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In situ synthesis of a Prussian blue nanoparticles/graphdiyne oxide nanocomposite with high stability and electrocatalytic activity

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ABSTRACT

Herein we report an in situ synthesis of Prussian blue nanoparticles (PB) on graphdiyne oxide (GDYO) which acts as an excellent substrate. The hybrid was then used as an electrode with high electrochemical catalytic activity towards hydrogen peroxide. The PB/GDYO hybrid was prepared by simply adding $FeCl_3$ to GDYO solution, and then mixing with $Fe(CN)_6^{3-}$ at room temperature. The GDYO was able to anchor PB in nanoparticle form and stabilize it in neutral and weakly basic solutions. The hybrid was investigated by transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and electrochemical measurements. The PB/GDYO hybrid showed high electrochemical catalytic activity and stability for the detection of hydrogen peroxide.

1. Introduction

Prussian blue (PB), a classical prototype of mixed-valence transition metal hexacyanometalates, generally acts as an artificial peroxidase and for this reason it is an excellent material for biosensors [1,2]. Due to its superior electrochemical and photoelectrochemical properties [3], a number of applications for PB and its analogues have been developed: these include the detection of molecules such as dopamine (DA) [4], morphine [5], cysteine [6], and ascorbic acid (AA) [7]. Nevertheless, PB suffers from low stability at the neutral and weakly basic pH values [8] employed in some biosensors. One strategy used to improve PB stability is to use various carbon substrates to load the PB nanomaterials; examples of these include carbon black [9], carbon nanotubes [10], carbon fibers [11] and graphene [12,13].

A new carbon allotrope, two-dimensional graphdiyne (GDY), was first synthesized through cross-coupling on the surface of a copper foil using hexaethynylbenzene [14]. Compared with other carbon nanomaterials, GDY comprises sp^2- and sp.-hybridized carbon atoms and has a unique electronic structure, high chemical stability and electrical conductivity. These properties have been useful in various research fields [15–17]. Due to its excellent behavior, GDY has been considered to be an ideal substrate for the development of highly efficient catalysts [18–20]. Our group has demonstrated that GDY oxides (GDYO) could be used for electroless deposition of ultrafine Pd clusters, the prepared Pd/GDYO nanocomposite showing a high catalytic performance towards the reduction of 4-nitrophenol with sodium borohydride as reducing agent [21]. In view of the advantages of GDYO, the combination of PB nanoparticles with GDYO could lead to materials with excellent electrocatalytic activity and stability for use in biosensors, especially at neutral and weakly basic pH values.

In the present work, PB nanoparticles were reduced directly in situ on the GDYO surface; this made it possible to control the size of the nanoparticles and to prevent their dissolution during the electrochemical process. The PB/GDYO nanohybrids were employed as electrocatalysts for the detection of H_2O_2 in a neutral medium, exhibiting excellent electrochemical performance and higher stability than PB nanoparticles supported on graphene oxide (GO).

2. Results and discussion

The morphologies of GDYO and PB/GDYO were first investigated by TEM (see Fig. 1A and B, respectively). The as-prepared GDYO (Fig. 1A) is well-defined and has a wrinkled shape, similar to the structure of GO [22]. Fig. 1B shows that the PB nanoparticles are homogeneously dispersed on the surface of the GDYO sheets and have a diameter of about 5 nm. These results demonstrate that GDYO is an excellent substrate for in situ synthesis of PB nanoparticles, forming a PB/GDYO hybrid.

Fig. 1C shows the XRD patterns of both PB and PB/GDYO. In both

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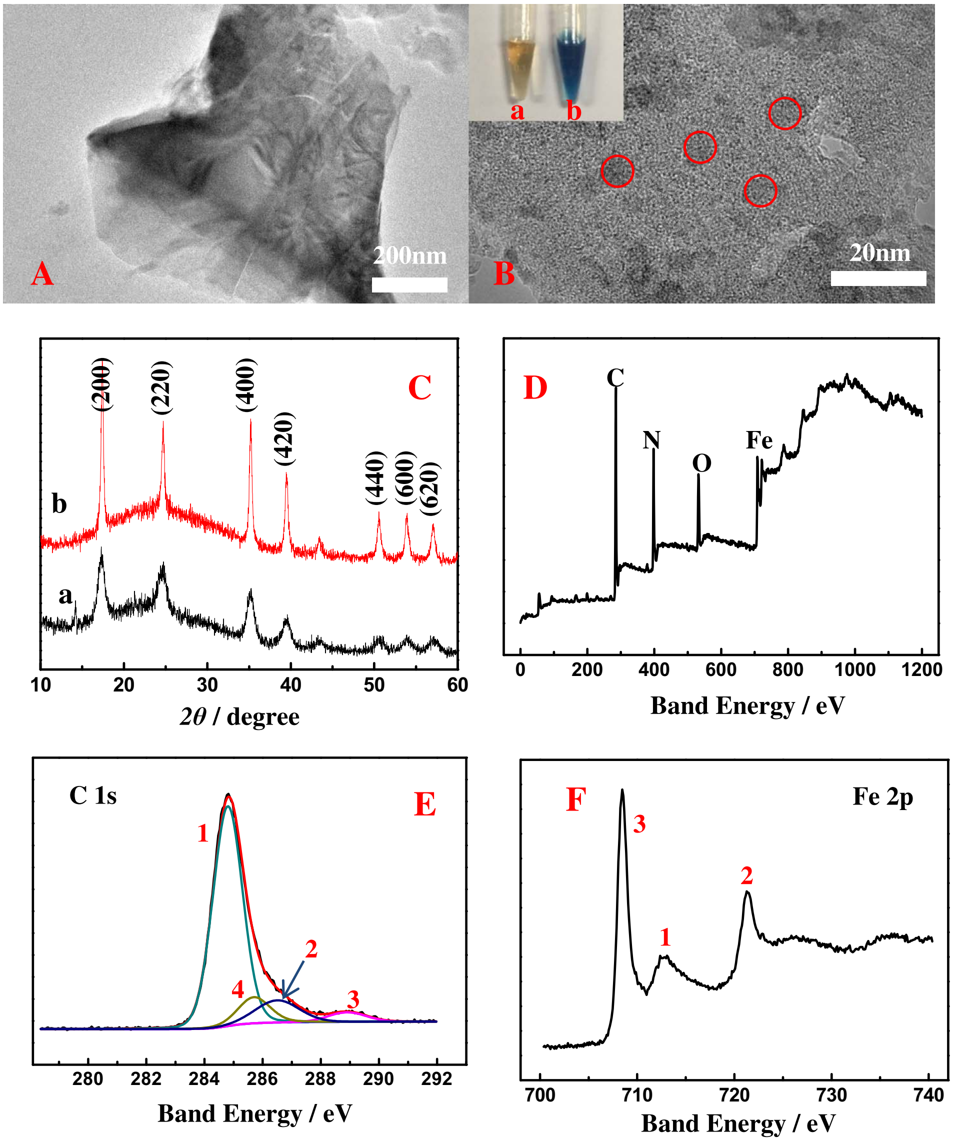

Fig. 1. Typical TEM image of (A) GDYO and (B) PB/GDYO, inset: photographs of (a) GDYO, and (b) PB/GDYO. (C) XRD patterns of (a) PB and (b) PB/GDYO. (D) Survey XPS data for PB/GDYO. High-resolution XPS for the elements (E) carbon and (F) iron in PB/GDYO.

samples, the same peaks were observed; more specifically, signals were detected at 2θ = 17.39°, 24.71°, 35.23°, 39.52°, 50.58°, 53.92° and 57.12°, which correspond to the (2 0 0), (2 2 0), (4 0 0), (4 2 0), (4 4 0), (6 0 0), and (6 2 0) planes of the cubic phase of PB, respectively [6].

The surface composition and the nature of the chemical bonds in the PB/GDYO hybrids were investigated by XPS. According to the wide scan XPS of PB/GDYO (Fig. 1D), the amount of carbon, nitrogen, oxygen and iron was 60.66, 21.59, 9.62 and 4.32 at.%, respectively. The XPS spectrum for C1s of PB/GDYO (Fig. 1E) indicated the presence of carbon atoms in different environments, including residual oxygen- and nitrogen-containing groups. Indeed, a number of different energy levels were detected: C=C bond at 284.5 eV (number 1 in the figure), C=O bond at 286.5 eV (2), O–C=O bond at 289.5 eV (3), and C–N bond at 285.7 eV (4) [21]. The results showed that there were no obvious changes in the molecular structure of the GDYO during the fabrication of the PB/GDYO hybrid. The Fe 2p signal of the PB/GDYO hybrid (Fig. 1E) was split into three peaks: Fe $2p_{3/2}$ (711.3 eV), Fe $2p_{1/2}$ (724.8 eV), and Fe(II) $2p_{3/2}$ (708.3 eV); these data indicate the presence of PB nanoparticles and therefore confirm the successful in situ synthesis of PB/GDYO [23].

The process of PB/GDYO formation was investigated by XPS (Fig. 2). When the $FeCl_3$ was added to the GDYO solution, the GDYO maintained its original elemental composition (Fig. 2A). Fe^{3+} ions were reduced to Fe^{2+} by the GDYO, as indicated by the Fe 2p signal [see Fig. 2B: Fe(II) Fe $2p_{3/2}$ satellite (716.2 eV) and Fe(II) $Fe2p_{1/2}$ satellite (729.9 eV)] [24]. This chemical reaction could be explained by the lower reduction potential of GDYO (− 0.21 V vs SHE), which implies the easy reduction of Fe^{3+} to Fe^{2+} with GDYO. Fig. 2 also shows