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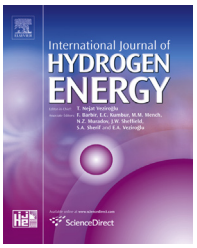

# Electrocatalytic activity of MWCNT supported Pd nanoparticles and $MoS_2$ nanoflowers for hydrogen evolution from acidic media

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ABSTRACT

Here, the hybrid material of $MoS_2$-coated Pd nanoparticles loaded on the multiwalled carbon nanotubes (Pd–$MoS_2$/MWCNT) was synthesized using chemical process and hydrothermal method. The nanohybrid was characterized by X-ray diffraction (XRD) patterns, Raman scattering, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Pd–$MoS_2$/MWCNT showed the high activity for hydrogen evolution reaction with a small onset overpotential of 70 mV, a high exchange current density of $7.1 \times 10^{-2}$ mA $cm^{-1}$ and Tafel slope of 54 mV $decade^{-1}$ as well as an excellent stability in acid media. It was found that these catalyst exhibited excellent HER activity compared to $MoS_2$ nanoflower, Pd–$MoS_2$ and $MoS_2$/MWCNT due to the synergistic effect of the high catalytic activity of $MoS_2$ nanoflowers and the excellent conductivity and large surface area of MWCNT and providing more free sites for the adsorption of H using Pd nanoparticles, exposing much more active sites and reducing intrinsic resistance. The turnover frequency per active site is also calculated. This work demonstrates the feasibility of increasing HER activity of $MoS_2$-based catalysts by combining $MoS_2$with MWCNT and Pd noble metal nanoparticles.



## Introduction

Hydrogen is counted as a promising clean energy and fuel carrier, because of its several advantages, such as high gravimetric energy density, sustainability, recyclability, $CO_2$ neutrality and pollution-free use [1]. To obtain a complete advantage of the desirable features of hydrogen, it should be produced from a renewable energy source in a sustainable manner. Electrochemically splitting water through hydrogen evolution reaction (HER), offers a favorable solution for this purpose [2–4]. To achieve an optimal performance, efficient electrocatalysts for HER are critical. At present, the most efficient and typical electrocatalysts for HER are Pt based compounds, which can realize excessive catalytic activity with almost no overpotential [5,6]. But the high cost and low abundance of Pt hinders the large-scale hydrogen production through acidic electrolyzers like polymer electrolyte membrane (PEM) electrolyzers [7]. Thus, it is highly attractive to design and synthesis of the cheap and efficient

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electrocatalysts for HER with earth-abundant materials and long term stability in acidic solution for large-scale hydrogen production. That's why several studies have been conducted on the development of electrodes with bi- or multi-metallic catalyst of low Pt loading, or non-precious metal catalysts in HER [8–12]. Mo-based dichalcogenides are known as effective candidates for replacing the Pt group metals due to their similar electronic structures to that of noble metals [11–14]. Among molybdenum dichalcogenides ($MoS_2$, $MoSe_2$ and $MoTe_2$), $MoS_2$, which basically consists of two-dimensional S–Mo–S layers that are stacked to various degrees, has led to the best electrocatalyst for the HER [11,12,15]. Therefore, great efforts have been made to design the composites and structures of $MoS_2$ that excellent HER activity can be obtained.

There are two general strategies for the improvement of the catalytic activation of $MoS_2$ (1) increasing the number or quantity of active sites per unit volume of catalyst and (2) improving the conductivity of catalyst [15–18]. For the increasing of the active sites number, different methods have been developed to reduce the size of $MoS_2$ to the nanoscale, such as chemical exfoliation, chemical vapor deposition, electrodeposition, solvothermal methods, hydrothermal method and gas phase synthesis [16,19,20]. High catalytic activity of nanostructured MoSx is due to a much higher specific surface area and more active sites compared with its bulk counterpart [20]. Furthermore, more highly conductive materials were added to nanostructured MoSx in order to improve the electrical contact, including reduced grapheme oxide, carbon nanotubes, carbon nanospheres, and so on [20–29]. For example, Cai et al. utilized SWCNT as a conductive support for loading $MoS_2$ [24]. Recently, Li et al. reported that amorphous molybdenum sulfide ($MoS_x$) layer directly bound at vertical N-doped carbon nanotube (NCNT) exhibited excellent HER activity, which can ascribe to the synergistic effects from the dense catalytic sites of amorphous $MoS_x$ surface and fluent charge transport along NCNT forest [20]. Ma et al. applied the reduced graphene oxide paper as a flexible straight solid support for adsorption of the $MoS_2$, which efficiently compensated the poor conductivity of nanosized $MoS_2$ [25]. Thus, synthesis the $MoS_x$ particles at a nanometer scale on the carbon-based supporting template would seem to present a perfect solution to fully organize the two general strategies detailed above, and thus be highly desirable to achieve high HER activity for $MoS_x$.

Doping other atoms into $MoS_2$ electrocatalyst is an additional way to improve their catalytic activity for HER. Recent reports have verified that the introduction of Co, Cu, Ni or Pd in $MoS_2$ could improve its electrocatalytic activity for HER [30–34]. Especially, Pd modified $MoS_2$ has been proved to be a superior electrocatalyst with excellent metal-like conductivity [33]. Based on these facts, it is more significant to explore whether the co-existence of carbon materials and promoters could obviously improve the electrocatalytic activity of nanoseized $MoS_2$.

Herein, we studied the catalytic performance of Pd–$MoS_2$/MWCNTs composite with respect to their application in HER. The structure is examined using transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman scattering X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) patterns. Because of the synergistic effect of the high catalytic activity of $MoS_2$ nanoflower and the excellent conductivity and large surface area of MWCNT and providing more free sites for the adsorption of H using Pd nanoparticles, this composite show high catalytic activity for HER performance with a small onset overpotential of 70 mV vs. reversible hydrogen electrode (RHE) at the high exchange current density of $7.1 \times 10^{-2}$ mA $cm^{-2}$ and a Tafel slope of 54 mV $decade^{-1}$, achieving high stability simultaneously. These highly active catalysts for HER should be the promising materials which can facilitate the development of electrochemical hydrogen production systems.

## Experimental

### Materials

All reagents used in this study were of analytical grade. MWCNT, cetyltrimethylammonium bromide and $K_2PdCl_4$ were obtained from Sigma–Aldrich. Sulfuric acid, nitric acid, ascorbic acid, sodium molybdate, thiourea, chitosan, ethanol, sodium hydroxide and citric acid were purchased from Merck (Darmstadt, Germany). All aqueous solutions were prepared with doubly distilled water. The chitosan solution (0.5%) was prepared by dissolving 0.05 g chitosan in 10 mL $CH_3COOH$ (2.0 mol $L^{-1}$)–N-Methyl-2-pyrrolidone with volume ratio of 4-1 by sonicating for 30 min. The chitosan solution was stored in refrigeration at 4 °C when not in use.

### Synthesis of $MoS_2$ nanoflowers

The $MoS_2$ nanoflowers assembled by nanosheets with few layers were prepared via a facile hydrothermal reaction. In a typical procedure, sodium molybdate (1.0 mmol) and thiourea (4.0 mmol) were dissolved in 10 mL of distilled water. 0.12 g citric acid dissolved in 5 mL of distilled water as pH adjusting agent, to adjust to an acid environment, was injected into the above solutions and stirred for 10 min. The final solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 48 h. Subsequently, the black product was centrifuged and washed with ethanol and distilled water alternately for several times to remove impurities, then dried in a vacuum at 60 °C for 6 h to obtain black $MoS_2$ powders [35,36].

### Synthesis of Pd–$MoS_2$ hybrid nanomaterials

The in situ growth of PdNPs on $MoS_2$ nanoflowers was carried out via wet-chemical synthesis [37]. 10.0 mg as-formed $MoS_2$ nanoflowers were dispersed into 40.0 mL fresh growth solution containing 20 mmol $L^{-1}$ cetyltrimethylammonium bromide (CTAB) and 0.5 mmol $L^{-1}$ $K_2PdCl_4$ in water. Into this solution, 300 mL aqueous solution of 250 mmol $L^{-1}$ ascorbic acid and 300 mL aqueous solution of 2.5 mol $L^{-1}$ NaOH were added in sequence with mild shaking. After 1 h, the resulting solution was centrifuged, and the precipitate was washed with distilled water. Pd nanoparticles modified $MoS_2$ nanoflowers were marked as Pd–$MoS_2$.

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