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Enlarged interlayer spaced molybdenum disulfide supported on nanocarbon hybrid network for efficient hydrogen evolution reaction

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ABSTRACT

We report a facile, one pot solvothermal route to prepare ultrathin molybdenum disulfide supported on nanocarbon hybrid (MoS_2@NCHy) network with varied mass loading of MoS_2 (20 wt%, 40 wt% and 60 wt %) for catalyzing hydrogen evolution reaction (HER). A large current density of $-451\ mAcm^{-2}$ at an overpotential of -480 mV *vs.* RHE, proves 40 wt% MoS_2@NCHy/GCE nanocomposite as a highly HER active catalytic material. This value was found to be 50 times, 6 times and 2.5 times higher compared to MoS_2/GCE ($-8\ mAcm^{-2}$), 20 wt% MoS_2@NCHy/GCE ($-75\ mAcm^{-2}$) and 60 wt% MoS_2@NCHy/GCE ($-180\ mAcm^{-2}$) respectively. Meanwhile, η_{10} (overpotential required to attain a current density of $-10\ mAcm^{-2}$) is -186 mV for 40 wt% MoS_2@NCHy/GCE, which is much lower to MoS_2/GCE (-498 mV), NCHy/GCE (-334 mV), 20 wt% MoS_2@NCHy/GCE (-264 mV) and 60 wt% MoS_2@NCHy/GCE (-204 mV). The overall activity of the catalyst was manifested by the least overpotential, $\eta_{10} = -186$ mV *vs.* RHE, Tafel slope of 53 $mVdec^{-1}$ and exchange current density (j_0) of $6.3 \times 10^{-2}\ mAcm^{-2}$. The superior performance of 40 wt% MoS_2@NCHy should be attributed to the highly conductive and porous support of three dimensional NCHy architecture as well as the enlarged interlayer spacing of MoS_2. This study paves a new paradigm to exploit the synergistic effect of MoS_2 and NCHy resulting in strong electronic coupling for enhancement in the HER activity.

1. Introduction

The global warming caused by burning of fossil fuels urges a strong demand for generation of green and renewable energy. Among the various possible alternatives, hydrogen is regarded as an eco-friendly fuel with high power density for future applications [1,2]. Electrolysis of water is one of the promising methods for hydrogen generation owing to its environment friendliness and high efficiency [3,4]. The key for efficient hydrogen production relays on developing cost-effective electrocatalyst which activate the hydrogen evolution reaction (HER) at a minimum required overpotential (η). Even though platinum (Pt) based materials rank as the best HER catalysts [5,6], the high cost and low abundance have significantly hindered their industrial applications. Replacement of Pt with other earth abundant and low cost materials is a real challenge for the research world at present. A number of electrocatalyst categorized as metal alloys [7], oxides [8], carbides [9], nitrides [10], borides [11], phosphides [12] and transition metal dichalcogenides [13] have been proposed by research community. Among various 2D transition metal dichalcogenide (2D-TMDs), molybdenum disulfide (MoS_2) has received much attention in the scientific community due to its amazing chemical and physical properties similar to graphene [14,15]. In MoS_2, Mo atoms are sandwiched between sulfur atoms by covalent bonds (S-Mo-S) in a trigonal prismatic arrangement, while the interlayers are held together by the weak Vander Waal's forces. It has been reported that the basal planes of MoS_2 are usually inactive towards the HER, whereas the rich edge sites at the border are HER active [16,17]. The density functional theory calculations and experimental results by Hinnemann et al. [17,18] have proven that the activity sites in MoS_2 stems from the uncoordinated sulfur edges and its electrocatalytic activity for HER scales up linearly with the edge sites. Though bulk MoS_2 is a poor electrocatalyst, engineering MoS_2 with more number of edge sites is one of the strategies to obtain an efficient HER electrocatalyst. But edge terminated structures are highly energetic and thermodynamically unstable compared to its basal planes [19]. At the same time MoS_2 being a semiconductor, improving its electrical conductivity is also equally important to achieve a high

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performing electrocatalyst. Thus, engineering MoS_2 nanostructures with ample number of active edge sites with good electrical conductivity and high stability is a real challenge on the application of MoS_2 as a HER electrocatalyst. Many synthetic strategies have been adopted by researchers to enhance the number of active sites: (1) reducing the terrace sites by constructing MoS_2 as vertically aligned structures [20,21], (2) intercalation of the anionic or cationic species between the interlayers of the MoS_2, thereby enhancing the interlayer spacing and exposing more active sites [22,23], (3) introducing defects and disorders in the planes, by developing polymorphic structure like 1T-MoS_2 [24], amorphous or low crystalline nanostructures [25], which expose higher density of active sites for the HER. The electronic structure modulation can be achieved by incorporation of metal atom [13,26] or implementing highly conductive materials that can act as scaffold/matrix/support like graphene, carbon nanotubes (CNT), carbon fiber, carbon cloth, amorphous carbon etc., forming hybrid nanostructures that can facilitate rapid electron transfer at the catalyst/electrolyte interface [27–42]. Coupling of MoS_2 nanosheets with carbon nanostructures improves the conductivity of the system, as well as, it is an effective way to overcome the restacking of the layers of MoS_2, which in-turn determines the activity of the catalyst. Recently, Jiang and co-workers reported MoS_2 catalyst supported on Gr/CNT/polyamide composite as a HER catalyst yielding a Tafel slope of 61 $mVdec^{-1}$ and exchange current density (j_0) = 11.5 μAcm^{-2} [40] 3D MoS_2-graphene hybrid aerogels were synthesized by Xu et al. with a Tafel slope of 51 $mVdec^{-1}$ and $j_0 = 0.03\ mAcm^{-2}$ [31]. All recent reports suggest the significance of carbon support in enhancing the electrocatalytic HER activity.

In this paper, we report a facile solvothermal method for coupling MoS_2 with 3D NCHy network for the preparation of a potential hybrid HER electrocatalyst. The NCHy represents a highly porous 3D interlinked network of rGO and *f*-MWCNT, where the CNT acts as a pillar and spacer for rGO and MoS_2 nanosheets. The solvothermal hydrazine reduction of GO has resulted in the formation of reduced graphene oxide (rGO) and incorporation of oxidized dimethylformamide (DMF) species between the MoS_2 layers resulting in interlayer expansion of MoS_2 from conventional 0.65 nm–~0.95 nm. The electrocatalytic activity towards HER with different mass loading has been analyzed using the linear sweep voltammetry (LSV), Tafel polarization and electrochemical impedance spectroscopy (EIS). The ideal combination of MoS_2 and NCHy *i.e* 40 wt% MoS_2@NCHy emerged to be a better electrocatalyst among MoS_2, NCHy and other MoS_2 loading ratios, manifesting a least overpotential (η) of −186 mV *vs.* RHE for attaining a current density (j) of $-10\ mAcm^{-2}$, Tafel slope of 53 $mVdec^{-1}$, exchange current density (j_0) of $6.3 \times 10^{-2}\ mAcm^{-2}$ with excellent stability during accelerated degradation test (ADT) for 5000 cycles under acidic conditions.

2. Experimental

2.1. Materials

Sodium molybdate ($Na_2Mo_4.4H_2O$, ≥ 99.5%, Merck), potassium thiocyanate (KSCN, ≥ 98.5%, Merck), hydrazine hydrate ($N_2H_4.4H_2O$, ≥ 80%, Merck), hydrogen peroxide (H_2O_2, ≥30%, Merck), DMF (99.8%, Merck), Graphite powder (≥99.5%, Merck), Multiwalled carbon nanotube (MWCNT, ≥ 98.5%, Sigma-Aldrich) were used for the synthesis. Nafion solution (5 wt%, Fuel Cells Etc.) was used for catalyst ink preparation and pure graphite rods (M/S Nickunj Catalyzing Transformation India) was employed as counter electrode. Commercial platinum catalyst (20 wt% Pt/C, Alfa-Aesar) was used for comparative HER activity studies. Ultrapure water (Resistivity: 18 MΩcm, Merck Millipore) was used throughout the experiment.

2.2. Synthesis of MoS_2

A facile one pot hydrothermal method was adopted for the synthesis of MoS_2 [43]. Typically, 3.63 g $Na_2MoO_4.4H_2O$ and 3.66 g KSCN was dissolved in 180 mL ultrapure water. The mixture was transferred to a stainless steel autoclave (100 mL) and maintained at a temperature of 260 °C for 24 h. The final product was obtained after purification by filtration, repeated washings and drying in a vacuum oven at 80 °C for 12 h.

2.3. Synthesis of NCHy

The NCHy was prepared by facile one pot solvothermal method. Typically, to prepare 1:1 ratio of rGO/CNT, 7.5 mg GO was dispersed in 75 mL of 10:1 DMF/H_2O mixture and ultrasonicated for 1 h. Further, 7.5 mg of *f*-MWCNT was added and sonicated for 10 min. The mixture was stirred for 30 min. 75 μL of $N_2H_4.4H_2O$ was added to the above solution. The resulting mixture was transferred to Teflon-lined stainless steel autoclave (50 mL) and kept at 260 °C for 6 h to complete the reaction. The product was collected and purified by centrifugation, washed with ultrapure water and dried at 80 °C in a vacuum oven for 12 h.

2.4. Synthesis of MoS_2@NCHy

Solvothermal route was adopted for the synthesis of MoS_2@NCHy. Typically, 0.03 g GO (Synthesis route of GO, explained in Section S1, Supplementary Information) was dispersed in 40 mL of 10:1 DMF/H_2O solvent mixture by ultrasonication for 1 h. 0.03 g of functionalized multiwalled CNT (*f*-MWCNT) (Supplementary Information, S2) was added to the above dispersion and sonicated for 10 min and stirred for another 30 min. To the above mixture, 0.06 g $Na_2MoO_4.4H_2O$ and 0.07 g KSCN was added followed by addition of 200 μL $N_2H_4.4H_2O$. The entire solution was transferred to a stainless steel-lined Teflon autoclave and heated at 260 °C for 24 h. The final product was obtained after purification by filtration, repeated washings and drying in vacuum oven at 80 °C for 12 h. The amount of MoS_2 was chosen so as to obtain a weight ratio of 40 wt% MoS_2@NCHy. Similarly, 20 wt% and 60 wt%. MoS_2@NCHy were also prepared using the same procedure.

2.5. Structural characterizations

The X-ray diffraction (XRD) patterns were acquired by Shimadzu XRD-600 equipped with Cu Kα radiation. The structural features of the samples were analyzed using Raman spectroscopy (Horiba-Jobin, LabRam HR) with 514 nm Argon laser source. JEOL JEM 2100 (200 kV) with a LaB_6 electron gun (Japan) was used for aquiring the transmission electron microscopic (TEM) images. SEM (Carl Zeiss EVO 18, operating voltage 30 kV) was used to record the scaning electron microscopic images. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a ESCA+, an Omicron Nanotechnology ESCA probe spectrometer with monochromatized Al Kα X rays (energy: 1486.6 eV). The peaks were deconvulated using peakfit V4 software and the binding energy (B.E) values were compared with the XPS database present in LaSurface.com.

2.6. Electrochemical measurements

All the electrochemical measurements were performed using an electrochemical work station (VSP multichannel model, M/S Bio-Logic Science, USA) with a conventional three-electrode cell with glassy carbon electrode (GCE, 3 mm in diameter) as working