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Nitrogen and sulfur co-doped graphene supported PdW alloys as highly active electrocatalysts for oxygen reduction reaction

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ABSTRACT

Nitrogen and sulfur co-doped graphene (NSG) is prepared by a facile microwave irradiation method and palladium-tungsten (PdW) alloy nanoparticles are supported on the NSG substrate. Several techniques, including X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, cyclic voltammetry and scanning electrochemical microscopy etc. are used to characterize the physical and electrochemical properties of the as-prepared samples. It is found that the PdW alloy nanoparticles are uniformly dispersed on the surface of NSG and the electrochemical performance of PdW/NSG is much better than those of Pd/NSG and Pd/G. The reason for the improved electrochemistry performance of PdW/NSG is considered to be the strong interactions and synergetic effects between PdW nanoparticles and NSG.

Introduction

Oxygen reduction reaction (ORR) played crucial roles in many energy conversion and storage systems, such as fuel cells [1,2], Zn-air [3,4] and Al-air batteries [5,6]. The application of electrocatalysts can obviously reduce the polarization, increase the reaction kinetics and therefore improve the overall efficiency of energy conversion. The Pt and Pt-based alloys were considered as the best electrocatalysts for ORR due to their high catalytic activity [7–9], however, their high cost, poor stability and CO-poisoning effect hindered the practical application. Therefore, one of the challenges for commercialization of these electrochemical energy devices is to develop low-cost and high-performance alternatives [10,11]. Recently, Pd-based alloys have attracted much attention owing to their catalytic activity comparable to that of Pt, and the advantages of low cost and good cyclic stability. In particular, Pd and transition metal complexes exhibited excellent catalytic activity since the addition of other metals changed the electronic structure of Pd [12–16].

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For example, Pd-Ag [17], Pd-Fe [18], Pd-Sn [19], and Pd-Ni [20] alloy electrocatalysts showed improved catalytic activity and cyclic stability. Tungsten is a transition metal with multiple valences and good redox character and the PdW alloys also exhibited electrochemical performance superior to Pd, indicating it is a promising alternative to Pt [21–24]. It was suggested that the oxygen molecules were adsorbed on the surface of the PdW alloy, and after two steps of hydrogenation on the surface, HO* and H_2O were obtained, respectively [25].

Graphene has large surface area and good electrical conductivity [26,27] and the catalytic activity of graphene was increased due to the introduced active sites after heteroatom-doping [28–31]. It was demonstrated that after the nitrogen atom doping to graphene, the spin density and charge distribution of carbon atoms was influenced by the neighbor dopants, which induced the "activation region" on the graphene, moreover the dispersion of metal alloy nanoparticles was increased, resulting in the enhanced catalytic activity [32–34].

Herein, nitrogen and sulfur co-doped graphene (NSG) was prepared by a facile microwave irradiation method and PdW alloy nanoparticles were supported on NSG and the catalytic performance of the PdW/NSG electrocatalyst was investigated. The microwave is a short-wave red light and it can make the vibration of polar molecules. During the microwave heating, the polar molecules are rapidly heated and will cause the molecular rotation, friction and collision in the directional fast changing electric field in which the ions in the solution will move rapidly. Meanwhile, the local temperature is increased due to the direction changing of ions, which accelerates the rate and reduces the temperature of chemical reactions [35]. The $NaBH_4$ was used in the preparation process because of the strong reduction ability in liquid phase at low temperature. Some other reducing such as oxalic acid, glycerin, etc. can be used, however, either the reduction occurred at high temperatures or the residual was difficult to remove. Therefore, by taking the advantages of using $NaBH_4$ combined with the characteristics of microwave-assisted heating, the reaction efficiency can be improved [36,37]. Moreover, the scanning electrochemical microscope (SECM) was used to study the electrochemical performance of PdW/NSG through the change of the probe current in the micron level by obtaining the electrical signal and its appearance of the substrate in the ORR reaction [38–40].

Experimental

Preparation of NSG

Graphene oxide (GO) was prepared by a modified Hummers' method reported elsewhere [41,42]. The mixture of GO and thiocarbamide (CH_4N_2S) at a mass ratio of 3:1 was placed in a microwave oven (MAS-II Plus, Shanghai, China) and heated at 600 W and 800 W for 2 min, respectively. The NSG was obtained by this simple microwave irradiation process.

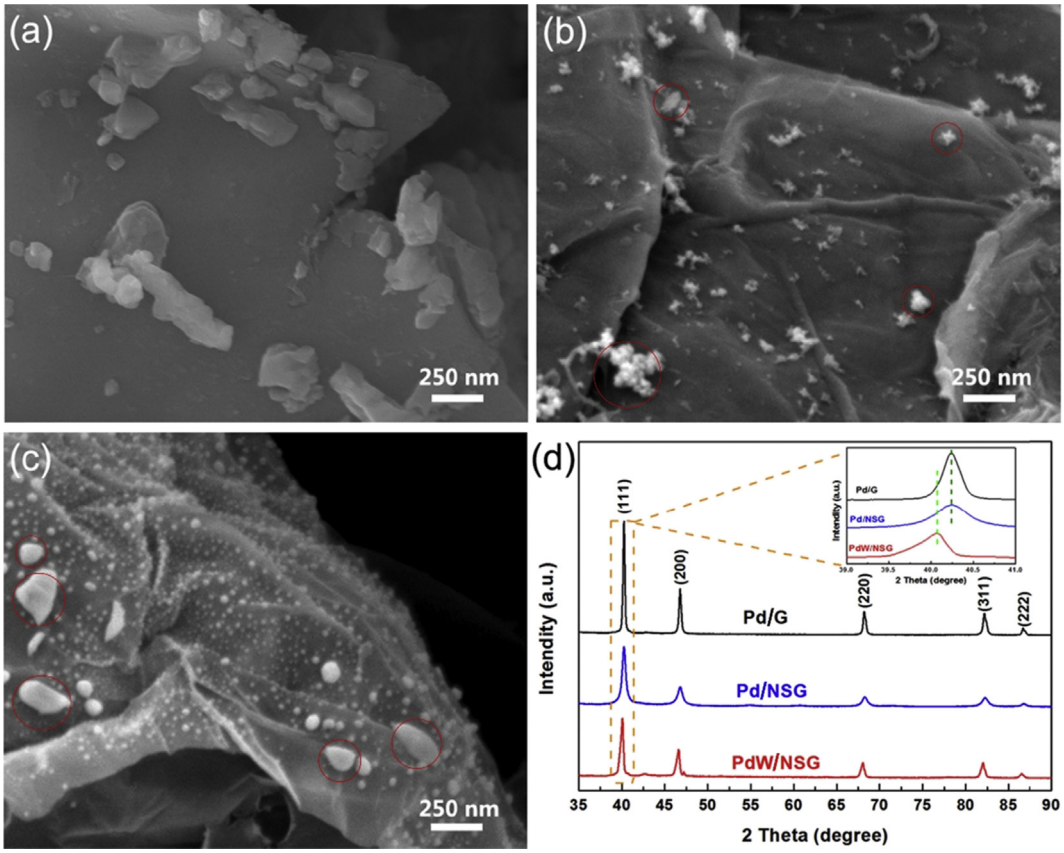

Fig. 1 – The SEM images of (a) Pd/G (b) Pd/NSG, (c) PdW/NSG and (d) XRD patterns of Pd/G, Pd/NSG and PdW/NSG.