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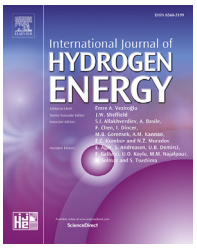

Palladium nanoparticles grown on β-Mo_2C nanotubes as dual functional electrocatalysts for both oxygen reduction reaction and hydrogen evolution reaction

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ABSTRACT

Developing efficient dual functional electrocatalysts for both oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) is critical for boosting the performance of fuel cells and metal air batteries, as well as production of clean and sustainable energy source. Herein, Pd nanoparticles grown on Mo_2C nanotubes were prepared as dual functional electrocatalysts for both ORR and HER. A series of samples with different Pd loadings were fabricated, while the morphology and the structural features were well examined by transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Interestingly, both the ORR activity and HER activity first increased then decreased with the increasing of Pd loading, and the sample of Mo_2C-Pd-9% exhibited the best performance among the series, superior than commercial Pd/C in both ORR and HER tests. Furthermore it also exhibited markedly higher long-term stability than Pd/C for both electrocatalytic reactions. The results may shed light on rational design of novel bi-functional electrocatalysts in the renewable energy field.

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Introduction

The global energy crisis and extensive environmental pollution caused by the heavily reliance of fossil fuels can be significantly mitigated by the rapidly developing green and sustainable energy technologies including water splitting, fuel cells and metal-air batteries [1–4]. Oxygen reduction reaction (ORR) plays a key role in fuel cells and metal-air batteries, while hydrogen evolution reaction (HER) is critical for production of clean energy [5–8]. Currently, Pt based nanomaterials have been widely considered as the state-of-art electrocatalysts for both ORR and HER thanks to their low overpotentials and large current densities [9–11]. Nevertheless, the low abundance and high costs of Pt significantly hindered their large-scale commercialization. Therefore, developing cost-effective, highly active and durable catalysts for ORR and HER as alternative of Pt is crucial and highly desirable [7,11–17].

Compared with Pt, palladium has demonstrated as a promising candidate to replace Pt due to its much lower costs and satisfactory catalytic activities in electrochemical reactions [18–22]. For instance, a series of Pd nanoparticles with various size exhibited effective catalytic activity toward ORR, and Zhou et al. successfully established the size effects [23]. Xia group synthesized 5–6 nm Pd nanocrystals with different shapes, and surface-structure-dependent ORR activities were observed [24]. By employing a top-down strategy, Xu group created a multisite HER catalyst on nano-Pd surface, where the water dissociation and hydrogen formation were balanced to achieve the highest efficiency for HER in alkaline media [25]. Recently, Liu et al. developed a facile approach to prepare Pd nanoparticle assemblies with porous structure for both HER and ORR, of which the Tafel slope was 30 mV dec^{-1} and the overpotential was 80 mV at 100 mA cm^{-2} for HER, while the half-wave potential and onset potential was 0.84 V and 0.93 V for ORR, respectively [26].

Nevertheless, when employing palladium nanoparticles alone to catalyze electrochemical reactions, the catalysts still suffer from low chemical susceptibility, as palladium nanoparticles would aggregate or decompose during the catalytic process. A matrix or support to integrate palladium nanoparticle as an intact hybrid catalyst is highly desirable [27]. In addition, such matrix or support would be easily accessible and the introduction of additional electrocatalytic activity is desired. Mo_2C nanotubes can be a great choice based on the following reasons: First of all, Mo_2C nanotubes can be fabricated under mild conditions in large scale with low costs; Secondly, previous studies have shown that Mo_2C nanotubes and/or their analogues exhibited a remarkable electrocatalytic performance toward HER [28–30]. Lastly and most importantly, through rational design, palladium nanoparticles can be grown on the surface of the Mo_2C nanotubes to form an integral composite, and enhancement of electrocatalytic performance via the synergistic effect is expected.

Herein, we report a facile approach to prepare palladium nanoparticles grown Mo_2C nanotubes. The as-prepared integral composite exhibited effective catalytic activities toward both ORR and HER. Among a series of samples tested, Mo_2C–Pd-9% demonstrated the best performance toward both ORR and HER, along with a most positive onset potential of +0.96 V and the largest diffusion-limited current density of 4.64 mA cm^{-2} at 1600 rpm for ORR, as well as an overpotential of 28 mV at the current density of 10 mA cm^{-2} for HER. Both the ORR and HER performance are superior than commercial Pd/C. Furthermore, Mo_2C–Pd-9% exhibited markedly higher long-term durability toward both ORR and HER than Pd/C.

Experimental section

Chemicals

Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ≥99.0% purchased from Damao Chemical Reagent, Tianjin, China), nitric acid (HNO_3, 65%–68%, purchased from Energy Chemicals, Shanghai, China), 3-hydroxytyramine hydrochloride (98%, purchased from Energy Chemicals, Shanghai, China), absolute ethanol (≥99.7%, purchased from Jinhuada Chemical Reagent, Guangzhou, China), ammonia solution (25%–28%, Cai Yunfei Chemical Industry), sodium tetrachloropalladate (II) (Na_2PdCl_4, 99.95%, purchased from Energy Chemicals, Shanghai, China). L-Ascorbic acid (AA, 98%, purchased from Energy Chemicals, Shanghai, China). All chemicals were used as received without purification. Deionized water was supplied by a Barnstead Nanopure Water System with a resistivity of 18.3 MΩ cm^{-1}.

Synthesis of MoO_3 nanorods

The MoO_3 nanorods were prepared by following a previously reported protocol [31]. In a typical reaction, 2.1 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 60 mL of mixed solvents of deionized water and HNO_3 (v: v = 5: 1). The mixed solution was then transferred into a Teflon-lined stainless steel autoclave (100 mL capacity) and heated at 200 °C for about 20 h. After cooling down, the product was collected by centrifugation and washed with deionized water and absolute ethanol for 3–5 times prior to drying at 70 °C overnight. The XRD patterns of the as-prepared MoO_3 nanorods can be found in Figure S1a, which agrees well with the previous reported results [28].

Synthesis of hierarchical β-Mo_2C nanotubes

The hierarchical β-Mo_2C nanotubes were prepared by following a previously documented synthetic method [28]. Firstly, 150 mg of the as-prepared MoO_3 nanorods were added into 30 mL of deionized water in a 250 mL glass beaker. After ultrasonic dispersion for 15 min, 300 mg of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 75 mg of 3-hydroxytyramine hydrochloride were gradually dissolved into the above solution, and the milky solution turned into orange-red suspension. Then, 60 mL of absolute ethanol was added into the above solution rapidly. After stirring for 5 min, 450 μL of 28–30% $NH_3\cdot H_2O$ was injected into the above solution quickly, and the mixture was kept stirring for 120 min. Subsequently, the orange-red precipitate was obtained by suction filtration and washed with absolute ethanol for several times, followed by vacuum drying at room temperature for 12 h. Such orange-red solid was Mo-

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