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# A novel solid-to-solid electrocatalysis of graphene oxide reduction on copper electrode

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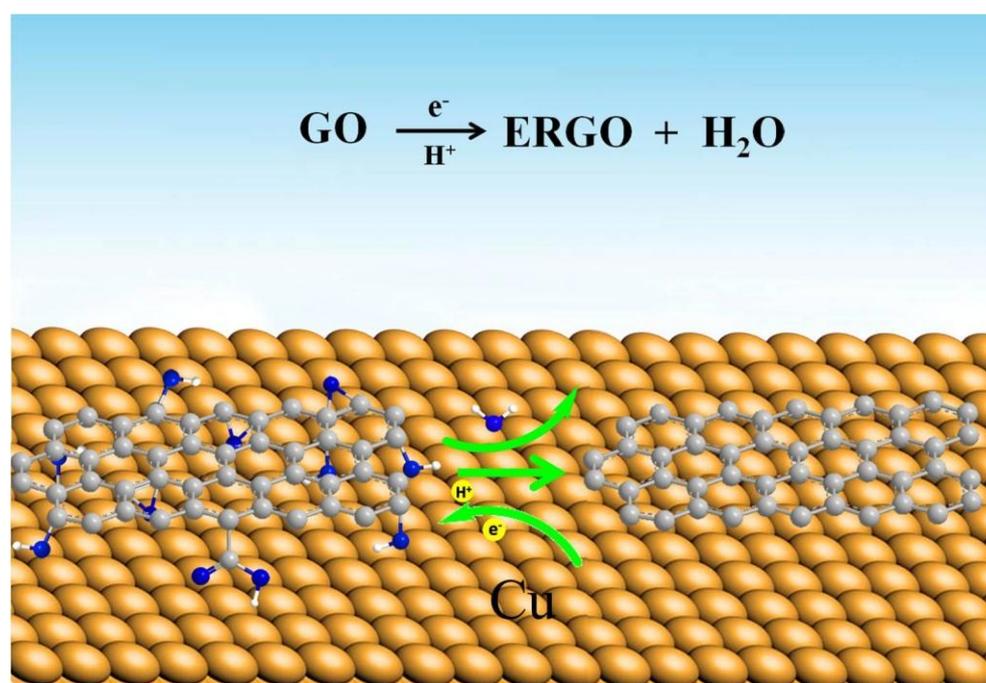
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## Graphical abstract



Graphene oxide could be efficiently reduced to graphene on Cu electrode through a novel electrocatalytic solid-to-solid reaction.

## ARTICLE

## A novel solid-to-solid electrocatalysis of graphene oxide reduction on copper electrode

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Graphene oxide (GO) could be efficiently reduced to graphene on Cu electrode through a novel electrocatalytic solid-to-solid reaction. Comparing to glass carbon (GC) inertial electrode, more oxygen-containing groups are removed on copper electrode under the same electrochemical reduction conditions for de-oxygenation of GO nanosheets. Especially, Cu catalyst could electrochemically catalyze the elimination of sp<sup>3</sup> carbon clusters in GO to restore sp<sup>2</sup> C=C conjugated network of graphene relative to GC electrode.

### Introduction

Graphene, as a two-dimensional crystal of one or few layers of carbon atoms, has attracted tremendous attention since its discovery in 2004<sup>1</sup>. Graphene has many outstanding properties including super electron mobility, excellent electrical conductivity, extremely high thermal conductivity, good optical transparency, strong Young's modulus, and high surface area<sup>2-4</sup>. Thus graphene has been intensively developed for various applications such as electronic devices, photonic devices, batteries, supercapacitors, fuel cells, sensors, thermal interface materials, interconnects, and biomaterials<sup>5-10</sup>. Synthesis method results in the actual properties and cost of graphene, which is currently a bottleneck for its large scale practical applications. There are two strategies to obtain graphene by bottom-up process from organics or by top-down procedure usually from graphite. Comparing to organics, graphite is a very abundant and cheap raw material. Bottom-up method includes chemical vapour deposition, epitaxial growth and organic molecules synthesis<sup>11</sup>. Top-down route includes micro-mechanical cleavage, ball-milling exfoliation, liquid phase exfoliation, and chemical exfoliation<sup>12,13</sup>. Among

all these methods, chemical exfoliation is one of the most promising procedures for low cost and large scale production of graphene<sup>14</sup>. The chemical exfoliation is first to prepare graphene oxide (GO) by oxidation of graphite which is a very mature technique, then reduction of GO to obtain graphene. The sp<sup>2</sup> conjugated network of pristine graphene is disrupted during the oxidation of graphite, thus reduction method is critical in restoring the structure and unique properties of graphene.

There are a lot of procedures for reduction of GO such as chemical reduction, thermal reduction, photocatalytic reduction, and electrochemical reduction<sup>15,16</sup>. Reducing agent is necessary for chemical reduction of GO, which might be harmful such as using hydrazine. In addition, it is not easy to completely remove the oxygen-containing groups in GO with only one reducing agent due to the selectivity. Thermal reduction needs high temperature, resulting in high cost and hard experimental conditions. Photocatalytic reduction involves photoactive materials under ultraviolet irradiation. Among the chemical reduction methods, electrochemical reduction of GO is a relatively simple, cheap, fast and environmentally friendly method to obtain graphene on a large scale<sup>17</sup>. Although many efforts have been devoted for electrochemical reduction of GO<sup>18</sup>, there is no report focusing on electrocatalytic reduction of GO to the best of our knowledge.

Here, we report a novel solid-to-solid electrocatalytic reaction of graphene oxide to graphene on copper catalyst electrode. During the electrochemical reduction of graphene oxide, Cu electrode demonstrates considerably larger peak current and lower starting reduction overpotential relative to glass carbon (GC) inertial electrode. Graphene with higher ratio of C/O and better sp<sup>2</sup> C=C conjugated structure is obtained on Cu electrode due to the electrocatalysis effect for GO reduction.

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## Experimental

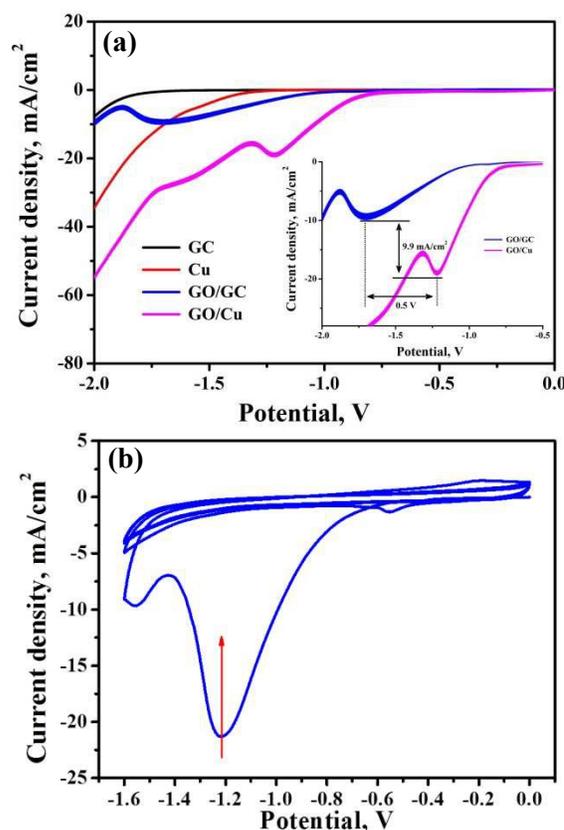
**Graphite oxide preparation.** Graphite oxide was synthesized from graphite powder by using a modified Hummers method. Exfoliation of graphite oxide to graphene oxide was achieved by ultrasonication of graphite oxide dispersion using an ultrasonic bath (500W) for 2 h. The obtained brown dispersion was then subjected to 10 min of centrifugation at 4000 rpm. to remove any unexfoliated graphite oxide. The concentration of the slurry was determined by drying a sample of graphene oxide in vacuum oven for 16 h, and was found to be 0.2 mg/ml.

**Electrode preparation.** The GC or Cu electrode (3.0 mm diameter) was polished with alumina slurry to get a mirror-like finish. Then it was washed with ethanol and dried at room temperature. GO coated GC (GO/GC) or Cu (GO/Cu) electrode was prepared by casting 6  $\mu$ L GO dispersion onto the GC or Cu electrode surface and allowed to dry at 30  $^{\circ}$ C for 30 min. Linear sweep voltammetry (LSV) and cyclic voltammograms (CV) experiments by using a CHI660E electrochemical workstation at a scan rate of 100 mV/s with the potential range of 0 V to -2.0 V. The conventional three-electrode cell for LSV test consisted of Ag/AgCl saturated KCl reference electrode, platinum foil auxiliary electrode, and working electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub>.

**Characterization.** The electrochemical reduced GO stripped from electrodes was used to conduct FT-IR spectra, Raman spectra, TEM and XPS analysis. The Fourier transform-infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 spectrometer in the range of 4000-400 cm<sup>-1</sup>. Raman spectra of the samples with the 514.53 nm line of an argon laser were measured by using Renishaw RM-1000 micro-Raman spectrometer. XPS analysis was recorded on a PHI 5800 XPS system, where Al K $\alpha$  excitation source was used. The TEM images were obtained by high resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 FEI). Atomic force microscopy (AFM) images were acquired by using the Multimode 8 (Bruker Co.) in tapping mode.

## Results and discussion

Graphite oxide (GO) nanosheets are synthesized from graphite powder by using a modified Hummers method. Then the GO nanosheets are coated on the GC and Cu electrodes for electrochemical reduction in a three-electrode cell using Pt counter electrode and Ag/AgCl reference electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Linear sweep voltammetry (LSV) technique is used to investigate the catalysis effect of electrochemical reduction of graphene oxide and the results are shown in Figure 1a. As the potential sweeps with 100 mV/s from 0 V to -2.0 V (vs. Ag/AgCl electrode), there is no reduction current until to -1.9 V and -1.3 V for the bare GC and Cu electrodes, respectively. The currents increase with the more negative potentials for the both electrodes, originating from the enhanced reduction of water to hydrogen at higher overpotentials<sup>16</sup>. It should be noted that the large overpotential of hydrogen evolution indicates the inertial property of GC electrode for water electrochemical reduction.



**Figure 1.** (a) LSV curves of glass carbon electrode (GC), Cu electrode (Cu), graphene oxide coated GC electrode (GO/GC), and graphene oxide coated Cu electrode (GO/Cu). (b) CV curves of graphene oxide modified Cu electrode.

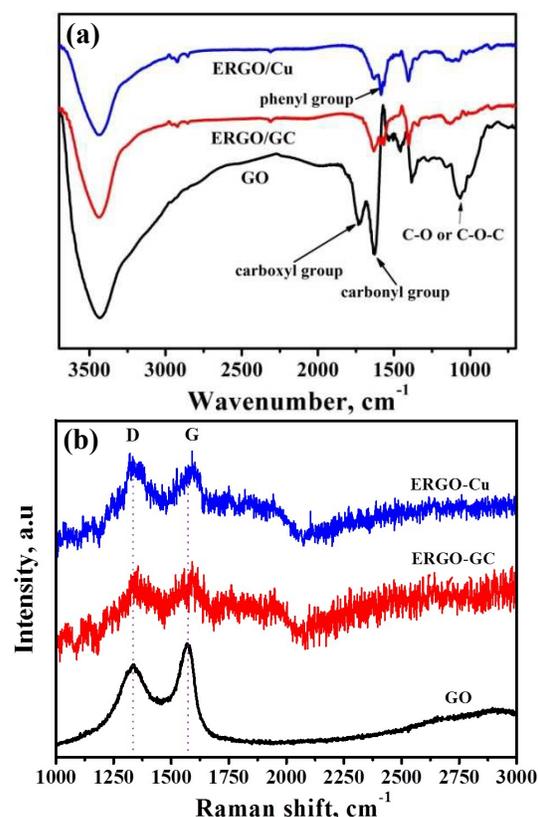
Comparing to the GC electrode, Cu electrode shows a larger cathodic current and more positive onset potential, suggesting that Cu possesses somewhat electrochemical catalytic activity towards electrochemical hydrogen evolution although it is much lower than the traditional metal catalysts such as Ni<sup>19</sup>, Pt<sup>20</sup>, Fe<sup>21</sup>, etc. This might be attributed to the highly conductive Cu that provides continuous and fast conducting pathways for electrons<sup>16, 22</sup>. Hydrogen evolution is a competing reaction for GO electrochemical reduction in the aqueous electrolyte. Electrocatalytic effect might be easily observed in the LSV test using Cu catalyst towards GO electrochemical reduction due to the higher overpotential of hydrogen evolution over Cu electrode than the above metal catalysts.

The reduction current occurs at -1.06 V for GO coated GC electrode due to the reduction of GO on the GC electrode ( $\text{GO} + \text{H}^+ + \text{e}^- = \text{ERGO} + \text{H}_2\text{O}$ )<sup>23</sup>. The H<sup>+</sup> could be from aqueous electrolyte and the electron is from the electrode. The highest reduction current appears at -1.70 V with ca. 9.9 mA/cm<sup>2</sup>. The reduction current decreases till -1.89 V, and then increases very close to the current of bare GC electrode as the potential sweeps to -2.0 V. The results suggest the reduction of GO on GC electrode in the main potential range between -1.06 V and -1.89 V under this LSV test condition. According to the following XPS and FT-IR results, it is

known that some oxygen-containing groups could not be removed although at higher overpotential for GO coated on GC electrode in the LSV test. The GO reduction current would decrease as the removable oxygen-containing species consumption under the electrochemical reduction condition. Then the major electrochemical reduction is hydrogen evolution at higher overpotential for GO coated GC electrode in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

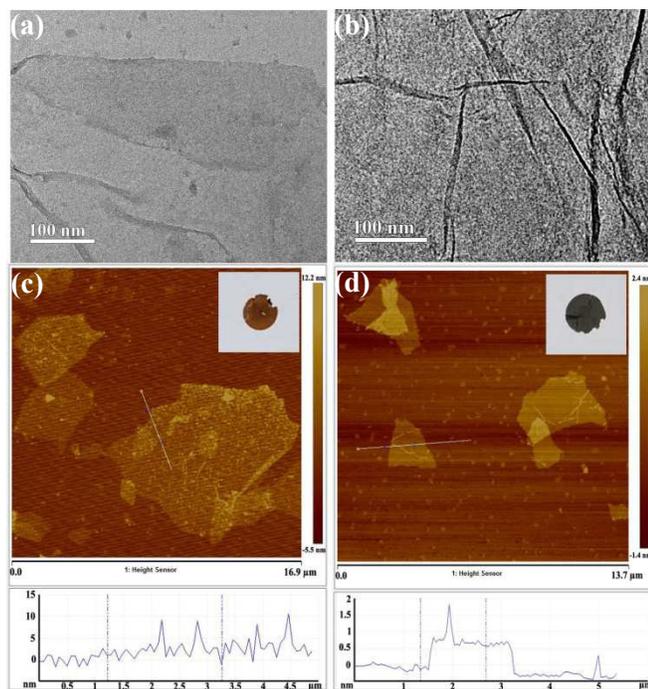
For GO coated Cu electrode, the reduction current starts at a lower potential of -0.8 V and the reduction peak also appears at a considerably lower potential of -1.2V with obviously larger reduction current (~19.4 mA/cm<sup>2</sup>) compared with GO coated GC in the LSV curves. The lower overpotential and larger current clearly indicate the electrocatalytic effect of Cu for GO reduction. The current decreases till to the water reduction potential of bare Cu electrode then increase as the overpotential increasing. It is similar to the GO coated GC electrode, the GO reduction current decreases as the consumption of removable oxygen-containing groups in GO. However, the current of GO coated Cu electrode is obvious larger than that of bare Cu electrode after the hydrogen evolution potential, which is obviously different from the phenomenon for GO coated GC electrode and GC electrode. The reason might be that the GO might improve the hydrogen evolution on the Cu electrode and/or the hydrogen evolution could improve the GO reduction over Cu electrode<sup>24</sup>. The CV of GO coated on the reused Cu electrode in a potential range from 0 to -1.6 V shows a large cathodic current peak at -1.2V (Figure 1b). This current density improvement of GO/Cu should be due to the enhanced reduction of the oxygen-containing group in GO with electrocatalytic effect of Cu electrode. In the second cycle, the reduction current density decreases considerably and disappears after several potential scans, suggesting the reduction of oxygen-containing group in Go occurs quickly and irreversibly and the exfoliated GO could be reduced electrochemically at negative potentials.

FT-IR is a useful technique to identify the oxygen-containing groups of GO and electrochemically reduced GO (ERGO). Figure 2a illustrates the FT-IR spectra of GO, GO reduction on GC and Cu electrodes after one time LSV test. The broad and intensive peak at about 3450 cm<sup>-1</sup> for GO is attributed to O-H stretching band of carboxyl groups and adsorbed water groups.<sup>25, 26</sup> After electrochemical reduction, the O-H stretching peak somewhat weaker and sharper. According to the previous reports,<sup>27</sup> the intensive peaks at approximately 1740 cm<sup>-1</sup>, 1630 cm<sup>-1</sup>, and 1060 cm<sup>-1</sup> for GO are assigned to C=O stretching vibration of carbonyl and/or carboxyl groups, deformation band of O-H groups, and alkoxy C-O-C stretching vibration, respectively. It could be observed that the peaks at 1740 cm<sup>-1</sup> and 1060 cm<sup>-1</sup> almost disappear as well as the intensity of peak at 1630 cm<sup>-1</sup> dramatically decreases after GO LSV tests, indicating the efficient electrochemical reduction of oxygen-containing groups in GO. The peaks at about 1590 cm<sup>-1</sup> for electrochemically reduced GO are ascribed C=C skeletal vibration of graphitic domain.<sup>27, 28</sup> Comparing to the GO reduced on GC electrode (ERGO/GC), the GO reduced on Cu



**Figure 2.** (a) FT-IR and (b) Raman spectra of GO, electrochemically reduced GO on GC electrode (ERGO/GC) and Cu electrode (ERGO/Cu).

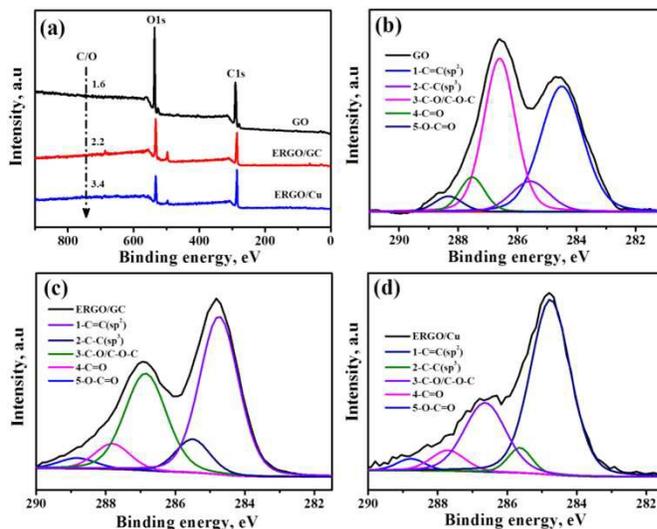
electrode (ERGO/Cu) shows higher peak intensity of C=C skeletal vibration and lower peak intensity of O-H deformation band, confirming the catalysis of Cu for GO electrochemical reduction. Raman spectroscopy is used to analyse the electrochemically reduced GO on surface of the different electrodes. As shown in Figure 2b, the GO displays a strong G-band and a weak D-band at 1586 cm<sup>-1</sup> and 1356 cm<sup>-1</sup>, respectively. In the Raman spectra of ERGO/GC and ERGO/Cu, the G-band are broadened and shifted upward, and are detected at 1601 cm<sup>-1</sup> and 1606 cm<sup>-1</sup>, respectively, which are mainly caused by stress<sup>29</sup>. Moreover, the width of D-band of ERGO on GC or Cu electrodes are also broadened. These upward- or broadened changes suggest the GO is electrochemically reduced on surface of the electrodes. In Figure 3a and b, large crumpled GO nanosheets are observed by TEM. The silk-veil-wave ERGO nanosheets for Cu electrode, however, show more folds and thinner thickness than ERGO nanosheets for GC electrode. These corrugated and scrolled resemblance of silk veil wave are nature of graphene nanosheets. Besides, AFM is currently the foremost methods allowing definitive identification of GO nanosheets. As shown in the Figure 3c and d, the thickness of the ERGO for Cu electrode is ca. 0.8 nm, which is more homogeneous and thinner than for GC electrode (ca. 2 nm). The homogeneous and thinner GO electrochemically reduced on



**Figure 3.** TEM and AFM images of electrochemical reduced GO on (a, c) GC electrode (ERGO/GC) and (b, d) Cu electrode (ERGO/Cu). Inset: the corresponding photographs of ERGO stripped from GC and Cu electrode. The samples were prepared by drop-casting corresponding dilute ethanol dispersions onto mica sheets.

Cu electrode might be due to the reduction of oxygen-containing group.

The compositions of the oxygen-containing groups in GO and electrochemically reduced GO (ERGO) could be identified by XPS measurement. As the shown in Figure 4a, the peaks at about 530 and 284 eV in overview XPS curves are assigned to the O1s and C1s spectra, respectively. The peak intensity order of O1s peaks is GO, GO after reduction on GC electrode, and GO after reduction on Cu electrode. The GO after reduction on Cu electrode exhibits a higher C/O ratio (3.4) than those of GO after reduction on GC electrode (2.2) and pristine GO (1.6). The results quantitatively illustrate that more amount of oxygen atoms could be removed on Cu catalytic electrode during the electrochemical reduction of GO. That's why the current peak intensity of GO coated Cu electrode is larger than that of GO coated GC electrode during the LSV test. The C/O ratio of GO reduction on Cu electrode in this work is not as high as the previous result about electrochemical reduction of GO on inertial electrodes for long reduction time<sup>23</sup>. Because the high reduction ability of electrochemistry could deeply reduce GO even on inertial electrode with long reduction time. However, the catalytic effect might be overlapped in this case and more electrical energy would be consumed for practical application on inertial electrode. The aim in this article is to propose and investigate that GO could be catalytically reduced in the electrochemical reduction process. Thus we focus on the comparison of the electrochemical reduction degree of GO



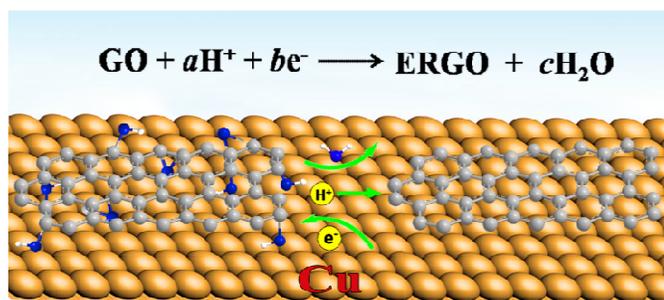
**Figure 4.** (a) XPS general spectra, C1s spectra of (b) GO, ERGO on (c) GC and (d) Cu electrodes.

with and without electrocatalyst under a suitable and same electrochemical condition such as LSV from 0 V to -2.0 V with a sweep rate of 100 mV/s.

The C1s XPS spectra (Figure 4b-d) for GO and electrochemically reduced GO could be further de-convoluted into five individual peaks that are attributed to  $sp^2$ -hybridized carbon (C=C, 284.6 eV),  $sp^3$ -hybridized carbon (C-C, 285.6 eV), carbons of alkoxy and epoxy groups (C-O/C-O-C, 286.6 eV), carbonyl-based carbons (C=O, 287.4 eV) and carboxyl-based carbons (O-C=O, 288.6 eV), respectively<sup>30, 31</sup>. The content of each group calculated from the C1s XPS spectra is listed in Table 1. The contents of -C-C ( $sp^3$ ) and -C=O have not been removed although the contents of -C-O/C-O-C and -O-C=O groups decrease for GO electrochemical reduction on the GC electrode. While for GO electrochemical reduction on Cu electrode, the contents of -C-C ( $sp^3$ ) and -C=O groups considerably decrease beside the decreasing contents of -C-O/C-O-C and -O-C=O groups thus the content of -C=C ( $sp^2$ ) of graphene increases obviously. The results suggest that Cu electrode can efficiently catalyze removal of -C-C ( $sp^3$ ) and -C=O to recover the conjugated structure of graphene and heal the defect while not just removing of oxygen-containing group like the electrochemical reduction of GO on GC electrode without Cu catalyst.

**Table 1** The C1s XPS data of GO and electro-chemical reduced GO on GC and Cu electrode (relative atomic percentage %).

	-C=C ( $sp^2$ ) 284.6 eV	-C-C ( $sp^3$ ) 285.6 eV	-C-O/C- O-C 286.6 eV	-C=O 287.4 eV	-O- C=O 288.6 eV
GO	41.9	9.1	38.6	6.9	3.4
ERGO/GC	48.6	9.1	32.2	7.0	3.1
ERGO/Cu	60.7	5.2	25.1	6.1	2.9



**Figure 5.** Mechanism of electrochemical reduction of GO on Cu electrode, (blue: O, white: H, gray: C).

It should be noted that the GO electrocatalytic reduction is very different from the traditional electrocatalysis which reactants and/or productions are liquid or gas. GO nanosheets are solid reactant and the product of ERGO nanosheets are also solid. There is no transfer/diffusion of GO/ERGO in the electrochemical reaction since the GO/ERGO solid nanosheets are all through on the Cu catalyst electrode during the reduction process. It is a novel solid to solid electrocatalytic reaction. Cu is an excellent catalyst for  $\text{CO}_2$  ( $\text{O}=\text{C}=\text{O}$ ) electrochemical reduction to hydrocarbons (C-C or C=C) in aqueous electrolyte<sup>32</sup>. Metal Cu atoms could absorb carbon oxide molecules then decrease the strength of C=O bond<sup>33</sup>. Thus the oxygen atoms would be easily removed to form carbon-carbon bond during electrochemical reduction (Figure 5). It might be similar to  $\text{CO}_2$  for GO electrochemical reduction on Cu electrode. As GO nanosheets are coated on the Cu electrode surface, the oxygen-containing groups are absorbed on the Cu atoms. The strength of C=O bond of GO then could be weakened on Cu electrocatalyst, resulting in the enhancement of the GO reduction with  $\text{H}^+$  from aqueous electrolyte to form water ( $\text{GO} + a\text{H}^+ + b\text{e}^- \rightarrow \text{ERGO} + c\text{H}_2\text{O}$ ).<sup>23</sup> Moreover, Cu is a very good electrical conductor, which could transfer the electrons on the reaction sites fast. Therefore, Cu demonstrates excellent catalytic activity toward GO electrochemical reduction.

## Conclusions

GO nanosheets could be efficiently reduced to graphene on Cu electrode through a novel solid-to-solid electrocatalysis. More oxygen-containing groups are removed and more  $\text{sp}^2$  conjugated structures are restored for GO electrochemical reduction on Cu electrode compared with GC electrode due to the Cu electrocatalytic activity.

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