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Spontaneous redox synthesis of Prussian blue/graphene nanocomposite as a non-precious metal catalyst for efficient four-electron oxygen reduction in acidic medium

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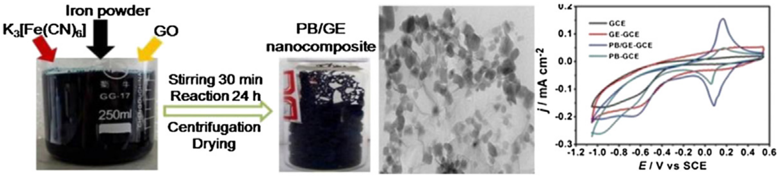
HIGHLIGHTS

- Prussian blue/graphene (PB/GE) is synthesized by a spontaneous redox method.
- ORR occurs mainly inside the PB lattice via the $4e^-$ reduction pathway at $E > -0.5$ V.
- ORR occurs mainly on GE nanosheets via the "2 + 2" mechanism at $E < -0.5$ V.
- PB/GE exhibits favorable electrocatalytic activity and long-term stability toward ORR.

GRAPHICAL ABSTRACT



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ABSTRACT

A Prussian blue/graphene (PB/GE) nanocomposite is synthesized as a non-precious metal catalyst by a spontaneous redox reaction in acidic solution with Fe powder, $K_3[Fe(CN)_6]$, and graphene oxide as precursors. The resulting PB/GE nanocomposite is characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The PB/GE nanocomposite-modified glassy carbon electrode (PB/GE–GCE) exhibits good electrocatalytic activity and long-term stability toward the oxygen reduction reaction (ORR). The reduced form of PB, Prussian white, has favorable electrocatalytic activity for the reduction of O_2 and H_2O_2 in acidic solutions. Rotating ring-disk voltammetric measurements clearly show that the dominant product of ORR at the PB–GCE is water produced by the $4e^-$ reduction of O_2 at all potentials. ORR at the PB/GE–GCE occurs mainly inside the PB lattice through the $4e^-$ reduction pathway at $E > -0.5$ V and on GE nanosheets through the "2 + 2" mechanism involving H_2O_2 as the intermediate product at $E < -0.5$ V. The PB/GE nanocomposite is a potentially efficient and cost-effective catalyst for fuel cells.

1. Introduction

Molecular oxygen is widely used as an electron acceptor for cathodes in many fuel cells because of its low cost, sustainability, and environment-friendliness [1–6]. Generally, the electrochemical oxygen reduction reaction (ORR) occurs via the $2e^-$, direct $4e^-$, or two $2e^-$ pathways ("2 + 2 mechanism"), depending on the electrode material, its surface properties, and the solution pH [7]. The $4e^-$ reduction process is ideal for fuel cells that acquire more electric energy. However, the kinetics of ORR is usually very slow, thereby limiting the practical applications of the reaction. Improving the design of electrocatalysts is thus very important to enhance the performance of cathodes, especially in fuel cells, by reducing the overpotential and achieving the $4e^-$ pathway of ORR.

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Prussian blue (PB) has a face-centered cubic structure in which alternating Fe^{II} and Fe^{III} centers are bridged by cyanide ions in a $Fe^{II}{-}C{\equiv}N{-}Fe^{III}$ fashion, forming an infinite three dimensional network [8]. Itaya et al. [9] first found that PB-modified electrodes have excellent electrocatalytic activity for ORR in acidic aqueous solutions. The ORR mechanism of the PB-modified electrode includes two fundamental steps. First, PB is reduced at the cathode, and the reduced form of the polycrystal is denoted as Prussian white (PW) [10]. Second, PW is oxidized into PB by O_2 with the simultaneous formation of water [9]. These steps are described in Eqs. (1) and (2) as follows:

$$Fe_4^{3+}\left[Fe^{II}(CN)_6\right]_3 + 4e^- + 4K^+ \rightarrow K_4^+Fe_4^{2+}\left[Fe^{II}(CN)_6\right]_3 \tag{1}$$

$$K_4Fe_4^{2+}\left[Fe^{II}(CN)_6\right]_3 + O_2 + 4H^+ \rightarrow Fe_4^{3+}\left[Fe^{II}(CN)_6\right]_3 + 2H_2O + 4K^+ \tag{2}$$

where Fe^{3+} and Fe^{II} are the high-spin and low-spin Fe ions, respectively.

Graphene (GE), a new class of two-dimensional nanomaterials consisting of a single layer of C atoms with an sp^2 network, has recently received increased research attention because of its unique nanostructure, excellent electron-transfer capacity, high stability, and large accessible surface area [6,11]. GE nanosheets can be facilely obtained from graphene oxide (GO) by different reduction methods, such as hydrothermal reduction [11–14], chemical vapor deposition [15], chemical reduction [16–19], electrochemical reduction [6,20], and microbial reduction [21].

Fan et al. [18] synthesized GE nanosheets based on Fe reduction of exfoliated GO via a green and facile approach. The present study also synthesizes a PB/GE nanocomposite in situ by a spontaneous redox reaction in an acidic aqueous solution containing Fe powder, $K_3[Fe(CN)_6]$, and GO as precursors. The resulting nanocomposite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The electrocatalytic ORR on the PB/GE nanocomposite was evaluated by cyclic voltammetry (CV), chronocoulometry/chronoamperometry, and the rotating ring-disk electrode (RRDE) method in acidic medium.

2. Experimental

2.1. Reagents

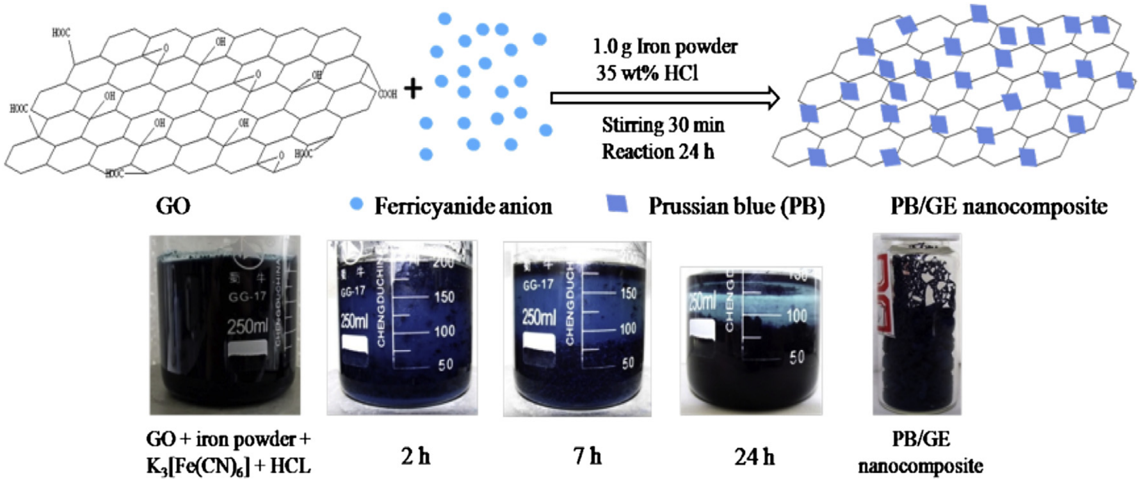
Graphite powder (325 mesh, spectrum pure), $K_3[Fe(CN)_6]$, $NaNO_3$, KCl, K_2SO_4, and Fe powder (average particle size: 10 μm) were obtained from Shanghai Chemical Reagent Co. (China). H_2O_2 (30 wt%) and other reagents were purchased from Beijing Chemical Reagent Plant (China). All of the reagents employed in the experiment were of analytical grade and used as received without further purification. Aqueous solutions were prepared with double-distilled water from a Millipore system (>18 MΩ cm).

2.2. Synthesis of PB/GE nanocomposite

GO was synthesized from natural graphite powder using a modified Hummers method [22,23]. The PB/GE nanocomposite was prepared by a spontaneous one-pot redox synthesis method. The general synthesis procedure for the PB/GE nanocomposite is described in Scheme 1. Briefly, 1.0 g of Fe powder, 1.0 g of $K_3[Fe(CN)_6]$, and 30 mL of HCl (35 wt%) were directly added to 100 mL of a GO suspension (0.5 mg mL^{-1}) at ambient temperature. The mixture was stirred for 30 min to ensure complete homogeneity and then allowed to stand for 24 h. The brown GO rapidly darkened in color in the presence of both Fe powder and H^+. After reduction, 20 mL of HCl (35 wt%) was again added to the solution to completely remove the excess Fe powder. Finally, the mixture was centrifuged, washed several times with pure water and ethanol, and then dried at 60 °C for 12 h in a vacuum oven. For comparison, GE and PB nanocomposites were also synthesized by the same method, except that the $K_3[Fe(CN)_6]$ and GO suspensions were changed to double-distilled water.

2.3. Characterization

SEM images were obtained using an XL30 ESEM FEG SEM instrument operating at 5 kV. TEM images were obtained using a JEOL JEM-2000 EX TEM instrument by dropping the complex solution onto Cu grids. Raman spectra were collected using a Renishaw inVia M2000 spectrometer (UK) operating with He–Ne laser excitation at a wavelength of 623.8 nm, laser power of 35 mW, and beam spot size of about 2 μm. XPS analysis was performed on an ESCALAB MK II X-ray photoelectron spectrometer.



Scheme 1. Synthesis procedure of the PB/GE nanocomposite.