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Interlocked graphene–Prussian blue hybrid composites enable multifunctional electrochemical applications

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ABSTRACT

There has been increasing interest recently in mixed-valence inorganic nanostructure functionalized graphene composites, represented by *Prussian blue*, because they can cost-effectively apply to biosensors and energy devices. In this work, we present a one-pot green method to synthesize interlocked graphene–*Prussian Blue* hybrid composites as high-performance materials for biosensors and supercapacitor electrodes. Given the fact that graphene oxide (GO) can act as an electron acceptor, we used iron(II) and glucose as co-reducing agents to reduce GO under mild reaction conditions without introducing toxic agents. High quality *Prussian blue* nanocubes with no or little coordinated water were generated simultaneously. Reduced graphene oxide (rGO) was thus functionalized by *Prussian blue* nanocubes via chemical bonding to form a kind of interlocked microstructure with high stability and good conductivity. The as-synthesized composites were tested for biosensing of hydrogen peroxide (H_2O_2) and as supercapacitor electrode materials. The specific capacitance of the microcomposite based electrodes can reach 428 F g^{-1} , with good cycling stability. The microcomposite also displays high performance catalysis towards electroreduction of H_2O_2 with a high sensitivity of $1.5 \text{ A cm}^{-2} \text{ M}^{-1}$.

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1. Introduction

Prussian blue (PB), as a non-enzymatic but enzyme mimicking catalyst, has been explored for applications in chemical sensors (Chi and Dong 1995; Liu et al., 2014a, 2014b; Yang et al., 2015a, 2015b; Zhao et al., 2005), biosensors (Arduini et al., 2006; Gao et al., 2014; Sekar et al., 2014; Wang et al., 2014; Zhu et al., 2013), energy devices (Okubo et al., 2010; Pasta et al., 2012) and water quality monitoring (Hao et al., 2015). PB and its analogs are considered as promising energy storage materials, because the theoretical specific capacity of PB can be as high as 170 mA h g^{-1} (Okubo et al., 2010). In addition, the facile synthetic procedure, nontoxicity and low cost of PB based materials make them have potential favoring for large-scale production and multifunctional applications. However, to date these great potentials have been far from exploitation, as the practically achieved specific capacity of PB is much lower than theoretical expectation. PB also suffers from low Coulombic efficiency and poor cycling stability, which has limited its practical utilization as energy materials. This has largely originated in the poor process used in PB crystal growth, in which coordinated water is hardly avoided and occupies most vacancies of the PB crystal. Moreover, the water-occupied vacancies may

induce a lattice distortion, which dramatically affects specific capacity and Coulombic efficiency, and deteriorates overall electrochemical performances. In most cases, PB prepared by the direct precipitation reaction of the $\text{M}^{\text{m}+}$ cations and the $[\text{M}(\text{CN})_6]^{\text{n}-}$ anions in a neutral aqueous solution always contains a large number of vacancies occupied by coordinated water, because of the fast precipitation process. However, a recent report showed that high-quality PB nanocubes or/and analogs without coordinated water can be synthesized by employing $\text{Na}_4\text{Fe}(\text{CN})_6$ as a single iron-source precursor, and the resulting material was tested as cathode electrodes for sodium-ion battery with impressive electrochemical performances (Yang et al., 2015a, 2015b; You et al., 2014). This was achieved by a slow process for growth of PB crystals, so that the number of vacancies occupied by coordinated water is dramatically reduced or even completely eliminated in some cases.

Graphene-based materials have captured great attention among physicists, chemists and materials scientists. Graphene is a two-dimensional (2D) sheet of carbon atoms in a hexagonal configuration connected by sp^2 bonds. This unique nanostructure holds considerable promise for its potential applications in many technological fields such as nanoelectronics (Berger et al., 2004; Cernetic et al., 2014), sensors (Dong et al., 2012; Li et al., 2014; Song et al., 2010), functional nanocomposites (Klein et al., 2015; Zhang et al., 2010a, 2010b; Zhu et al., 2013), and energy devices (Liu et al., 2014a, 2014b; Wang et al., 2011; Xiong et al., 2015; Xu

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et al., 2015; Yang et al., 2011). Graphene has been prepared by a variety of methods, including mechanical exfoliation (Li et al., 2008; Novoselov et al., 2004), modified Hummers' methods (Chen et al., 2009; Compton et al., 2010), and chemical vapor deposition (CVD) (Cernetic et al., 2014; Wu et al., 2011). Among these methods, wet-chemical reduction of exfoliated GO is an efficient approach to large-scale production of graphene nanosheets at low cost. However, the most commonly used methods for reduction of GO are carried out using hydrazine and its derivatives (Domingues et al., 2013; Park et al., 2011) as reducing agents. The use of highly toxic and dangerously unstable hydrazine or dimethylhydrazine to reduce GO is not desirable for many applications. Recently, mild conditions were reported to reduce GO, such as L-ascorbic acid (Zhang et al., 2010a, 2010b), reducing sugars (Zhu et al., 2010) and others. Among many green reducing agents, glucose is of particular interest in reducing GO because of its high ability, relatively low-cost, and enabling environmentally friendly reactions. In this work, we used glucose as a co-reducing agent. Based on the fact that GO is an efficient electron acceptor (Akhavan and Ghaderi, 2012; Salas et al., 2010; Guo et al., 2013), GO can be reduced by electron-rich materials such as metals, metal ions, biomolecules or bacteria. This has been demonstrated by several recent reports (Fan et al., 2011; Guo et al., 2013; Liu et al., 2014a, 2014b; Mei et al., 2012). In general, to obtain rGO based functional hybrid materials two steps including reduction and functionalization are normally involved. For example, PB functionalized graphene materials were prepared by mixed PB nanoparticles (PBNPs) directly with rGO, so that PBNPs were confined by electrostatic attraction in rGO papers (Zhu et al., 2013). Zhang et al. (2012) and Qian et al. (2013) used various reducing agents to reduce GO and Fe^{3+} to prepare rGO-PB hybrid materials. In the present work, we report the preparation of high-quality PB nanocube-rGO hybrids by using $\text{K}_4\text{Fe}(\text{CN})_6$ as the only iron-source. As schematically illustrated in Fig. 1, simultaneous reduction and functionalization of GO have been achieved by a one-step procedure with the green nature of reactions. The as-synthesized PB nanocubes were wrapped by rGO nanosheets to form an interlocked stable structure. This unique structured microcomposite not only can act as an electron mediator, but also can stabilize PB nanocubes in electrochemical environments, which altogether enables this hybrid materials to hold multifunctional applications.

2. Material and methods

2.1. Materials and reagents

Graphite power (< 20 μm , synthetic), H_2O_2 (30%), sulfuric acid

(H_2SO_4 , 95–97%), hydrochloric acid (HCl, 34.5–36.5%), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, $\geq 99\%$), phosphorus pentoxide (P_2O_5 , $\geq 98\%$), potassium permanganate (KMnO_4 , $\geq 99\%$), hydrochloric acid (HCl, 34.5–36.5%), glucose ($\geq 99\%$) and potassium hexacyanoferrate (II) trihydrate ($\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, $\geq 99\%$) were obtained from Sigma-Aldrich. All chemical reagents are of at least analytical grade and were used as received without further purification. Milli-Q water (18.2 $\Omega \text{ cm}$) was used throughout the experiments.

2.2. Synthesis of G-rGO-PB composite

To synthesize high-quality PB modified rGO (G-rGO-PB), 2 mL GO (1 mg/mL) solution was mixed with 10 mL $\text{K}_4\text{Fe}(\text{CN})_6$ (10 mM), 2 mL (40 mg/mL) glucose and 1 mL 0.5 M HCl. The mixed solution was stirred for 10 min and then heated at 60 $^\circ\text{C}$ in a microwave for 3 h. The raw product was collected and purified by centrifugation and filtration. rGO-PB was prepared in the same procedure but in the absence of glucose and is used as a reference sample.

Other details of experiments, including GO synthesis, optimization of reaction conditions for the composite synthesis, construction of electrochemical electrodes and instrumental methods, are provided in the Supporting Information.

3. Results and discussion

3.1. One-step eco-friendly synthesis of G-PB-rGO composites

High quality and stable GO was prepared by the modified Hummer's method (Zhu et al., 2013). GO was well dispersed in pure water, and its UV-vis spectrum is shown in Fig. 2 (brown curve). We compared the efficiency of glucose and PB precursor for the reduction of GO. In comparison with PB-rGO (Fig. 2), GO was further reduced in the presence of glucose. The glucose-rGO (G-rGO) exhibits an absorption peak at 260 nm, while the PB-rGO retains a shoulder peak at 300 nm due to the $n-\pi^*$ transitions of $\text{C}=\text{O}$ bonds. This indicates that glucose is a stronger reducing agent for GO reduction. However, PB precursor offers electroactive functionalization of GO, as evidenced by the new absorption peak around 725 nm from the PB component (Zhu et al., 2013). Therefore, we used both PB precursor and glucose as co-reducing agents to simultaneously reduce GO and functionalize rGO in microwave-assisted one-step synthesis to obtain G-PB-rGO composite. To gain more details, Raman spectra were recorded (Fig. S1). The D band of GO, rGO-PB and G-rGO-PB that originated in the defects of graphitic planes is located at 1363, 1363 and 1365 cm^{-1} , respectively; and the G band related to the in-plane vibrations of sp^2 is observed at 1594, 1594 and 1595 cm^{-1} . The $I_{\text{D}}/I_{\text{G}}$ ratio of GO,

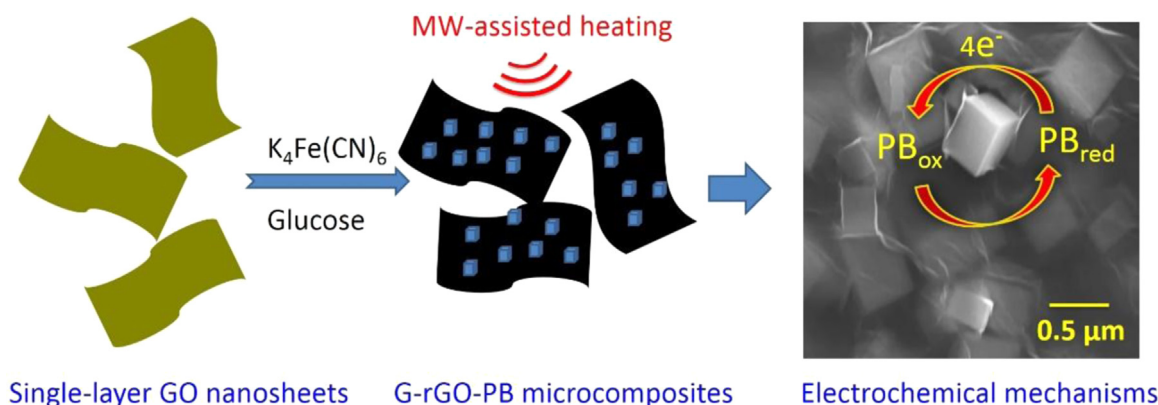


Fig. 1. Schematic representation of the preparation procedure and electrochemical activity of G-rGO-PBs.

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