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Short communication

Preparation of reduced graphene oxide nanosheet/glutathione-Pd hydrogel with enhanced catalytic activity

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ABSTRACT

In this manuscript, we have prepared reduced graphene oxide nanosheet/glutathione-Pd (rGS/G-Pd) hydrogel with the help of glutathione by a hydrothermal method. During the synthesis, glutathione not only improved cross-linking of hydrogel via reacting with functional groups on graphene oxide nanosheet (GS) surface; but also deeply reduced GS to improve the conductivity. Additionally, the diameter of Pd nanoparticles (NPs) was decreased to 1.7 nm by taking advantage of synergistic effect between glutathione and Pd^{2+} ions. The final hydrogel displayed three-dimensional hierarchical porous structure with ultra-small Pd NPs uniformly decorated on the surface. In heterogeneous catalytic reaction, the rGS/G-Pd hydrogel showed superior catalytic performance towards the counterparts synthesized without glutathione, indicating it was a suitable candidate for catalyst.

Recently, graphene/metal nanoparticles (NPs) hydrogels have received considerable attention in catalysis, because hydrogels not only well disperse metal NPs on surface, but also prevent restacking of individual graphene nanosheets. Moreover, they can generate three dimensional (3D) hierarchical porous structure to improve mass diffusion and transfer during catalytic reactions. The typical approach for preparation of graphene/metal NPs hydrogel is hydrothermal method by using graphene oxide nanosheets (GSs) and metal salts as raw materials, in which GSs are assembled into cross-linking reduced graphene oxide nanosheet (rGS) hydrogel, and metal salts are reduced to the NPs. Based on this strategy, graphene/Au and graphene/Pt hydrogels were prepared and displayed excellent catalytic activity [1,2]. Although hydrothermal method is simple, it is difficult to control the size of metal NPs. As commonly known, the catalytic performance of metal NPs is mainly determined by the first or first few layers of metal species. To increase their amount, it is necessary to synthesize uniform NPs with the diameter as small as possible [1]. Therefore, how to further reduce the diameter of NPs without sacrificing simple process is still a great challenge.

Taking advantage of multiple-functional groups in molecule, glutathione was usually used as reducing agent to synthesize fluorescent metal nanoclusters with ultra-small diameter (Scheme S1) [3,4]. Inspired by the related work and continued with the line of our study [5,6]; herein, we have prepared rGS/glutathione-Pd (rGS/G-Pd) hydrogel in the presence of glutathione. Their enhanced catalytic activity towards the reduction of 4-nitrophenol (4-NP) was studied and compared with the referenced samples synthesized without glutathione.

Fig. 1 shows the Fourier-transform infrared (FT-IR) spectra of GS and rGS/G-Pd hydrogel. In hydrogel, the peaks located at 1431, 1342, 1218 and 1170 cm^{-1} are ascribed to GS [7]. The peaks emerged at 1515 and 1107 cm^{-1} are assigned to bending vibration of C—N bond, indicating glutathione is successfully grafted on GS surface during hydrothermal reaction. Importantly, the peaks located at 1722, 1626 and 1048 cm^{-1} are attributed to C═O, C═C and C—O groups on GS surface (Fig. 1a). These groups disappear in hydrogel (Fig. 1b), revealing reaction takes place between them and glutathione. In light of previous study, such reactions were beneficial for promoting cross-linking among neighboring GS, leading to an enhanced stability [8].

SEM images of rGS/G-Pd hydrogel at different magnifications are shown in Fig. 2a–c. rGS acts as the basic skeleton in hydrogel, and their morphology is shown in Fig. 2a. We can see rGS well preserves sheet-like morphology and many wrinkles appear on their surface. During the hydrothermal reaction, these rGSs assemble into bulk-phase hydrogels. In Fig. 2b, the neighboring rGSs are adhered together through self-assembly behavior, which leads to the appearance of numerous macropores with sizes ranging from several micrometers to tens of micrometers at the junctions of adjacent rGSs. In low magnification image (Fig. 2c), an interconnected and porous 3D network of hydrogel can be seen clearly. Obviously, such 3D hierarchical porous structure is favorable for mass diffusion and transfer during catalytic reactions. Fig. 2d shows the digital image of freshly-prepared rGS/G-Pd hydrogel. It represents a cylindrical shape, further indicating individual rGSs assemble into bulk-phase hydrogel during the hydrothermal reaction.

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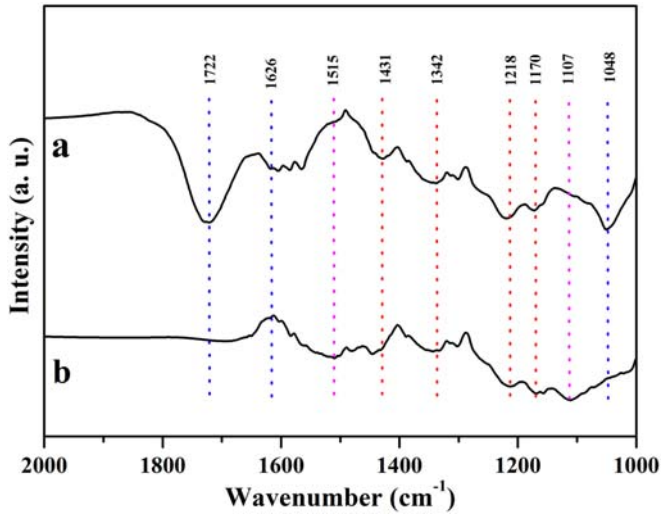

Fig. 1. FT-IR spectra of (a) original GSs and (b) rGS/G-Pd hydrogel. The peaks appeared in both GSs and hydrogel are appointed by red dotted line; the peaks only appeared in hydrogel are appointed by pink dotted line; the peaks only appeared in GSs are appointed by blue dotted line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Transmission electron microscope (TEM) images of rGS/G-Pd hydrogel in Fig. 3a and b exhibit the highly dispersed Pd NPs densely decorate on the curling rGS surface. From a statistical analysis of 100 NPs (Fig. S1a), their sizes mainly fall between 1.0 and 2.5 nm, and the average diameter is only 1.7 nm, which is much smaller than previous study (Table S1) [9–12]. Their crystalline lattice is measured to be 2.3 Å, which matches well with the (111) lattice of Pd NPs (inset of Fig. 3b). Due to small size and low loading (0.84 wt%), no diffraction peaks of Pd NPs can be observed in X-ray diffraction pattern (Fig. S2). To classify the important role of glutathione in reducing the size of Pd NPs, a controlled experiment was carried out with the similar recipe except no glutathione addition. As shown in Fig. 3c and d, although Pd NPs still represent high dispersity and uniformity, their average diameter dramatically increases to 3.7 nm (Fig. S1b), which is about 2.2 times larger than samples in Fig. 3b. Considering the experimental conditions were the same except glutathione was used; apparently, functional groups including amino and mercapto groups in glutathione molecule contributed greatly to the small size of Pd NPs, because of the coordination interactions between Pd^{2+} ions and these groups through sharing the electron pairs. This was consistent with the reported synergistic effect [13,14].

X-ray photoelectron spectroscopy (XPS) analysis was done to gain further insights into the surface compositions of rGS/G-Pd hydrogel. In core-level Pd 2d XPS spectrum (Fig.4a), two peaks centered at 337.3 and 342.5 eV are corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, indicating the oxidation state is Pd^0 [15,16]. The fitted N 1s spectrum in Fig.4b demonstrates two N species at 399.7 and 402.2 eV, which are attributed to the —NH— and N^+ groups in glutathione. The core-level S 2p spectrum can be curve-fitted into three peaks with binding energies at 162.8, 164.0 and 168.8 eV (Fig.4c) [17]. The former two peaks are corresponding to C—S—C bond and the last peak is assigned to the —C—SO_3^- group. There is no —C—SO_3^- group in glutathione molecule (Scheme S1); therefore, its appearance further confirms the reaction occurs between glutathione and functional groups on GS surface. The carbon species in GS are divided into four peaks (Fig. 4d): C—C/C═C (284.6 eV), C—O (286.2 eV), C═O (286.9 eV) and O—C═O (288.4 eV) [18]. The core-level spectrum of C 1s in rGS/G-Pd hydrogel can be fitted into three peaks (Fig. 4e). Compared with Fig. 4d, besides appearance of C—N/C—S peak centered at 285.1 eV, the peaks belonged to C═O and O—C═O groups vanish. The amount of oxygen-containing groups dramatically decreases from 54.1% (GS) to 24.1% (hydrogel). In contrast, the core-level spectrum of C 1s in rGS/Pd hydrogel is fitted into three peaks assigned to C—C/C═C, C—O and C═O groups, respectively (Fig. 4f). The amount of oxygen-containing groups is about 28.0%, which reveals GS can be deeply reduced in the presence of glutathione. Deep reduction was beneficial for enhancing conductivity of rGSs; and hence, accelerating transfer of electrons during the catalytic reaction [19].

Highly dispersed Pd NPs with ultra-small size, 3D hierarchical porous structure, together with high conductive rGSs, made rGS/G-Pd hydrogel act as suitable catalyst in heterogeneous catalysis [1,2,17,19]. Herein, the typical reduction of 4-NP was selected as a model reaction to evaluate their catalytic property. Fig. S3 shows only 12.5% of 4-NP is reduced without catalysts even after 26.0 h. Conversely, the 4-NP can

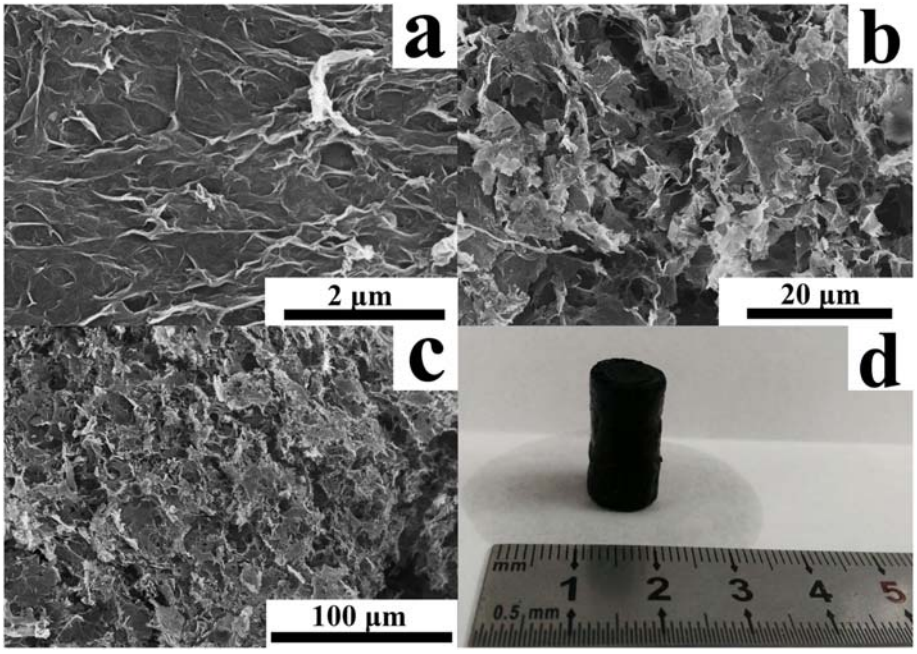

Fig. 2. (a–c) SEM images of rGS/G-Pd hydrogel with gradually reduced magnifications. (d) Digital image of freshly-prepared rGS/G-Pd hydrogel.