Hollow PdCu nanocubes supported by N-doped graphene: A surface science and electrochemical study

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ABSTRACT

N doped graphenes (NGs) are believed to be promising materials for constructing novel hybrid composites with desirable functionalities and applications in many fields. Therefore, a better understanding of the NGs holds the key to a better performance of the hybrid properties. A facile and low-cost preparation of NGs supported hollow PdCu alloy nanocubes (H–PdCu) catalysts were introduced in this paper. To increase the stability and efficiency of the catalysts, a two-step strategy was employed, which included the preparation of NGs and the synthesis of hollow PdCu alloy nanocube catalysts. A series of NGs using melamine, polypyrrole (ppy) and polyaniline (PANI) as nitrogen source, respectively. The influence of the different N species (pyridinic N, pyrrolic N and graphite N) on the morphologies and corresponding electrical properties of H–PdCu nanoparticles were studied. The results indicate that NGs are successfully synthesized, and hollow PdCu alloy nanocubes are well-dispersed on the surface of them with a relatively narrow particle size distribution. Electrochemical characterizations reveal that the H–PdCu/melamine-NG catalyst has excellent catalytic activity and stability toward alcohols oxidation in alkaline electrolyte, which can serve as promising anode catalysts in direct alcohols fuel cells (DAFCs).

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Introduction

Of the various types of fuel cells, the direct alcohols fuel cells (DAFCs), which are based on liquid fuels, have attracted significant attention as a power source for portable electronic devices owing to its high energy density, low operating temperature and because it is non-toxic, which is not true for gaseous fuels [1–4]. However, lower oxidation activity of...
alcohols and higher cost of Pt-based catalysts are the major drawbacks to limit DAFCs’ practical application [5–7]. To solve these problems, tremendous efforts have been made to find catalysts with high activity, stability, and low cost.

On the one hand, less expensive and more abundant non-platinum catalysts with acceptable performance have been widely studied. For instance, Pd catalysts have been found to be effective in controlling and regulating the shape and size of metal nanoparticles on the surface of graphenes can play an important role in controlling and regulating the shape and size of metal nanoparticles. However, there is scarce research about a systematic study on the influence of different N atom species in the formation course of hollow PdCu alloy nanocubes. Therefore, to further improve the performance of catalyst, it is very important to study the effect of the N atom species of the graphenes surface on the catalyst activity.

In this work, a series of NGs were synthesized by heat treatment process using polypyrrole (ppy), melanine and polyaniline (PANI) as the source of nitrogen, respectively. And hollow PdCu alloy nanocubes were prepared on the surface of the different N doped graphenes. The influence of the different N atom species (pyridinic N, pyrrolic N and graphite N) on the morphologies and electrical properties of the catalysts were also studied. Electrochemical characterizations reveal that the H–PdCu/melamine-NG catalyst has excellent catalytic activity and stability toward alcohols oxidation in alkaline electrolyte, which can serve as promising anode catalysts in DAFCs.

Experimental

Preparation of different N doped graphenes

GO was prepared based on the modified Hummers’ method [30]. The melamine-NG was synthesized via grinding and thermal annealing. GO and melamine were mixed together with a mass ratio of 1:1 under grinding for 2 h. The mixture was heated at 800 °C for 2 h under the protection of N2. The final product was air-cooled to room temperature and labeled as melamine-NG.

The ppy-NG was synthesized by in situ chemical oxidative polymerization of pyrrole monomer and carbonization of the ppy. The GO (0.4 g) was dispersed in 50 mL ethanol aqueous solution (volume ratio 1:1) by ultrasonic treatment for 30 min. 80 mg pyrrole monomer was added to the above suspension and stirred for 10 min. Then 50 mL of Na2S2O8 (2.289 g) aqueous solution was added slowly to the suspension with constant stirring for 12 h in ice-water bath. After reaction, the obtained ppy-GO powder was dried and heated at 800 °C for 2 h under the protection of N2, which was labeled as ppy-NG.

The PANI-GO was prepared under the same condition except using aniline replaced pyrrole monomer. For comparison, the reduced graphene oxide (RGO) was also prepared under the same thermal treatment condition and labeled as RGO-NG.

Synthesis of hollow PdCu alloy nanocube catalysts

An aqueous solution of PdCl2 (3.3 mg/mL, 3.8 mL), 20 mg of CuSO4·5H2O, and 50 mg of glutamate were mixed together in EG (50 mL) in 40 mL of EG. The pH of the system was adjusted to 11 by the dropwise addition of 8 wt% KOH/EG solution with vigorous stirring. Subsequently, 30 mg of the as-prepared melamine-NG were added, and the solution was ultrasonicated and stirred for 2 h to obtain a homogeneous suspension. Upon completion, the suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed, heated at 160 °C for 6 h, and air-cooled to room temperature. Finally, the product was collected by filtration and washed several times with DD water. The product was dried at 40 °C under vacuum for 8 h. The catalyst thus obtained was denoted as H–PdCu/melamine-NG. The H–PdCu/ppy-NG, H–PdCu/PANI-NG and H–PdCu/RGO were also prepared under identical conditions.

Characterization

The morphology of the samples was characterized by transmission electron microscopy (TEM) (JEOL-100CX) at 200 kV. The crystal structure of the products was analyzed by X-ray diffraction (XRD) recorded on a D/max-2200/PC X-ray
diffractometer with Cu Kα radiation source. Field emission scanning electron microscope (FESEM) images and energy dispersive X-ray spectroscopy (EDX) results were obtained with ZEISS SUPRA 40 and X-MAX 20. The X-ray photoelectron spectroscopy (XPS) measurements were made using ESCALABMKLL electron spectroscope from VG Scientific (West Sussex, UK).

The electrochemical measurements in this study were conducted with a conventional three-electrode electrochemical cell on a CHI 660E electrochemical workstation. A glassy carbon electrode (3 mm o.d.) coating catalyst was used as working electrode, a saturated calomel electrode (SCE) was applied as the reference electrode and Pt foil (1 cm²) was used as the counter electrode. The cyclic voltammetric (CV) and chronoamperometry curves for ethanol or glycerol electrooxidation experiments were carried out in 1 M KOH containing 1 M ethanol or glycerol. Electrochemical CO-stripping voltammograms were conducted by bubbling CO into 0.5 M H₂SO₄ for 30 min at a potential of 0.1 V (vs. SCE electrode). All electrochemical experiments were performed at 25 ± 1 °C.

Electrochemical CO stripping voltammograms were obtained by oxidizing preadsorbed CO (COad) in 0.5 M H₂SO₄ at a scan rate of 50 mV s⁻¹. CO was purged through 0.5 M H₂SO₄ for 30 min to allow complete adsorption of CO onto the catalyst. The working electrode was stayed at 0.1 V, and excess CO in the electrolyte was removed by purging with high-purity N₂ for 30 min. The amount of COad was evaluated by integrating the COad stripping peak and correcting for the capacitance of the electric double-layer.

Results and discussion

The TEM images demonstrated that hollow PdCu nanocubes with a uniform size and distribution can be obtained with the different supports. Fig. 1 shows the TEM images of the as-prepared catalysts from H–PdCu/melamine-NG (a), H–PdCu/ppy-NG (b), H–PdCu/PANI-NG (c), and H–PdCu/RGO (d). As shown in Fig. 1a, the individual cubes are composed of an empty core with a uniform shell, and well-dispersed on the surface of support with a relatively narrow particle size distribution. The particle diameters vary from 40 to 65 nm, and the average diameter is about 50 nm. To better understand the formation mechanism of hollow nanocubes in our system, we have monitored their formation process by running the reactions under the same conditions but for different support. From Fig. 1(b–c), hollow PdCu nanocubes with a relatively narrow particle size distribution are evenly deposited on the surface of the supports, and no significant change in either the structure or composition can be observed. Fig. 1d shows the TEM image of the H–PdCu/RGO, in which little H–PdCu are

Fig. 1 – TEM images of the as-prepared catalysts from H–PdCu/melamine-NG (a), H–PdCu/ppy-NG (b), H–PdCu/PANI-NG (c), and H–PdCu/RGO (d).
formed, instead of abundant hollow nanocubes with a uniform shell and internal cavity. Additionally, compared with RGO, the morphology of NG is not changed obviously after doping by N and the presence of N appears to reduce the particles agglomeration. From the above results, it is believed that the graphenes doped by N is important for the formation of uniform H–PdCu catalysts with a good distribution.

The surface chemical states and elemental compositions of NG supports were analyzed by XPS. Fig. 2(a–c) shows the survey-scan spectra of melamine-NG, ppy-NG and PANI-NG, respectively. The survey-scan spectra of NG supports are mainly dominated by the signals of C 1s, N 1s, and O 1s elements. The presence of N1s peak at about 400 eV demonstrates the successful incorporation of nitrogen in NG supports, which is in good accordance with the results of EDX elemental mapping. The high resolution N 1s spectra of melamine-NG, ppy-NG and PANI-NG are shown in Fig. 2(d–f), respectively. All of the N1s spectra can be further deconvoluted into three peaks, which correspond to three individual N-containing species. The peak at about 400.1 eV can be assigned to pyrrolic N species from the pentagonal ring of ppy, 398.1 eV to pyridinic N, and 401.1 eV to graphitic N, respectively [31]. Pyridinic N and pyrrolic N represent nitrogen atoms bonding with two carbon atoms and donate one or two p-electron to the aromatic π-system. Graphitic N, also called “quaternary nitrogen”, refers to nitrogen atoms that substitute the carbon atoms in graphene layers [32]. Table 1 lists N species compositions of different NG supports determined

![Fig. 2](image_url) – XPS spectra and the corresponding high-resolution N1s spectrum of the melamine-NG (a,d), ppy-NG (b,e), PANI-NG (c,f).
Nitrogen distributions of different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pyrrolic N</th>
<th>pyridinic N</th>
<th>graphite N</th>
</tr>
</thead>
<tbody>
<tr>
<td>melamine-NG</td>
<td>0.54</td>
<td>0.32</td>
<td>1.34</td>
</tr>
<tr>
<td>ppy-NG</td>
<td>0.55</td>
<td>0.43</td>
<td>0.63</td>
</tr>
<tr>
<td>PANI-NG</td>
<td>0.68</td>
<td>0.25</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table 1 – Nitrogen distributions of different samples.

Fig. 3 shows the XRD patterns of the as-prepared catalysts from H–PdCu/melamine-NG (a), H–PdCu/ppy-NG (b), and H–PdCu/PANI-NG (c). On the mapping images of all samples, a homogeneous distribution of N, Pd and Cu elements can be clearly observed, except from C element. It can be seen that Pd and Cu of all samples are uniformly distributed in the mappings, which is in agreement with the TEM results. The N is well distributed on the mappings of melamine-NG, ppy-NG and PANI-NG, respectively. The results reveal that the graphenes were doped by N successfully and the N atoms are all homogeneous distributed in a series NGs. In the process of N dope, the N sources react with the oxygen functional groups like carbonyl, carboxyl, and lactone in GO to achieve the insertion of nitrogen and give more effective deoxygenation of GO. Therefore, the graphenes doped using melamine, ppy and PANI as N sources have a similar composition distribution and nanostructure.

The catalytic activity of the prepared catalysts towards alcohols oxidation under alkaline conditions was evaluated through electrochemical measurements. Fig. 5 shows the CV curves of H–PdCu/melamine-NG, H–PdCu/ppy-NG, H–PdCu/PANI-NG, and H–PdCu/GO modified electrodes in 1 M NaOH solution containing 1 M ethanol (Fig. 5a), 1 M NaOH solution containing 1 M glycerol (Fig. 5b), respectively. The data were collected at a scan rate of 50 mV s\(^{-1}\) from −0.8 to 0.2 V at 25 °C. And all the results were normalized on the basis of the amount of Pd loading (mass activity). As Fig. 5a shows, the ethanol electrooxidation is characterized by two well-defined current peaks on the forward and reverse scans. In the forward scan, the oxidation peak corresponds to the oxidation of freshly chemisorbed species which come from the ethanol adsorption. The reverse scan peak is primarily associated with the removal of carbonaceous species which are not completely oxidized in the forward scan. The value of the peak current in the forward scan represents the electrocatalytic activities of the electrocatalysts. Clearly, the maximum peak current density of the H–PdCu/melamine-NG catalyst (ca. 710 mA mg\(^{-1}\)) is much higher than that of the others. Fig. 5b is a comparison of corresponding CV curves for glycerol electrooxidation from the as-prepared different catalysts. From the curves, two main peaks for the glycerol electrooxidation are observed in both the forward and reverse scan directions. The mass values of H–PdCu/melamine-NG, H–PdCu/ppy-NG, H–PdCu/PANI-NG, and H–PdCu/GO are 1300 mA mg\(^{-1}\), 320 mA mg\(^{-1}\), 450 mA mg\(^{-1}\), and 186 mA mg\(^{-1}\), respectively. It demonstrates that H–PdCu/melamine-NG modified electrode reveals extraordinarily high electrocatalytic activity relative to the electrode modified by other electrocatalysts, and the activities towards the ethanol and glycerol electrooxidation both decrease in the following order: H–PdCu/melamine-NG > H–PdCu/PANI-NG > H–PdCu/ppy-NG > H–PdCu/GO. Both graphitic N and pyridinic N have been proposed to serve as sites for Pt nucleation and to retard Pt diffusion and particle coalescence. The abundance of graphitic N and pyridinic N species on NGs should assist the catalytic activity of catalysts. The total ratio of graphitic N and pyridinic N in melamine-NG, PANI-NG and ppy-NG is 1.66%, 1.27%, 1.06%, respectively. Therefore, H–PdCu/melamine-NG shows extraordinarily high electrocatalytic activity for alcohols oxidation.

Fig. 3 – XRD patterns of the as-prepared different catalysts.
In order to compare the electrochemical stability of the as-prepared catalysts for alcohols oxidation, chronoamperometry tests were carried out at \(-0.3\) V for 6500 s in 1 M NaOH solution containing 1 M ethanol (Fig. 6a), 1 M NaOH solution containing 1 M glycerol (Fig. 6b), respectively. Evidently, the H–PdCu/melamine-NG catalyst shows much higher anodic currents and much slower degradation in currents, demonstrating better activity and stability than that of the other catalysts under the same conditions. The result further demonstrates that the NG using melamine as N sources can significantly enhance the activity and stability of catalyst toward alcohols electrooxidation.

The electrochemical active surface area (EAS) of the catalysts was determined by CO-stripping CV measurements, which were performed in 0.5 M H₂SO₄ electrolyte at a scan rate of 50 mV s⁻¹, at 25 °C. Fig. 7 shows the cyclic voltammograms obtained with CO adsorbed onto the catalysts (the solid curves) and without CO adsorbed onto the catalysts (the

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**Fig. 4** — FESEM images and corresponding chemical mapping of the as-prepared catalysts from H–PdCu/melamine-NG (a), H–PdCu/ppy-NG (b), and H–PdCu/PANI-NG (c).

**Fig. 5** — CV curves of the as-prepared catalysts from H–PdCu/melamine-NG (curve 1), H–PdCu/ppy-NG (curve 2), H–PdCu/PANI-NG (curve 3), and H–PdCu/RGO (curve 4) in different electrolytes: 1 M KOH + 1 M ethanol (a) and 1 M KOH + 1 M glycerol (b) aqueous solution, sweep rate of 50 mV s⁻¹, at 25 °C.
dashed curves) of H–PdCu/melamine-NG (a), H–PdCu/ppy-NG (b), H–PdCu/PANI-NG (c), and H–PdCu/RGO (d). The corresponding EAS of the catalyst was obtained from the following equation:

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EAS = \frac{Q}{m \cdot C}
\]

in which \( Q \) is the charge of the CO desorption–electrooxidation in microcoulombs (mC), \( m \) represents

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**Fig. 6** – The chronoamperometry of the as-prepared catalysts from H–PdCu/melamine-NG (curve 1), H–PdCu/ppy-NG (curve 2), H–PdCu/PANI-NG (curve 3), and H–PdCu/RGO (curve 4) in 1 M KOH + 1 M ethanol (a), 1 M KOH + 1 M glycerol (b) aqueous solution, at a scan rate of 50 mV s\(^{-1}\), at 25 °C.

**Fig. 7** – CV curves for the oxidation of preadsorbed CO at the as-prepared catalysts from H–PdCu/melamine-NG (a), H–PdCu/ppy-NG (b), H–PdCu/PANI-NG (c), and H–PdCu/RGO (d) in 0.5 M H\(_2\)SO\(_4\), scan rate of 50 mV s\(^{-1}\), at 25 °C. Dashed curves were CVs for these electrodes without CO\(_{\text{ad}}\) and solid curves for adsorbed CO\(_{\text{ad}}\).
the total amount of Pd (mg) on the electrode and C denotes the quantity of electricity when hydrogen molecules are adsorbed on Pd with a homogeneous and single layer (here, it is 420 μC cm²). The calculated EAS was 426.81, 268.37, 330.46 and 137.64 m² g⁻¹ Pd for H–PdCu/melamine-NG, H–PdCu/ppy-NG, H–PdCu/PANI-NG, and H–PdCu/RGO, respectively. In addition, the activity varied in keeping with the same law as for alcohols oxidation. Obviously, it can further demonstrate that N doped graphenes can effectively increase the active sites, and thereby can enhance the catalytic activity and stability of the electrocatalysts.

Conclusions

In this work, a series of hollow PdCu alloy nanocubes supported on nitrogen-doped graphene support (H–PdCu/ppy-NG) were successfully synthesized using a simple one-pot template-free method. Compared with RGO, the NGs used as supports can provide more active sites and increase the dispersibility of H–PdCu, which could improve the electrocatalytic activity and utilization ratio of the catalyst. Additionally, different N source doped different mass ratio of N species in NGs. More pyridinic N and graphitic N species on NG surfaces should be helpful to load more H–PdCu for enhancing the catalytic activity of the H–PdCu/NG. H–PdCu/melamine-NG shows the highest catalytic activity and stability, which makes it the candidate for direct alcohols fuel cells catalysts.

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