Synthesis of AuPd/g-C₃N₄ nanocomposites and their electrochemical properties

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Abstract. In the present work, AuPd/g-C₃N₄ nanocomposites were prepared by the facile chemical reduction method. The TEM results show that the metal nanoparticles were uniformly deposited on the surface of the g-C₃N₄ surface. The electrochemical properties towards the sensing of H_2O_2 were tested. It was found that the AuPd/g-C₃N₄ shows the superior electrochemical performance compared with the Au/g-C₃N₄ and Pd/g-C₃N₄.

1. Introduction

In the past years, quantitative detection of H_2O_2 has received considerable attention, since H_2O_2 is an essential intermediate in biomedical, pharmaceutical, environmental protection, and electrochemistry. Many traditional techniques, such as chemiluminescence, titrimetric spectrophotometry, fluorescence and electrochemical method were used to quantitative detection of H_2O_2. Especially, non-enzymatic electrochemical method gained a great of interests among various techniques owing to its high sensitivity, low cost, easy operation, and the possibility for real-time detection. In the past decades, many nanomaterials, including metal nanoparticles, metal hexacyanoferrate, metal oxide, have been empolyed to fabricate the electrochemical H_2O_2 sensors [1, 2]. Our group has recently synthesized Ag/C nanocomposites and silver deposited porous graphitic g-C₃N₄ nanocomposites for nonenzymatic electrochemical H_2O_2 sensing which exhibited high sensitivity and low detection limit [3]. Compared with the single-component metal nanoparticles, the bimetallic nanoparticles shown superior electrochemical properties towards the detection of H_2O_2. For example, Chen and co-workers recently constructed RGO/Ag-Au/Cu₂O ternary nanocomposites electrochemical sensor for the detection of H_2O_2, and the sensor exhibited good electrocatalytic activity, with a linear response range from 0.05 to 50.75 mmol/L at -0.2 V and a sensitivity of 0.14 μA mmol/L^{-1} cm^{-2} [4]. However, up to date, there is no report on the construction of g-C₃N₄/bimetallic nanoparticle nanocomposite electrochemical sensor. In this work, AuPd/g-C₃N₄ nanocomposites were prepared by a facile chemical reduction method. The TEM results show that the metal nanoparticles were uniformly deposited on the surface of the g-C₃N₄ surface. The electrochemical properties towards the sensing of H_2O_2 were tested. It was found that the Au-Pd/g-C₃N₄ shows the superior electrochemical performance compared with the Au/g-C₃N₄ and Pd/g-C₃N₄.

2. Experimental

2.1. Preparation of AuPd/g-C₃N₄, Au/g-C₃N₄ and Pd/g-C₃N₄ samples

2.1. Preparation of AuPd/g-C$_3$N$_4$, Au/g-C$_3$N$_4$ and Pd/g-C$_3$N$_4$ samples
All chemical reagents were of analytic purity and used directly without further purification. The g-C$_3$N$_4$ nanosheets were prepared by a thermal polymerization strategy [5]. The AuPd/g-C$_3$N$_4$ was prepared by a facile chemcial reduction method. In a typical synthesis, 100 mg of g-C$_3$N$_4$ was first dissolved in 100 mL of distilled water, followed by the sonication for 30 min. Then, the 0.5 mL of HAuCl$_4$ (0.01 mol·L^{-1}) and 0.94 ml H$_2$PdCl$_4$ (0.01 mol·L^{-1}) was added into the above solution under vigorous stirring for 30 min, followed by added of 20ml NaBH$_4$ (0.15 mol·L^{-1}). Then the solution was heated to 100℃ and kept for 24 h. Then, the sample was washed with deionized water and ethanol and eventually dried under vacuum at 60 °C for 6 h. For comparison, the Au/g-C$_3$N$_4$, Pd/g-C$_3$N$_4$ sample was prepared by the simialr method in the absence of HAuCl$_4$ or H$_2$PdCl$_4$, respectively.
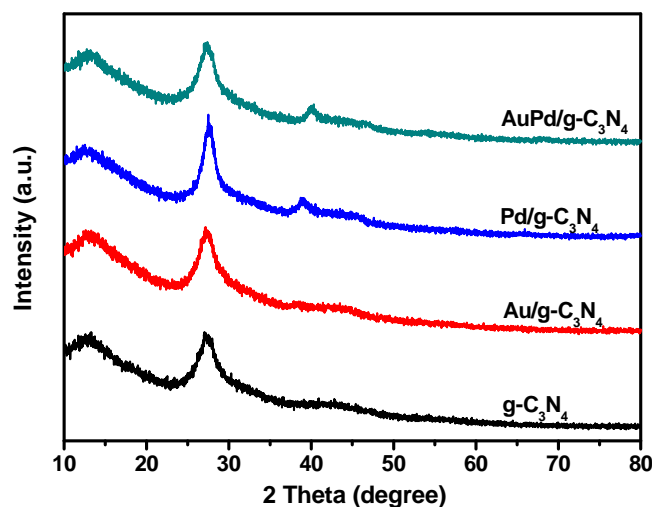
2.2. Characterization

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The morphology of the as-prepared samples was examined by transmission electron microscopy (TEM) instrument (Tecnai G2F30 S-TWIN, Philips). The phase purity and crystal structure of the obtained samples were examined by X-ray diffraction (XRD) using D8 Advance X-ray diffraction (Bruker axs company, Germany) equipped with Cu-KR radiation (λ) 1.5406 (Å). The chemical states of the as-prepared sample were examined by X-ray photoelectron spectroscopy (XPS, PHI 5300C ESCA System) with Al Kα radiation operating at 250W.

2.3. Preparation of the modified electrode and electrochemical measurements

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1.0 mg of AuPd/g-C$_3$N$_4$ composite and 10 mL of Nafion solution (5 wt%) were dispersed in 1 mL water–isopropanol mixed solvent (3 : 1 v/v) by at least 30 min sonication to form a homogeneous catalyst solution. Then 10 mL of the catalyst solution was dropped onto the surface of pretreated GCE and lefto dry at room temperature to get AuPd/g-C$_3$N$_4$-modified GCE (denoted as AuPd/g-C$_3$N$_4$/GCE). Amperometric and cyclic voltammetry (CV) experiments were carried out by a CHI 650D electrochemical analyzer (CH Instruments, Inc., Shanghai), in a home-made three-electrode electrochemical cell consisting of a twisted platinum wire as an auxiliary electrode, a saturated calomel electrode (SCE) as a reference electrode and a modified-GCE (0.07 cm^2) as a working electrode. All experiments were carried out at the ambient temperature. Prior to the experiment, the electrolyte, consisting of a solution of 0.2 M phosphate buffer solution (PBS, pH 7.4), was purged with high-purity nitrogen for at least 30 min and a nitrogen atmosphere was maintained over the solution.
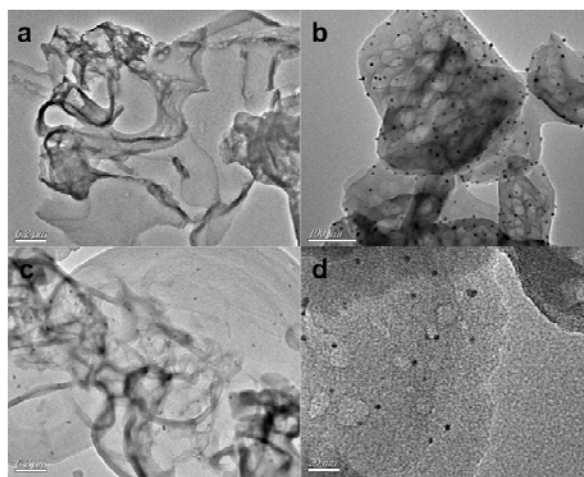
3. Results and discussion

The XRD patterns of Au/g-C$_3$N$_4$, Pd/g-C$_3$N$_4$ and AuPd/g-C$_3$N$_4$ binary alloy composites were measured to investigate the crystal structure. As shown in Fig. 2, there are two distinct peaks at 13.0° and 27.4°can be indexed as the (100) and (002) peaks for graphitic materials, respectively. For the Au/g-C$_3$N$_4$ sample, due to the low content of Au metal nanoparticles, the characteristic diffraction peaks of Au cannot be observed. In contrast, the diffraction peak centered at 38.2° in the Pd/g-C$_3$N$_4$ and Au/g-C$_3$N$_4$ sample which can be ascribed to the (111) plane of Pd nanoparticles. However the peak ascribed to the (111) plane of the Pd shifted to higher degrees, probably due to the formation of alloyed nanoparticles.

Fig. 1. XRD patterns of the as-prepared g-C_3N_4, Au/g-C_3N_4, Pd/g-C_3N_4, and $AuPd$/g-C_3N_4.
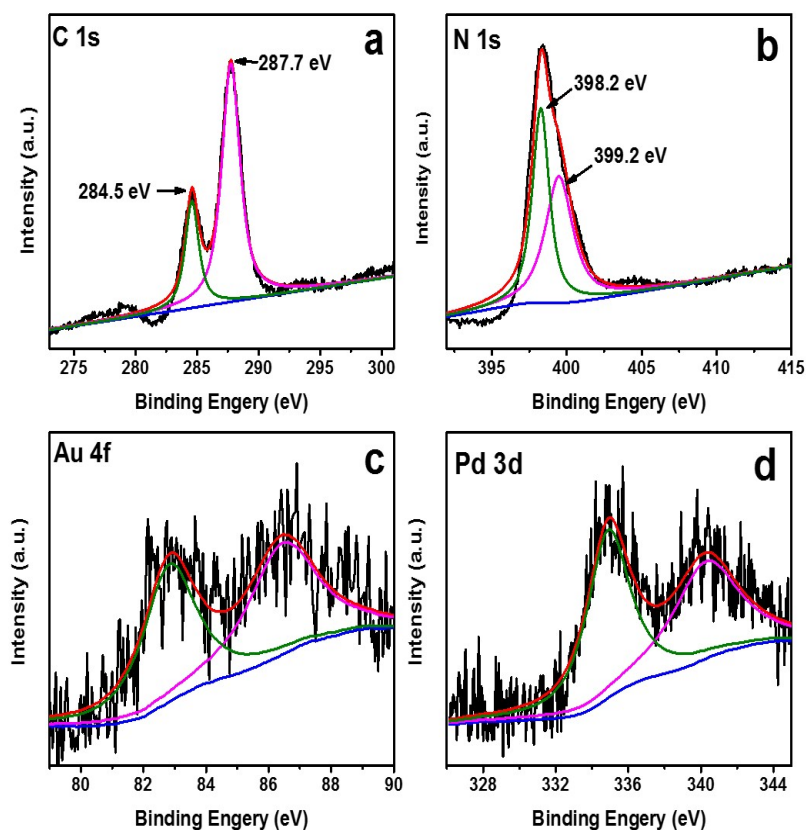
The morphology and microstructure of the as-prepared samples were then investigated by TEM. Fig. 2a shows that some mesopores with several tens of nanometres in size can be observed in the g-C_3N_4 sheets, which could serve as a support for the loading of metal particles in this composite system. The TEM image for the Au/g-C_3N_4 sample shows that a few of the Au nanoparticles were deposited on the surface of g-C_3N_4 sheets (Fig. 2b). Similarly, the Pd nanoparticles with 2-5 nm in size was deposited on the surface of g-C_3N_4 sheets in the Pd/g-C_3N_4 samples (Fig. 2c). For the $AuPd$/g-C_3N_4 sample, tiny AuPd bimetatic nanoparticles were loaded on the g-C_3N_4 nanosheet.

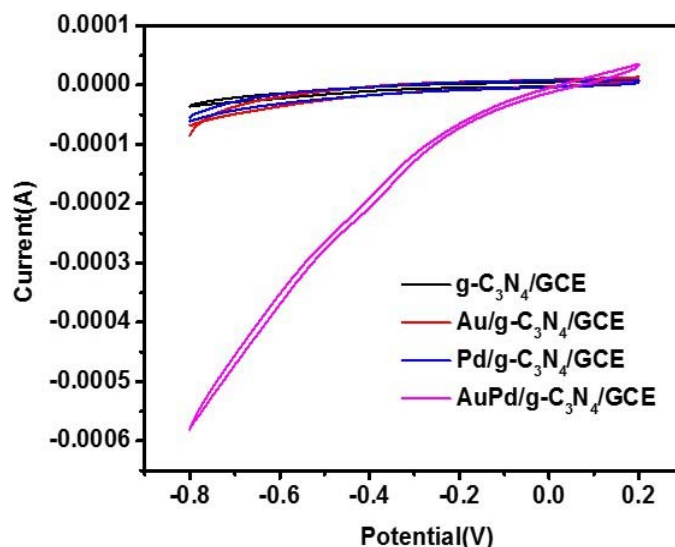**Fig. 2.** Typical TEM images of (a) g-C_3N_4, (b) Au/g-C_3N_4, (c) Pd/g-C_3N_4, and (d) $AuPd$/g-C_3N_4.

The chemical composition of the $AuPd$/g-C_3N_4 composites were characterized by XPS. Fig. 3a displays the C 1s XPS spectra, and it can be ascribed to carbon and defect-containing sp^2-hybridized carbon atoms present in graphitic domains. The second peak at 287.5 eV is assigned to the sp^2-bonded carbon (the major carbon species in the g-C_3N_4 polymer) in N-containing aromatic rings (N-C=N). The high resolution N 1s spectrum of Au-Pd/g-C_3N_4 (as shown in Fig. 3b) can be also fitted into two different peaks at binding energies of 398.2 and 399.2 eV, respectively, which are attributed to sp^2 hybridized N bonded with C (C-N=C) and the bridging tertiary N (N-(C)$_3$). The Au 4f XPS signal can be deconvoluted into two peaks at around 88.0 and 84.3 eV, indicating that metallic Au^0 is the main species. As exhibited in Fig. 3d, the Pd $3d_{5/2}$ and Ag $3d_{3/2}$ peaks are located at 335.3 eV and 340.6 eV,

respectively, confirming the existence of metallic Pd in the binary samples. These XPS results further confirm formation of AuPd/g-C$_3$N$_4$.

Fig. 3. XPS spectra of the AuPd/g-C$_3$N$_4$ composite: (a) C 1s, (b) N 1s, (c) Au 4f and (d) Pd 3d.

The AuPd/g-C$_3$N$_4$ binary nanocomposites are potential electrochemical sensor materials. An enzymeless H$_2$O$_2$ sensor has been constructed by direct deposition of the as-prepared catalysts on a bare GCE surface to study their electrochemical activities. Fig. 4 displays the CVs of the g-C$_3$N$_4$/GCE, Au/g-C$_3$N$_4$/GCE, Pd/g-C$_3$N$_4$/GCE, and AuPd/g-C$_3$N$_4$/GCE nanocomposites in the presence of 1 mM of H$_2$O$_2$ in N$_2$-saturated PBS solution (0.2 M, pH=7.4), and the scan rate is 50 mV s^{-1}. The responses of the bare g-C$_3$N$_4$/GCE, Au/g-C$_3$N$_4$/GCE and Pd/g-C$_3$N$_4$/GCE toward the reduction of H$_2$O$_2$ are insensitive. There is no obvious change in current density with the increase of electric potential. When the AuPd bimetallic nanoparticles anchored on the surface of g-C$_3$N$_4$ nanosheets, the electrode shows a sensitive response towards the reduction of H$_2$O$_2$. This might be because of the presence of alloyed metal nanoparticles with good electrical conductivity which could accelerate the electron transfer of the electrode.

Fig. 4. CVs of different materials modified electrodes in the absence and presence of H_2O_2 for the bare g-C_3N_4/GCE, Au/g-C_3N_4/GCE, Pd/g-C_3N_4/GCE, and AuPd/g-C_3N_4/GCE in N_2-saturated 0.2 M pH 7.4 PBS with presence of H_2O_2, scan rate: 50 mV s^{-1}.

4. Summary

In summary, AuPd/g-C_3N_4 nanocomposites were synthesized by the facile chemical reduction method. The TEM results show that the metal nanoparticles were uniformly deposited on the surface of the g-C_3N_4 surface. The electrochemical properties towards the sensing of H_2O_2 were tested. It was found that the AuPd/g-C_3N_4 shows the superior electrochemical performance compared with the Au/g-C_3N_4 and Pd/g-C_3N_4.

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