of MoS_x with filler crystallites; (b, c) SEM images of originally prepared unconfined MoS_x; (d, e) SEM images of MoS_x from confined growth; (f, g) SEM images of MoS_x from finely confined growth with grinded filler crystallites. The previous granular product will change its shape and become rather uniform after confined growth.

Please cite this article in press as: Chen L, et al., Versatile synthesis of molybdenum sulfide from confined spaces for efficient hydrogen evolution, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.09.106