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Investigation on direct electrochemical and electrocatalytic behavior of hemoglobin on palladium-graphene modified electrode

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ABSTRACT

Palladium-graphene (Pd-GR) nanocomposite was acted as modifier for construction of the modified electrode with direct electrochemistry of hemoglobin (Hb) realized. By using Nafion as the immobilization film, Hb was fixed tightly on Pd-GR nanocomposite modified carbon ionic liquid electrode. Electrochemical behaviors of Hb modified electrode were checked by cyclic voltammetry and a pair of redox peaks originated from direct electron transfer of Hb was appeared. The Hb modified electrode had excellent electrocatalytic activity to the reduction of trichloroacetic acid and sodium nitrite in the concentration range from 0.6 to 13.0 mmol·L^{-1} and from 0.04 to 0.5 mmol·L^{-1}. Therefore Pd-GR nanocomposite was proven to be a good candidate for the fabrication of third-generation electrochemical biosensor.

1. Introduction

Electrochemistry of redox proteins/enzymes is difficult to achieve due to the deeply buried of electroactive centers inside of their polypeptide structures [1]. To solve this problem multifarious chemically modified interfaces have been designed to improve the process of electron transfer [2]. Due to the similarities between the electron transfer on the electrode and on the biological membrane in living bodies, the investigation can be applied to understand the mechanism inside the biological system. Also the results can be used to build biosensors and bioreactors [3]. As a redox protein consisted of two α and two β polypeptides, hemoglobin (Hb) has the responsibilities to restore and transfer oxygen [4]. The shape of Hb is almost sphere with its molecular weight about 64,500 Da with the size of 6.5 × 5.5 × 5.0 nm. Because of its well-known structure, Hb is often selected as the model molecule in direct electrochemistry of protein and electrochemical sensors [5].

Ionic liquid (IL) is organic compound with specific electrochemical performances, which is widely used in electrochemistry with good stability, high conductivity, easy to dissolve and wide electrochemical window [6]. Carbon ionic liquid electrode (CILE) is defined as carbon paste electrode (CPE) that used IL as the binder and the modifier [7]. CILE exhibits the superior characteristics than CPE, including high conductivity, certain catalytic activity and good anti-fouling ability. Therefore CILE is reported as the working electrode in electroanalysis [8–10].

With the development of nanoscience various nanomaterials and hybrid materials have been synthesized and used in different fields including catalyst, sensors, drug and gene delivery, photodynamic therapy, optogenetics, and so on [11–20]. Dhand et al. reviewed the methods and strategies for the synthesis of diverse nanoparticles and their applications [21]. Loh et al. summarized the delivery of gene materials with inorganic materials [22]. Therefore nanomaterials play important roles with various applications. Graphene (GR) is a carbon nanosheet that consists of single layer of carbon atom, which has many specific characteristics including high conductivity, low resistance, easy to produce and large surface area [23,24]. Due to its large surface area, GR can be decorated by other nanometerials to obtain nanocomposite that shows synergistic effects [25]. Nanosized Pd is a commonly used catalyst in the electrochemical reaction, which can lower the active energy and fast the electrochemical reaction due to its high activity. Maleki et al. applied nanosized Pd modified electrode for electrocatalytic determination of hydrazine [26]. Wang et al. fabricated a glucose sensor with porous Pd nanotubes on glassy carbon electrode (GCE) [27]. Yang et al. described the formation of Pd-based nanoporous metal with improved catalytic activity towards glucose oxidation [28]. Ke et al. prepared a Pd-decorated nanoporous gold/Ni foam electrode for the evaluation of H_2O_2 electroreduction [29]. Huang et al. proposed a ratiometric electrochemiluminescence (ECL) immunosensing method by introducing the lumiol/palladium nanoclusters@graphene oxide probe to the ECL immunosensor [30]. By decorating GR with nanosized Pd, Pd-GR nanocomposite exhibits

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the enhanced performance with the obvious synergistic effects. Shi et al. fabricated a Pd-GR catalyst modified GCE for 4-chlorophenol analysis [31]. Dong et al. prepared flower-like palladium nanoclusters on electrodeposited GR electrode for hydrogen gas analysis [32]. Kumar et al. used a Pd-GR nanocomposite modified GCE for electrochemical determination of ethanol [33]. GR related hybrid materials have also been used for the realization of direct electrochemistry of redox proteins. For example, Zhan et al. applied Co_2Al layered double hydroxide and GR nanocomposite on CILE surface for the immobilization of Hb [34]. Wen et al. constructed an electrochemically reduced graphene oxide and Hb modified GCE for the detection of nitromethane [35]. Mohammadrezei et al. used Hb-GR quantum dots-chitosan for

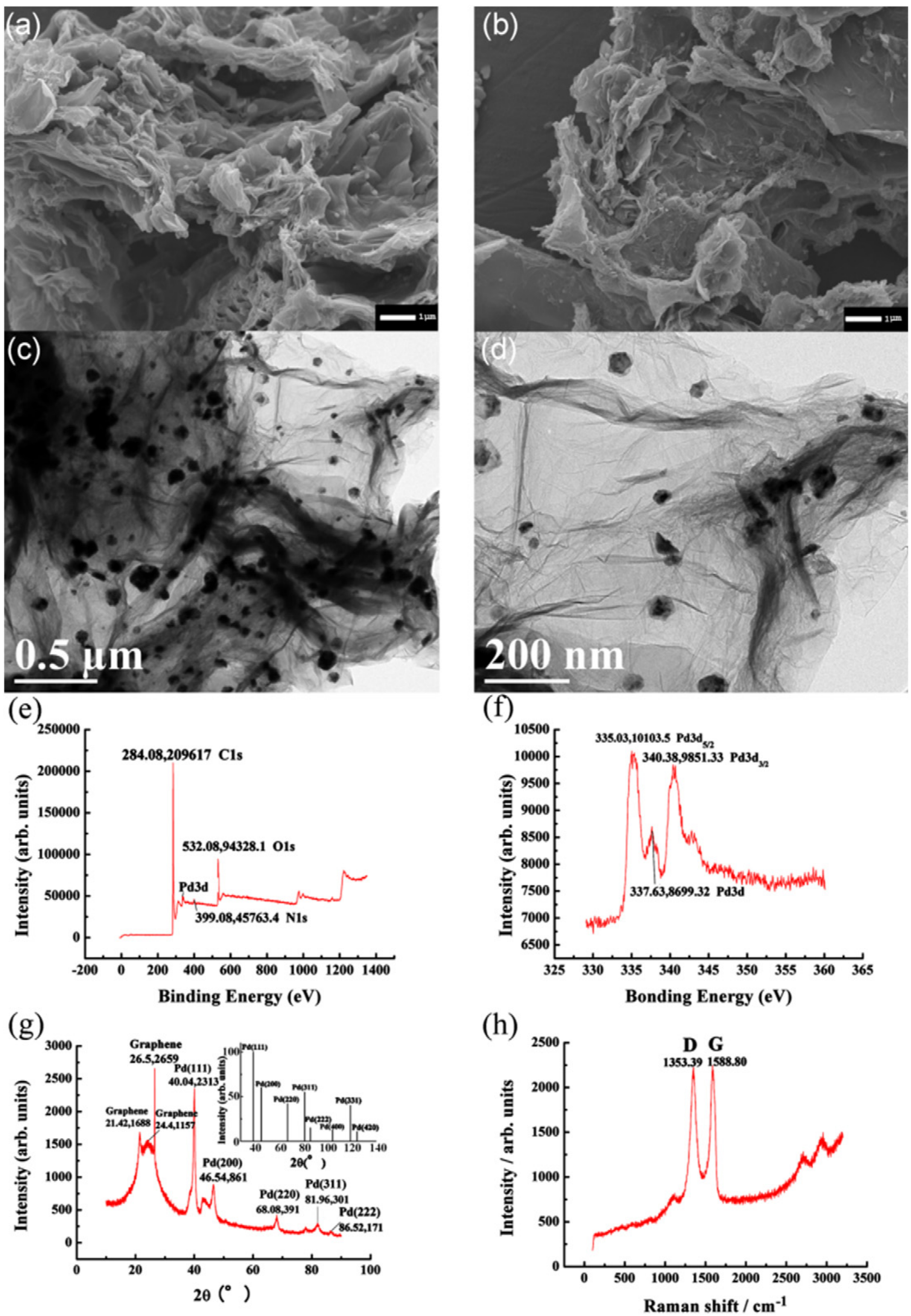

Fig. 1. SEM images of Pd-GR nanocomposite on CILE (a and b), TEM images of Pd-GR nanocomposite under different magnifications (c and d); XPS spectrum of Pd-GR composite (e); XPS spectrum of Pd in local zoom area (f); XRD pattern of Pd-GR nanocomposite (g), (inset was the standard XRP pattern of Pd); Raman spectrum of Pd-GR nanocomposite (h).