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Three-dimensional graphene promoted by palladium nanoparticles, an efficient electrocatalyst for energy production and storage

Ali A. Ensafi *, E. Heydari-Soureshjani, B. Rezaei*

Department of Chemistry, Isfahan University of Technology, Isfahan 84156–83111, Iran

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ABSTRACT

Three-dimensional (3D) graphene was easily obtained by a simple hydrothermal method from two-dimensional (2D) graphene to create the interspace sites and active surface area. So, the fabrication of the 3D-graphene nanocomposite is promising for advanced energy production and storage application. The structure of the 3D-graphene nanocomposite was characterized by various techniques. Then, 3D-graphene was decorated with Pd nanoparticles. Morphological characterization shows the porous structure of 3D-Pd/rGO, so it has a high electroactive surface area. The function of the electrocatalyst toward the supercapacitor, hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) were investigated. The obtained results as a supercapacitor displayed that the supercapacitor on 3D-Pd/rGO has a high specific capacitance of 582.0 F g^{-1}, the high energy density of 180 (W h Kg^{-1}), high power density of 3750 (W Kg^{-1}), long potential window of 1.00 V and long life. The electrocatalyst shows the small onset potential of −0.08 V (*vs.* RHE), Tafel slope of 29 mV dec^{-1} and high durability. Also, in the electroanalytical application of the nanocompound as an electrocatalyst for ORR shows an excellent onset potential of 0.90 V (*vs.* RHE), slow drop in the current density (34% in the presence of MeOH) and the reduction process via a four electrons pathway.

Introduction

Graphene is a well-defined single atom thick sheet with a honeycomb-shaped lattice of carbon atoms that taken from graphite [1,2]. Due to the unique properties, such as huge electrical conductivity, surface area, and active site, graphene has grown rapidly in the experimental progress in the last decade. However, there are many problems in the usage of graphene in the form of two-dimensional (2D) materials. It's likely that the enabled sites of graphene oxide (GO) be covered when the oxygen-containing functional groups of GO are hydrated by dispersion of GO in aqueous solutions and formed hydration shell around its oxygen-containing functional groups [3,4]. GO has a low conductivity because of oxygen-containing functional groups and surface defense [5]. So, for the electrochemical application, GO be converted to reduced graphene oxide (rGO) by facile methods. The structure defects can appear in the reduction process, which impacts on the mechanical property and electrical conductivity [1]. Although rGO has a less conductivity rather than the pristine graphene, rGO sheets can aggregate together because of remaining oxygen-containing functional groups [5]. Also, a van der Waals and π-π stacking attraction between the basal planes of

* *Corresponding author.*
E-mail addresses: Ensafi@cc.iut.ac.ir, aaensafi@gmail.com, ensafi@yahoo.com (A.A. Ensafi).
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GO or rGO create low friction and rapid transitions between the layers [6]. Due to this π-π bonding, GO, or rGO layers tend to stick to each other and formed a graphitic structure which it reduced the specific surface area [6].

In many applications such as energy generation and storage devices, the restocking of graphene layers is important [6]. When GO or rGO sheets, stick to each other, the permeation of electrolyte ions is difficult through the densely packed graphene sheets, and thus the power of energy generation and storage devices have come down [6].

To solve this problem of 2D-graphene, three-dimensional (3D), porous graphene materials have much attraction. The structure of 3D-graphene remained stable by using spacer materials between graphene layers, which is an impressive way to maintain graphene structure. 3D-graphene not only has a unique property of 2D-graphene but also have a huge surface area, porosity, excellent electrical conductivity and so on. 3D-graphene network is a great substrate for making nanocomposite, which has a synergistic effect for progressing in energy generation and storage application such as supercapacitors and fuel cells. This spacer material may include noble metals (Pt, Pd. Au), polymers (aniline, pyrrole), metal oxide (Co_3O_4), metal-organic framework (MOF), carbon nanocomposite, etc. [6].

With the evacuation of the fuel cell and environmental deterioration, demand for alternative energy increased [7]. Supercapacitors between other forms of energy device have a higher power density, long life cycle and low maintenance cost [8]. According to the charge storage mechanism, supercapacitors categorized into two kinds: Electrical double layer capacitors (EDLC) and pseudocapacitors (PCs) [9–11]. Meanwhile, hydrogen as a no carbon emission energy needs a way to generate hydrogen through water electrolysis [12], and in the proton exchange membrane fuel cell (PEMFC), ORR has a considerable task [13,14], so control the efficiency of this energy generation and storage device [15]. HER has a high overpotential at the surface of unmodified electrodes that expends plenty of electrical energy [16,17]. ORR has an intricate reaction pathway and two-step electron-proton transfer [18]. Finally, HER and ORR processes are a very sluggish kinetic, so the expansion of the clean, cost-effective and high-stability electrocatalyst are important.

In addition, many studies have been done on the Pd and Pt-based nanocomposite, in the field of supercapacitors, oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), methanol oxidation, etc. Chao et al. synthesized the robust three 3D N-doped porous graphene (R_3DNG) by Pd nanoparticles via a polyol-assisted reduction strategy and applied for methanol oxidation in alkaline media with a remarkable electrocatalytic activity (2.71 A mg^{-1} Pd) [19]. Cardoso et al. developed a Pd based alloy nanocomposite, namely rGO-AuPd and rGO-FePd and used for HER. rGO-AuPd and rGO-FePd show the onset potential of 80 and 140 mV [20]. Wu et al. prepared Pt/GNS@TiC catalyst and applied for ORR. The power density of fuel cells with its catalyst reaches to 853 mV cm^{-2} [21]. Yan et al. prepared PdAu alloyed clusters supported on carbon nanosheets as an electrocatalyst of ORR. The hybrid materials demonstrated effective ORR activity in alkaline media [13]. Li et al. described a series samples with different Pd loading and checked for ORR and HER activity. Their results show that the Mo_2C–Pd-9% exhibited the best performance among series [22]. Yan et al. prepare palladium nanoclusters encapsulated in porous carbon nanosheets as an electrocatalyst for ORR in alkaline media. Among the synthesized sample Pd/CNS-20% shown the positive onset potential and high diffusion-limited current density toward ORR [23].

Although there is some study about Pd nanocomposite, this work has some advantage rather than other works. So, in following some of them are reviewed. In this work, the 3D structure was synthesized in the facile and one step process by the Pd nanoparticles, while in other works the Sacrificial Support Method (SSM) was used for the synthesis of 3D structure and after that the nanoparticles decorated on it [24,25]. Also, in this work, low amount of Pd was consumed, while in other works, another materials were used [26,27]. Finally, those nanocomposites were used in alcohol oxidation and catalytic performance, but this electrocatalyst was applied in three applications such as supercapacitors, HER and ORR and the results show that it's applicable in three different fields.

In this study, a 3D-graphene network was prepared using Pd nanoparticles, as a spacer material, in a facile and one step process. This form of graphene is a good choice for making the nanocomposite, which can be applied to an energy production and storage device owing to a synergetic effect and porous structure. The morphology of 3D-Pd/rGO was checked by scanning electron microscopy (SEM) and transition electron microscopy (TEM). Other properties of 3D-Pd/rGO were evaluated by FT-IR, XRD, BET, AFM, and EDX. The work introduced in this paper is centralized on the operation of 3D-Pd/rGO for PCs, HER and ORR. The results showed that the 3D-Pd/rGO has good efficiency and power toward these processes.

Experimental section

Materials and analytical characterizations

All of the materials and solvents were reagent grade and commercially available. Palladium (II) chloride ($PdCl_2$), glucose, H_2SO_4 and KOH were gathered with high purity from Merck Company. FT–IR spectra over the wavenumber of 400–4000 cm^{-1} were obtained using JASCO FT–IR (680 plus) spectrophotometer. Transition electron microscopy (TEM) image and energy dispersive X-ray spectroscopy (EDX) have been achieved with an on a Philips CM120. X-ray diffractometry (XRD: D/MAX–255) with an accelerating voltage of 20 kV and SEM were made on a Philips XI30. Dynamic light scattering instrument (DLS) was used for obtaining particle size distribution of the Pd nanoparticles with a Malvern ZEN 3600, UK. Induction coupled plasma Mass spectrometer (ICP-MS) measurement was obtained by Perkin Elmer ELAN 6100.

Synthesis of 3D self-assembled porous structure

The modified Hummers method was applied to the synthesis of graphene oxide (GO) according to the previous literature [28]. The homogenous suspension of GO (1.0 mg mL^{-1}) was prepared by ultrasound bath. After that, it placed under gentle