Materials Letters 216 (2018) 243–247

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Facile synthesis of MoS_2/rGO-MOF hybrid material as highly efficient catalyst for hydrogen evolution

Chuanping Zhu [a], Kunchan Wang [a], Ting Lei [a,*], Tao Xiao [b], Lihong Liu [b]

[a] State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China
[b] 2nd Xiangya Hospital, Central South University, Changsha 410011, China

ARTICLE INFO

Article history:
Received 8 November 2017
Received in revised form 10 January 2018
Accepted 22 January 2018

Keywords:
Hydrogen evolution reaction
Composite materials
Energy storage and conversion
Reduced graphene oxide
Nanocomposites
Metal-organic framework

ABSTRACT

MoS_2/rGO-MOF hybrid material as a highly effective electrocatalyst for hydrogen evolution reaction (HER) has been synthesized by a two-step hydro- and solvothermal process by loading MoS_2 on the surface of copper-centered metal organic framework (Cu-MOF) and graphene oxide (GO) hybrid. The obtained MoS_2/rGO-MOF hybrid catalyst exhibits an excellent electrocatalytic HER activity with small onset overpotential of 60 mV and a low Tafel slope of 36 mV decade^{-1}. The enhancement of catalytic activities was ascribed to the higher specific surface area beneficial from the mesoporous structure of GO-MOF hybrid and synergetic effect between MoS_2 nanosheets and GO-MOF matrix.

1. Introduction

Recently, MoS_2 has been highlighted as a promising HER catalyst and has attracted more attention because of its low cost and high chemical stability [1,2]. However, MoS_2 exhibits extremely poor conductivity and insufficient number of active edge sites [3]. Therefore, developing high performance electrocatalysts for HER has been one of the most critical challenges.

Graphene has good conductivity, chemical durability and large surface area, which makes it suitable for loading and confining nanosized materials [4]. Until now, tremendous research efforts have been reported on the development of MoS_2/graphene hybrids, which exhibit significantly enhanced electrochemical performances for HER [5–10].

Metal-organic frameworks (MOFs), as an efficient catalyst or as the support for catalysts, have drawn focused attention because of its large surface areas and high porosities [11]. Recently, some MOF-based hybrid materials were used in hydrogen evolution reaction [12–14].

In this work, we designed for the first time a new MoS_2/rGO-MOF composite material by a two-step hydro- and solvothermal process. The as-obtained hybrid material, with integration of advantages of excellent electrocatalysis activity of MoS_2, porous structure and high specific surface area of MOFs and high electrical conductivity of reduced graphene oxide (rGO), exhibits excellent HER performance.

2. Experimental procedures

Graphene oxide (GO) was synthesized by a modified Hummers's method [15]. GO-MOF composite was synthesized based on previous reported hydrothermal method [16].

For the preparation of MoS_2/rGO-MOF hybrid material [5], 40 mg of GO-MOF composite was dispersed in 40 mL DMF by ultrasonic for 15 min, followed by adding 88 mg of $(NH_4)MoS_4$ and sonicated for another 15 min. Then, 0.4 mL of $N_2H_4{\cdot}H_2O$ was added. The mixture was sonicated for 30 min to get a well-dispersed suspension and then transferred to a 100 mL Teflon liner and heated up to 200 °C for 10 h in an oven and cooled naturally to room temperature, followed by washing and drying.

The SEM, TEM and XRD were performed on field-emission scanning electron microscope (NOVA NANOSEM 230), transmission electron microscopy (FEI Tecnai G^2 F20, TEM) and D/MAX-255 X-ray diffractometer, respectively. Nitrogen isotherms were carried out at 77 K on a Monosorb rapid surface area analyzer instrument.

All electrochemical measurements were conducted at room temperature on a CHI 660D electrochemical work station (Shanghai Chenhua Instrument Co., China). The catalyst loaded GCE electrode, graphite rode electrode and saturated calomel electrode

* Corresponding author.
E-mail address: tlei@mail.csu.edu.cn (T. Lei).

https://doi.org/10.1016/j.matlet.2018.01.123

(SCE) are used as working electrode, counter electrode and reference electrode, respectively.

3. Results and discussion

Fig. 1a is a SEM image of GO, illustrating that GO is dense fakes of graphene sheets stacked together. Fig. 1b reveals the surface appearance of GO-MOF hybrid, which is regular shaped thin platelets stacked together. The inset TEM image clearly indicates the uniform distribution of MOF on GO sheets. The SEM image of MoS_2/rGO-MOF in Fig. 1c clearly shows well dispersed flower-like MoS_2 particles on the surface of GO-MOF matrix. The EDS analysis by inset indicates the atomic ratio of S to Mo was about 1.8, close to the stoichiometric ratio of MoS_2. The TEM image in Fig. 1d indicates that MoS_2/rGO-MOF hybrid material has a layered structure, where the flower-like MoS_2 particles are consisted of ultrathin MoS_2 nanosheets, which are well anchored on the matrix. The high-resolution TEM (HRTEM) image in Fig. 1e shows the typical lattice fringes of MoS_2 nanosheets with a d spacing of 0.62 nm, corresponding to the (002) plane [17]. This result further demonstrates that MoS_2 particles are successfully decorated on the surface of GO-MOF matrix

The XRD pattern of GO in Fig. 1f displays a single peak at around $2\theta \approx 9°$, indicating an interlayer distance of 0.93 nm [18]. The diffraction peaks of GO-MOF match those of MOF crystal, indicating the existence of the well-defined Cu-MOF units in the composite. The XRD pattern of MoS_2/rGO-MOF exhibited the typical (002) and (100) planes of the 2H-MoS_2 (JCPDS card no. 37-1492) in accordance with literatures previously reported. Notably, the broadened diffraction peaks indicated that MoS_2 on the surface of rGO-MOF matrix have low degree of crystalline with a small particle size.

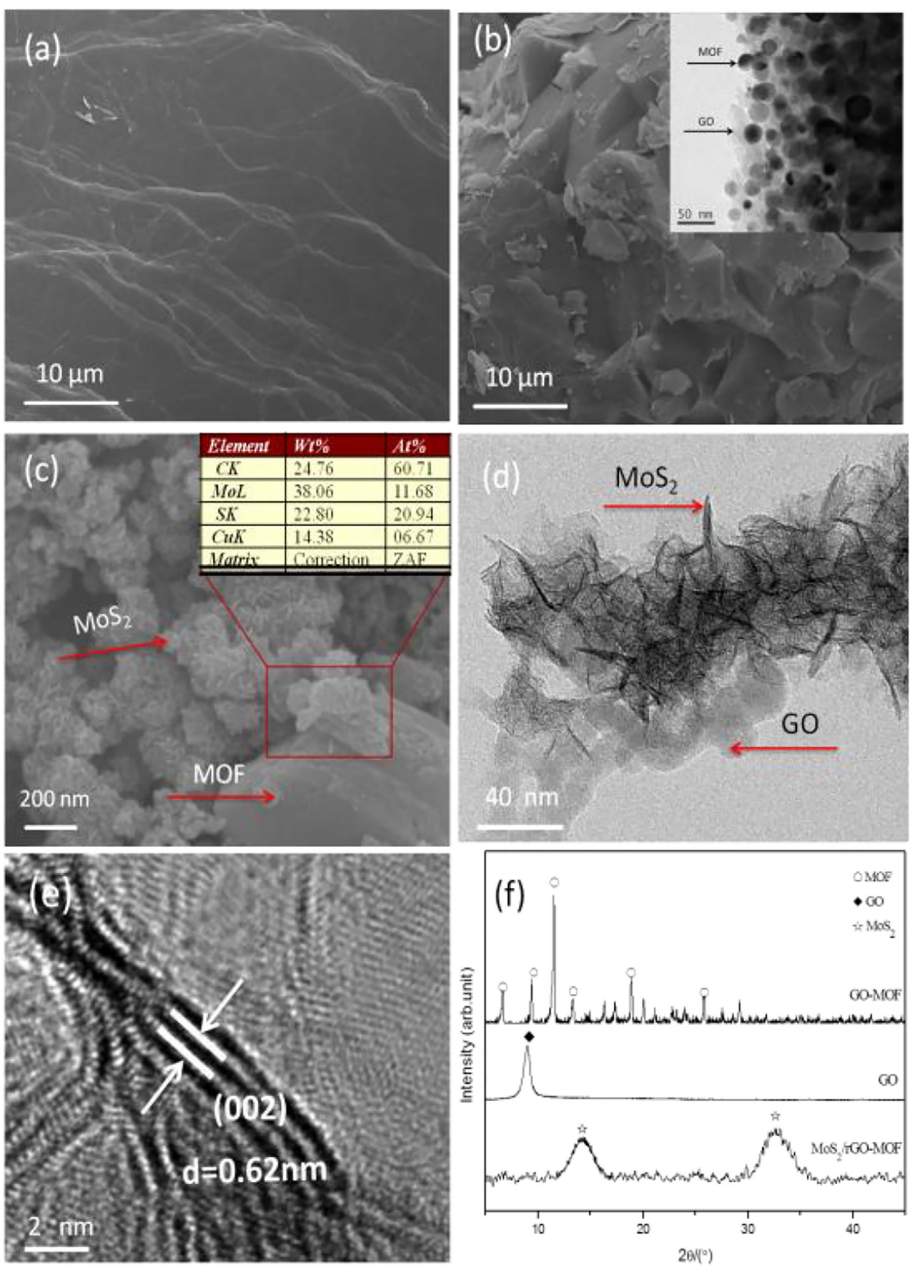

Fig. 1. SEM images of (a) GO, (b) GO-MOF. The inset is TEM image, (c) MoS_2/rGO-MOF, The inset is EDS analysis for assigned area, (d) TEM image, (e) HRTEM image of layered MoS_2, (f) XRD patterns of GO, GO-MOF and MoS_2/rGO-MOF.