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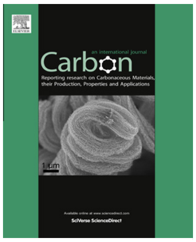

Letter to the Editor

Galvanic displacement induced reduction of graphene oxide

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ABSTRACT

Copper–silver or copper–gold galvanic displacement could induce the reduction of graphene oxide, resulting in a fast and effective removal of the oxygen-containing groups in graphene oxide and formation of silver or gold nanoparticles on graphene sheets. A graphene oxide mediated long-range electron transfer process between copper and silver or chloroauric ions is proposed for the occurrence of the reactions.

Graphene draws world-wide interests in recent years, due to its broad applications in transparent conductive films, sensors and clean energy devices [1]. Many approaches have been reported to produce graphene, including chemical vapour deposition, epitaxial growth, mechanical exfoliation of graphite and chemical reduction of graphene oxide (GO) [2]. Chemical reduction is of great significance, for its feasibility in large-scale graphene production [3]. As the reductants in this method, hydrazine hydrate and H_2 have been widely used [3–4]. On the other hand, reductants with less toxicity and at lower reaction temperatures are still desired for the green and easy production of graphene. Metals, such as iron, zinc and aluminium, have been introduced to avoid the usage of hazardous reagents and greatly simplify the reduction procedures of GO [5–7]. All the metals reported to reduce GO, have lower standard reduction potentials than hydrogen. Copper, with a standard reduction potential much higher than hydrogen, has never been reported to reduce GO under ambient conditions.

Galvanic displacement, occurring between two materials with different reduction potentials, is regarded as the mechanism to form various fascinating nanomaterials including gold nanocages [8]. Herein, we demonstrated that copper–silver or copper–gold galvanic displacement could trigger the fast and effective reduction of GO.

As shown in Fig. 1a, GO solution shows a prominent peak at 240 nm in its ultraviolet–visible (UV–vis) spectrum. After the addition of copper powders for 12 h, the solution remained yellowish brown and transparent (shown in Fig. 1 inset), without obvious change in the UV–vis spectrum (Fig. 1b). To induce the reaction, silver nitrate or chloroauric acid solution was added after copper powders. Brownish grey (Cu–Ag–rGO) or black precipitate (Cu–Au–rGO) was produced instantly, leaving transparent and colorless supernatants (shown in Fig. 1 inset). Peaks at ~210 nm appear in the UV–vis spectra of the above supernatants with a vanished peak of GO at 240 nm, owing to the existence of hydrated Cu^{2+} (Fig. 1c and d).

Compared with the C1s X-ray photoelectron spectra (XPS) of GO (in Fig. 2a), those of Cu–Ag–rGO (in Fig. 2b) and Cu–Au–rGO (in Fig. 2c) show dramatic decreases of the –C=O bond (at 286.7 eV) intensity. The peak of –C=C bond (at 284.6 eV), standing for the π–π conjugating structure of carbon atoms, remains evident. The C/O atom ratios increase from 3.02 (in GO) to 11.78 (in Cu–Ag–rGO) and 7.46 (in Cu–Au–rGO), indicating an effective removal of the oxygen-containing groups in GO.

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Fourier transform infrared (FT-IR) spectrum of the original GO in Fig. 3a shows the vibration peaks of various oxygen-containing groups (1724, 1608, 1215 and 1048 cm^{-1} for C=O, C–O, C–OH and C–O–C, respectively) [7]. All these peaks almost vanish in the spectra of Cu–Ag–rGO and Cu–Au–rGO, further suggesting the removal of these oxygen-containing groups in GO. The corresponding Raman spectra in Fig. 3b show two graphene characteristic bonds: the D bond at 1350 cm^{-1} and the G bond at 1585 cm^{-1}. The intensity ratio of D and G bonds (I_D/I_G) increase from 0.73 (in GO) to 0.90 (in Cu–Ag–rGO) and 0.83 (in Cu–Au–rGO), indicating the occurrence of the chemical reduction process, for the numerous defect-rich graphite domains were produced [6]. Slight peak shifts (indicated by the dash line in Fig. 3b) of the G bonds from 1595 (in GO) to 1585 cm^{-1} (in Cu–Ag–rGO and Cu–Au–rGO,) suggest the restoration of the sp^2 carbon conjugated structure [7].

X-ray powder diffraction (XRD) patterns of the solid products are shown in Fig. 4a and b, where evident diffraction peaks of Ag (JCPDS No. 04-0783) and Au (JCPDS No. 04-0784) are indexed, respectively. The morphologies of Cu–Ag–rGO and Cu–Au–rGO were further examined by transmittance electron microscopy (TEM), as shown in Fig. 4c and d, respectively. Besides the graphene sheets with clear edges and wrinkles, nanoparticles with diameters of 30–50 nm could be observed on the reduced graphene oxide (rGO) sheets. In the corresponding high-resolution TEM (HR-TEM) images (shown in the insets), the lattice-fringe inter-planar spacing of the nanoparticles are measured to be 0.206 and 0.234 nm, which are indexed to the (200) and the (111) crystal planes of Ag and Au, respectively. The existences of Ag and Au nanoparticles on the graphene sheets were also confirmed by the evident characteristic energy dispersive spectra (EDS) peaks of Ag and Au in Fig. 4e and f.

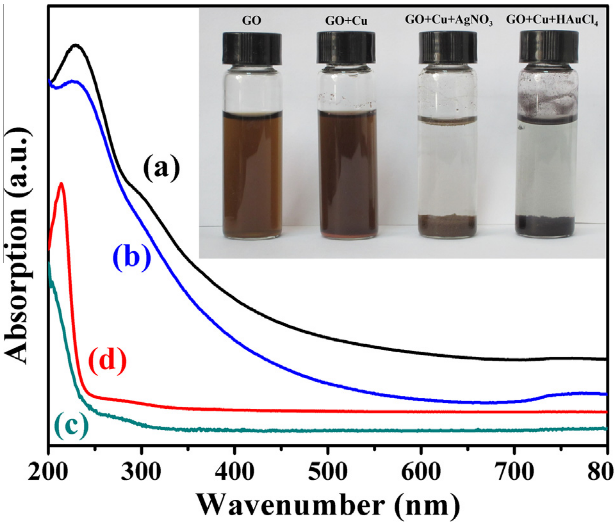

Fig. 1 – UV–vis spectra of GO solution (a), with the addition of copper powders after 12 h (b), with additions of silver nitrate (c) and chloroauric acid (d) solution after copper powders after 2 min. Inset: corresponding photographs of GO solution and the products. (A color version of this figure can be viewed online.)

According to the reference, the reduction of GO by metals could be attributed to the differences of the reduction potentials between GO and metals [6]. For the standard reduction potential of zinc (Zn^{2+}/Zn) is −0.76 V versus standard

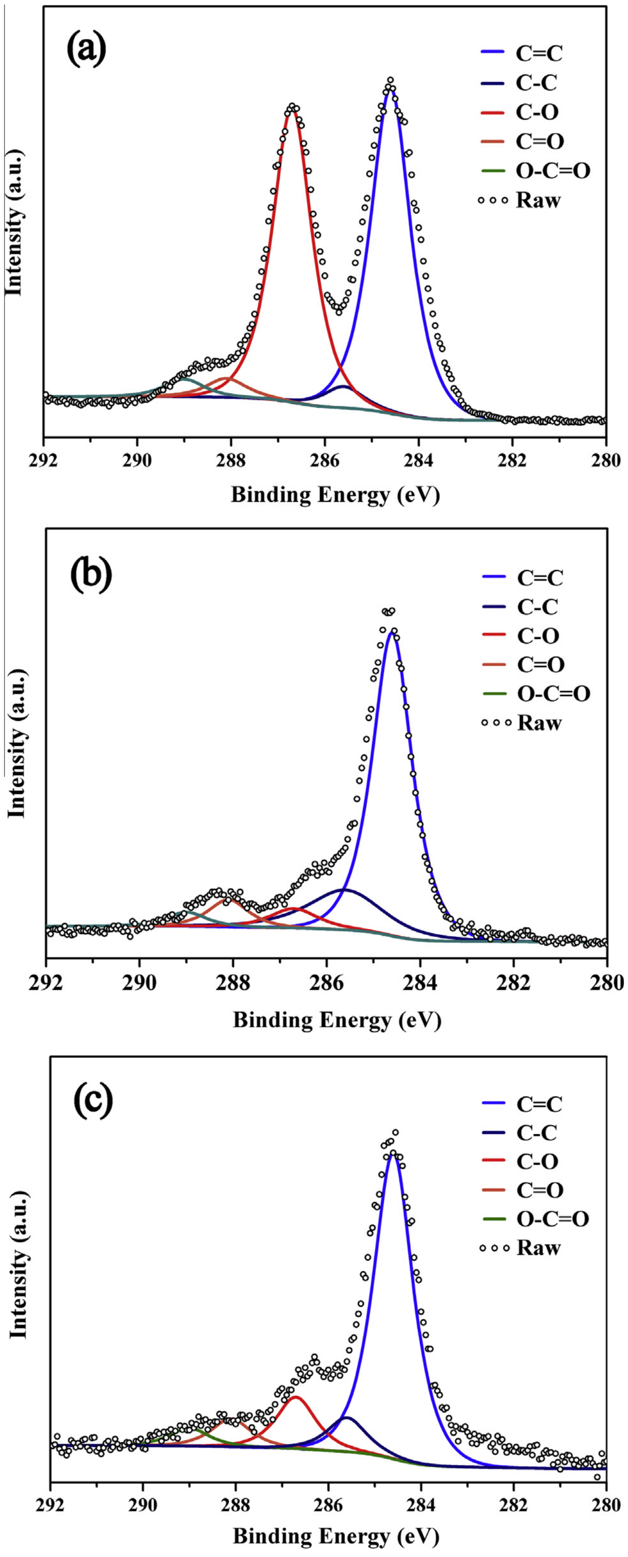

Fig. 2 – C1s XPS spectra of GO (a), Cu–Ag–rGO (b) and Cu–Au–rGO (c) with peak separations and fittings. (A color version of this figure can be viewed online.)