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Molybdenum/graphene – Based catalyst for hydrogen evolution reaction synthesized by a rapid photothermal method

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ABSTRACT

Catalysis of the hydrogen evolution reaction (HER) is important in the development of an energy economy based on clean hydrogen gas. In this work, we report a new catalyst material for the generation of hydrogen via hydronium reduction. The new material, which consists of MoO₂, sulfur, and graphene, was prepared by co-reduction of molybdenum salt and graphite oxide in air in the presence of focused solar radiation. The potential utility of this material for HER catalysis was evaluated by cyclic and linear-sweep voltammograms and compared against a Pt/C commercial catalyst. The MoO₂/graphene hybrid nanocomposite exhibits a Tafel slope of 47 mV/dec and hydrogen evolution at a potential only ~120 mV more negative than the standard Pt/Carbon catalyst at 10 mA/cm² current density. The hydrogen gas generated by the catalytic material was measured using gas chromatography. The simple synthesis and low overpotential suggests that this hybrid composite has potential as an HER catalyst.

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Introduction

The generation and utilization of hydrogen gas for the hydrogen energy economy is a promising area of research since the oxidation of hydrogen to generate energy in electrochemical fuel cells produces H₂O rather than CO₂. However, the realization of an effective hydrogen-based energy economy is very challenging due to, among other factors, the lack of energy-efficient and cost-effective techniques for large-scale production of hydrogen gas. This is primarily a result of the high overpotential required for the hydrogen evolution reaction (HER):



Currently, platinum-based catalysts offer the best performance for HER [1,2]. However, the high cost and low earth abundance of Pt and Pt group metals severely hinder their use for HER applications and present an economic obstacle to a hydrogen energy economy. In order for a hydrogen economy to be realized, the HER catalyst materials should be cheap and readily available.

Intense research has been ongoing to find a cost-effective alternative to platinum for the photo/electrocatalytic

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production of hydrogen. Xu et al. have reported an ordered mesoporous composite of quantum-sized CdS/Ta₂O₅ as a visible light-driven photocatalytic material with considerable hydrogen evolution from stimulant waste water [3]. Faber et al. have reported earth-abundant transition metal disulfides on graphite disk substrates as electrocatalytic HER material [4]. Natural catalysts such as hydrogenase and nitrogenase enzymes have also been shown to be efficient for HER applications [5,6]. Notably, these enzymes contain non-noble metals such as Mo, Fe and Ni as key players in the HER catalytic mechanism [5,6]. Inspired by these natural materials, non-noble metal chalcogenides such as MoS₂ and NiS have been designed to catalyze the electrochemical production of hydrogen [7,8]. Nickel-based materials operate efficiently in alkaline electrolytes [9], but HER generally requires acidic conditions and the long-term stability of these materials in acidic electrolytes needs to be improved [10]. Bulk MoS₂ has been shown to be a relatively poor HER catalyst, but nanocrystallized MoS₂ has been identified as a promising HER material. Recent literature reports have focused on engineering MoS₂ structures in order to preferentially expose edge sites by synthesizing thin films of highly ordered double-gyroid MoS₂ bicontinuous network [11], and preparing MoS₂ nanoparticles of different sizes to create more active-edge sites for HER [12]. Graphene, which consists of extended 2-dimensional sheets of sp²-bonded carbon atoms, has also been investigated as a potential conducting matrix for the semi conductive MoS₂ for electrocatalytic hydrogen evolution [13]. The honeycomb graphene structure shows superior properties such as fast mobility of charge carriers, exceptional conductivity and large theoretical specific surface area [14,15]. Moreover, graphene behaves like metals owing to its large work function (4.42 eV) [16]. This enables graphene to accept photoelectrons from conduction band of most of the semiconductors and hence it has been investigated as a cost effective and efficient co-catalyst to enhance the electron separation and transfer from semiconductors and catalyze the proton reduction in photocatalytic water splitting [17].

The layered structure of MoO₂ has low electrical resistivity, high electrochemical activity and high stability and therefore employed as anode material in Li-ion batteries [18]. It is reported that MoO₂ has high theoretical Li storage capacity making it a promising anode material in lithium-ion batteries. But since irreversible volume expansion of bulk MoO₂ can result in plastic deformation and a decrease in performance, nanostructured MoO₂ [19] as well as MoO₂–carbon composite [20] have been investigated. It is found that the nanostructured MoO₂ with high surface area and MoO₂–carbon composite with improved conductivity arising from the carbon coating layer could effectively solve the issue of detaching the active material from current collector leading to substantial loss in capacity. Recently, solid MoO₂ dispersed in a graphene “nano-architecture” matrix has been reported as an attractive lithium-ion battery electrode material [21]. It is reasonable to expect that such a material could have potential HER applications. The photocatalytic activity of gold nanoparticle/molybdenum/graphene oxide nanocomposite, prepared by UV irradiation of the precursor materials in isopropanol, has been recently reported for the degradation of Rhodamine B [22]. However, most synthesis procedures of MoO₂/graphene

involve long processing time, high-temperature conditions, calcination under inert atmosphere, and toxic reagents in some cases. Several examples include the use of toxic hydrazine hydrate for graphite oxide reduction with calcination under H₂/Ar atmosphere [18], preparation by long-time high-temperature hydrothermal reaction followed by long hours of processing and calcination under inert atmosphere [21], and pre-heating of precursor materials [23].

In the current work we present an HER catalyst material composed of MoO₂ dispersed in a graphene matrix (MoO₂/Graphene) by a photothermal reduction method, as an effort to develop a green, economically-feasible, and earth-abundant HER catalyst. Unlike the synthesis procedures reported in the literature, the current technique is simple, rapid, facile, and environmentally green as it involves in-situ reduction of molybdenum salt and graphite oxide compounds using focused solar radiation. The material is stable under acidic conditions and is an excellent HER catalyst as evidenced from low overpotential and Tafel slopes.

Materials and methods

Graphite oxide (GO) was prepared by Hummer's method [24]. MoO₂/Graphene was prepared by co-reduction of ammonium tetrathiomolybdate (ATM, Alfa Aesar, 99.95%) and GO using focused solar radiation. To prepare MoO₂/graphene compound, different ratios of ATM and GO were taken and then were mixed together in de-ionized (DI) water by ultra sonication and magnetic stirring. The solvent was then evaporated by slow heating in air (~50 °C). The dried ATM-GO composite was ground with a mortar and then spread in a petri dish. The in-situ reduction of ATM and GO into MoO₂ and graphene was performed outside on sunny days by a simple technique utilizing natural sunlight. The incident flux of solar radiation was focused towards the material in petri dish using a convex lens of diameter 100 mm (Fig. 1) under ambient conditions. As soon as focused light falls on the material in petri dish, a popping sound is heard. This is similar to the photoacoustic effect reported for flashing of single-walled carbon nanotubes in which acoustic waves are generated upon flashing light [25]. When the material is irradiated with sunlight, the absorbed energy may be transmitted as heat resulting in a local increase in temperature and thermal expansion of the material which in turn leads to mechanical motion. Due to the localized thermal excitation and rapid temperature increase of the compound, simultaneous reduction of GO to graphene and ATM to MoO₂ occurs spontaneously. The mechanism of reduction of GO to graphene can be termed as deflagration, which is the removal of insulating functional groups over basal planes of GO by the opto-thermal effect. During this process, the ATM is reduced in air to MoO₂ containing sulfur, releasing other constituents in gaseous form. This is similar to the simultaneous reduction/exfoliation of metal salt-GO composites to corresponding metal-graphene composites under focused sunlight [26].

The “popping” sound signals the reduction of GO to graphene. The material was mixed using a spatula and the position of the focused light was continuously moved to ensure the completeness of reaction and homogeneity of the product.

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