LETTER

Effective electron transfer between heteropoly blue and graphene oxide: a green approach to graphene synthesis†

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A facile electrochemical approach for the synthesis of graphene is developed by highly effective electron transfer from electron-rich heteropoly blue to graphene oxide. Reduced graphene oxide immobilized on a glassy carbon electrode (GCE) shows more positive potential for hydrogen evolution owing to the presence of the polyoxometalate electrocatalyst.

Graphene, a monolayer graphite sheet, has stimulated the research interest of the scientific community in the last ten years due to its various potential applications in nanoelectronics,¹ biosensors,² supercapacitors³ and nanocomposite materials.⁴ Rapid development in synthesis technologies enriches the preparation of graphene by mechanical or chemical exfoliation,⁵ epitaxial growth on metal surfaces,⁶ chemical⁷ or thermal reduction,⁸ template-directed method,⁹ photocatalytic reduction¹⁰ and electrochemical reduction of graphene oxide (GO).¹¹ Among these methods, the electrochemical reduction of exfoliated GO is a green and facile method which has been desirably adopted by many researchers to prepare graphene. Moreover, the electron-transfer pathway and the electron-transfer rate between the electrode and the active species determine the efficiency of electrochemical reduction of GO to reduced graphene oxide (RGO). In recently published results, a necessary low cathodic potential (−1.2 to −1.5 V vs. Ag/AgCl) was applied to ensure the full reduction of GO on a glassy carbon electrode surface.^{11–15} The main reason is low effective electron transfer between the glassy carbon electrode and the GO species. Hence, incorporation of an electrocatalyst into the GO electrochemical reduction

system may be considered to accelerate electron transfer across the electrode/GO interface so that the reduction potential of GO can shift to more positive values in terms of energy conservation for bulk production.

Polyoxometalates (POMs) are well-organized metal–oxygen clusters which are water soluble and exhibit a great diversity of sizes, nuclearities and shapes.¹⁶ Most importantly, POMs can be reduced reversibly without any structural change and can often be utilized as electron-transfer mediating catalysts in many redox reactions.¹⁷ Upon a series of one/two-electron reduction processes, near-colorless POMs composed of saturated-valence metals form intensely blue mixed-valence species. The blue species are customarily termed as ‘heteropoly blue’.¹⁸ Heteropoly blue, acting as electron carriers, can provide electrons for the substrates in the redox reactions and they change back to the initial POM species. Recently, Wang *et al.* chose a Keggin-type $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW_{12}) electrocatalyst to prepare a POM–graphene nanocomposite.¹⁹ However, such an acidic-form SiW_{12} ion is stable only in a narrow pH range of 1 to 3 in aqueous solution without structural degradation. Li *et al.* reported the photoelectrochemical synthesis of hybrids based on graphene–POM–poly(ionic liquids).²⁰ A Pressler-type heteropolytungstate $\text{K}_{12.5}\text{Na}_{1.5}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ ($\text{NaP}_5\text{W}_{30}$) cluster is extraordinarily stable toward hydrolysis at room temperature from pH 0 to 11 and can be reducible to heteropoly blue species.^{16,21} Owing to the presence of a large number of tungsten atoms (W^{6+}) within a single cluster, the Pressler-type ions can store more electrons stably than other types of POM and they have been proved to be green, reusable and ecofriendly catalysts for many reactions. Herein, we selected $\text{NaP}_5\text{W}_{30}$ (preparation, $\text{ESI}^\dagger$) as a precursor to obtain an electron-rich heteropoly blue cluster, which was employed for the preparation of RGO by transferring electrons to GO (preparation, $\text{ESI}^\dagger$). In order to investigate the electron-transfer process between heteropoly blue and GO, two methods were carried out as follows.

For the first method (Method I), two hundred cycles of cyclic voltammetry (CV) were operated in 5 mmol L^{-1} $\text{NaP}_5\text{W}_{30}$

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Fig. 1 (A) UV-vis absorption spectra of 5 mmol L⁻¹ as-made NaP₅W₃₀ heteropoly blue solution (a), blue solution with a small amount of GO after 2 min (b) and 20 min (c), blank blue solution stored for 30 min (d). The insets show the photographs of NaP₅W₃₀ solutions representing curve a and curve c. (B) Absorbance values at 700 nm of 5 mmol L⁻¹ as-made NaP₅W₃₀ heteropoly blue solution as a function of time with/without GO addition.

aqueous solution between 0.1 V and -0.7 V. Then a deep blue NaP₅W₃₀ solution was obtained as shown in the photographic inset a of Fig. 1A, which showed a characteristic absorbance of heteropoly blue at 700 nm in the UV-vis absorption spectrum (curve a in Fig. 1A). As soon as 0.1 mg mL⁻¹ GO dispersion was dropped into the blue NaP₅W₃₀ solution, the color of the solution began to fade. Two minutes later the absorbance of the blue NaP₅W₃₀ aqueous solution decreased by nearly one-third, see curve b in Fig. 1A. Completely colorless solution (the photographic inset c of Fig. 1A) was produced after a period of twenty minutes, whose corresponding UV-vis absorption spectrum was measured as curve c in Fig. 1A. Actually, the color of the blue solution also gradually disappeared due to the presence of oxygen molecules in solution without GO addition. But the oxidation of NaP₅W₃₀ heteropoly blue by O₂ was a very slow process, its absorbance decreased by one-third after half an hour, as shown in curve d in Fig. 1A. In contrast to the fade process of blank NaP₅W₃₀ heteropoly blue solution (circle symbols in Fig. 1B), the decolor rate of blue NaP₅W₃₀ is doubled with the help of GO (square symbols in Fig. 1B). Simultaneously, some dark suspended solids appeared in the decolorized solution of NaP₅W₃₀, which were the reduced product of GO. The facts prove that electrons can be quickly transferred from heteropoly blue to GO. X-ray diffraction (XRD) results of the reduced products prove that the reduced GO is mixed with unreduced GO species (Fig. S1, ESI†). This indicates that such a method in which electrons are prestored in heteropoly blue, easily causes the incomplete and heterogeneous reduction of GO. On one hand, it is difficult to control the number of electrons stored in heteropoly blue and the number of electrons needed by the reduction of GO during the preparation and reduction procedure. On the other hand, the above uncertainty easily induces the partial electron transfer between heteropoly blue molecules and GO species.

Another method (Method II) was an instant reduction of GO by electrochemically scanning the mixture of NaP₅W₃₀ and

Fig. 2 CVs of bare GCE in a 0.5 mmol L⁻¹ NaP₅W₃₀ and 0.05 mg mL⁻¹ GO aqueous solution containing 5 mmol L⁻¹ HCl and 20 mmol L⁻¹ NaCl upon consecutive cycles. Scan rate is 20 mV s⁻¹.

GO solution. Three redox peak pairs were observable between 0 and -0.6 V in Fig. 2, which corresponded to two reduction steps of four electrons each at -0.35 V and -0.48 V and one additional multi-electron step at -0.65 V in NaP₅W₃₀.²¹ With the increase of CV cycles, the redox current of all peaks gradually enhanced. The reason is proposed that consecutive electron transfer from heteropoly blue species of NaP₅W₃₀ to GO triggered by electrochemical reduction cycles accelerates the formation of RGO. Enrichment of more and more RGO around the electrode surface enhances the electrochemical signal of NaP₅W₃₀ by providing a fast path for electron migration. Therefore, reduction of GO happened at a higher cathodic potential of -0.75 V with the help of heteropoly blue species, than the applied potentials reported elsewhere.¹¹⁻¹⁵ Essentially, NaP₅W₃₀ acted as a stable electrocatalyst for the reduction of GO, which received electrons from electrodes and then endowed GO enough electrons for its reduction. Photographs provided us with direct information about the reduction of GO (Fig. S2, ESI†). The mixture solution of NaP₅W₃₀ and GO was uniform and pale yellow (photo A in Fig. S2, ESI†). After two hundred CV cycles, the electron-rich blue solution became colorless and some suspended solids appeared (photo B in Fig. S2, ESI†). The black suspended solids deposited on the bottom of container overnight (photo C in Fig. S2, ESI†). The deposits were separated, washed and dried by a series of procedures. More importantly, the remaining filtrate can be reused for the electrocatalytic reduction of a new batch of GO, showing a green and economic process.

The reduced products of GO were characterized by atomic force microscopy (AFM), XRD, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Fig. S3 (ESI†) shows the AFM images of GO and RGO, where sheet structures are clearly visible. From the height profiles, the GO sheets measure about 1.2 nm in thickness. Values on the order of 0.9–1.3 nm are regarded as typical of single-sheet GO. The thickness of 1.5–2.0 nm for the RGO sheets is larger than the reported apparent thickness of single-sheet graphene and its roughness is greater than that of GO sheets. This is possibly attributed to the adsorption of NaP₅W₃₀ molecules on the RGO sheet surface during the electrocatalytic process. The result from XPS also confirms the existence of trace NaP₅W₃₀ in RGO (Fig. S4, ESI†). Moreover, the presence

Fig. 3 XPS spectra of GO (a) and RGO (b). Raman spectra of GO (c) and RGO (d).

of $\text{NaP}_5\text{W}_{30}$ in RGO generates electrostatic repulsion between RGO sheets and results in a stable dispersion of RGO in aqueous solution without deposition (Fig. S5, ESI[†]). Results from XRD indicate the formation of RGO, where a broad peak around 24° appeared instead of a sharp peak for GO sheets (Fig. S6, ESI[†]).

XPS was also employed to confirm reduction of GO by comparing the amounts of epoxide and hydroxyl groups before and after electrochemical reduction. Four types of C 1s are present in the precursor GO (Fig. 3a), containing 3.5% of $\text{O}-\text{C}=\text{O}$ centered around 288.9 eV, 3.4% of $\text{C}=\text{O}$ centered around 288.0 eV, 39.4% of $\text{C}-\text{O}$ centered around 286.8 eV and 53.7% of sp^2 $\text{C}-\text{C}$ centered around 284.8 eV. After reduction, the content of sp^2 $\text{C}-\text{C}$ increased to 83.6% while a total of only 16.4% oxygenated carbon remained in RGO in Fig. 3b. This deoxygenation efficiency was similar to the value of RGO obtained at -1.1 V.¹⁵ Clearly, electron transfer from $\text{NaP}_5\text{W}_{30}$ heteropoly blue to GO for the reduction of GO was very effective by the electrochemical method. In addition, two strong peaks corresponding to a D peak at 1350 cm^{-1} and a G peak at 1595 cm^{-1} were observed in the Raman spectra of both GO sample (Fig. 3c) and RGO sample (Fig. 3d). Moreover, the D/G intensity ratio of RGO was larger than that of GO, suggesting an increased number of smaller RGO domains upon reduction of GO. In other words, GO has been reduced to RGO by the electrocatalytic role of $\text{NaP}_5\text{W}_{30}$.

Although a trace of $\text{NaP}_5\text{W}_{30}$ is present in RGO sheets after electrochemical reduction reaction, to some degree, RGO is actually endowed with electrocatalytic activity in electrochemical applications. Noble metal loaded graphene is generally utilized to electrocatalyze the hydrogen evolution reaction (HER),²² but there is no reported example of electrocatalytic HER by POM loaded RGO. In this case, the electrocatalytic activity of RGO immobilized GCE towards HER was investigated. As shown in Fig. 4a, HER occurs on bare GCE from the potential of -0.8 V in 0.5 mol L^{-1} H_2SO_4 aqueous solution. When RGO obtained by our method is immobilized on GCE, the reduction peak of H^+ in 0.5 mol L^{-1} H_2SO_4 aqueous solution is obviously shifted to a more positive potential (onset potential is -0.43 V) accompanied by largely enhanced current (Fig. 4c). For comparison, RGO prepared by electrochemical reduction at -1.5 V¹³ (ERGO) without any electrocatalysts was also modified on GCE and it displayed a slightly

Fig. 4 Linear sweep voltammetry of bare GCE (a), ERGO/GCE (b) and RGO prepared by $\text{NaP}_5\text{W}_{30}$ electrocatalysis immobilized on GCE (c) in 0.5 mol L^{-1} H_2SO_4 at a scan rate of 20 mV s^{-1} . Inset shows CV of RGO/GCE in 0.5 mol L^{-1} H_2SO_4 .

lower reduction potential (Fig. 4b) than RGO. This result suggests RGO has better electrocatalytic activity for HER in the presence of $\text{NaP}_5\text{W}_{30}$ than ERGO. The inset of Fig. 4 also provides evidence of the existence of $\text{NaP}_5\text{W}_{30}$ by showing some characteristic redox peaks of $\text{NaP}_5\text{W}_{30}$ on RGO modified GCE. Further investigation of the $\text{NaP}_5\text{W}_{30}$ -RGO composite for hydrogen generation by light-driven water splitting is ongoing. Based on this finding, it is possible for RGO to be applied in more catalytic fields by loading different POM clusters.

In summary, two facile strategies are proposed to investigate the electron transfer from heteropoly blue to graphene oxide for the synthesis of graphene. The method of prestoring electrons in $\text{NaP}_5\text{W}_{30}$ clusters in the form of heteropoly blue causes low-effective and heterogeneous reduction of graphene oxide. Another method of instantly transferring electrons from $\text{NaP}_5\text{W}_{30}$ heteropoly blue to graphene oxide can realize high-effective reduction of graphene oxide. By highly effective electron transfer from electron-rich heteropoly blue to graphene oxide, the reduction potential of GO shows a positive shift of nearly 750 mV, suggesting $\text{NaP}_5\text{W}_{30}$ acts as a stable electrocatalyst for the reduction of GO. The resultant RGO modified GCE electrode shows more positive potential for hydrogen evolution owing to the presence of the polyoxometalate electrocatalyst. Future prospects of this work are suggested by us from the following points: (1) the wheel-shaped polyoxometalates containing catalytic active metal atoms can be considered to electrocatalytically reduce GO for further oxygen reduction application, (2) Ru-containing polyoxometalate is chosen to prepare RGO-POM nanocomposites by electrochemical reduction for efficient water oxidation and (3) different polymolybdic POM electrocatalysts can be trialed due to the positive reduction potential.

Experimental

Preparation of $\text{NaP}_5\text{W}_{30}$ heteropoly blue by Method I

The electrochemical cell was filled with a 5 mmol L^{-1} $\text{NaP}_5\text{W}_{30}$ aqueous solution containing 5 mmol L^{-1} HCl and 20 mmol L^{-1} NaCl . A 2 cm^2 ITO working electrode, an Ag/AgCl reference

electrode and a Pt wire auxiliary electrode were immersed into the electrolyte solution. Preparation of $\text{NaP}_5\text{W}_{30}$ heteropoly blue was performed by carrying out CV in the potential range of 0.1 V to -0.7 V at a scan rate of 20 mV s^{-1} for 200 cycles with consecutive magnetic stirring. The resultant $\text{NaP}_5\text{W}_{30}$ heteropoly blue solution was used for further electron-transfer reaction.

Reduction of GO by Method II

A 5 mmol L^{-1} $\text{NaP}_5\text{W}_{30}$ aqueous solution, containing 5 mmol L^{-1} HCl and 20 mmol L^{-1} NaCl, was mixed with 0.05 mg mL^{-1} GO dispersion. The mixture was used to fill an electrochemical cell and purged with nitrogen for 30 min. A GCE working electrode with a diameter of 3 mm, an Ag/AgCl reference electrode and a Pt wire auxiliary electrode were immersed into the electrolyte solution. CVs were carried out in the potential range of 0.1 V to -0.75 V at a scan rate of 20 mV s^{-1} for 40 cycles with consecutive magnetic stirring. Reduction of GO proceeded with CV scanning and the reduced product RGO appeared at the bottom of the electrochemical cell after a period of deposition.

Separation of RGO

After the mixture of $\text{NaP}_5\text{W}_{30}$ and GO aqueous solution was electrochemically scanned for the required cycles, the composite solution was left for 24 h to deposit black RGO. By centrifugation at 5000 rpm, the black deposits were separated. The RGO was washed with deionized water several times and dried in vacuum to give black solids.

Modification of RGO on GCE for catalyzing hydrogen evolution reaction

To prepare RGO modified electrodes, 0.5 mg of RGO was dispersed into 1 mL water to give homogeneous suspension upon bath ultrasonication. A $5 \mu\text{L}$ sample of the suspension was dip-coated onto a GCE surface and dried at ambient temperature for 24 h to give a RGO immobilized GCE.

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Notes and references

- 1 X. L. Li, X. R. Wang, L. Zhang, S. W. Lee and H. J. Dai, *Science*, 2008, **319**, 1229–1232.
- 2 Q. L. Zhang, T. Q. Xu, J. Wei, J. R. Chen, A. J. Wang and J. J. Feng, *Electrochim. Acta*, 2013, **112**, 127–132.
- 3 K. Zhang, L. L. Zhang, X. S. Zhao and J. Wu, *Chem. Mater.*, 2010, **22**, 1392–1401.
- 4 Y. H. Ng, A. Iwase, A. Kudo and R. Amal, *J. Phys. Chem. Lett.*, 2010, **1**, 2607–2612.
- 5 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183–191.
- 6 A. Zangwill and D. D. Vvedensky, *Nano Lett.*, 2011, **11**, 2092–2095.
- 7 H. Wang, D. Zhang, T. Yan, X. Wen, L. Shi and J. Zhang, *J. Mater. Chem.*, 2012, **22**, 23745–23748.
- 8 S. Park and R. S. Ruoff, *Nat. Nanotechnol.*, 2009, **4**, 217–224.
- 9 H. Wang, D. Zhang, T. Yan, X. Wen, J. Zhang, L. Shi and Q. Zhong, *J. Mater. Chem. A*, 2013, **1**, 11778–11789.
- 10 G. Williams, B. Seger and P. V. Kamat, *ACS Nano*, 2008, **2**, 1487–1491.
- 11 H. L. Guo, X. F. Wang, Q. Y. Qian, F. B. Wang and X. H. Xia, *ACS Nano*, 2009, **3**, 2653–2659.
- 12 M. Zhou, Y. Wang, Y. Zhai, J. Zhai, W. Ren, F. Wang and S. Dong, *Chem. - Eur. J.*, 2009, **15**, 6116–6120.
- 13 Y. Y. Shao, J. Wang, M. Engelhard, C. M. Wang and Y. H. Lin, *J. Mater. Chem.*, 2010, **20**, 743–748.
- 14 L. Y. Chen, Y. H. Tang, K. Wang, C. B. Liu and S. L. Luo, *Electrochem. Commun.*, 2011, **13**, 133–137.
- 15 X.-Y. Peng, X.-X. Liu, D. Diamond and K. T. Lau, *Carbon*, 2011, **49**, 3488–3496.
- 16 M. Jiang, E. B. Wang, G. Wei, L. Xu, Z. H. Kang and Z. Li, *New J. Chem.*, 2003, **27**, 1291–1293.
- 17 M. Jiang, X. D. Zhai and M. H. Liu, *J. Mater. Chem.*, 2007, **17**, 193–200.
- 18 G. L. Cao, J. Xiong, Q. Xue, S. T. Min, H. M. Hu and G. L. Xue, *Electrochim. Acta*, 2013, **106**, 465–471.
- 19 S. Wang, H. Li, S. Li, F. Liu, D. Wu, X. Feng and L. Wu, *Chem. - Eur. J.*, 2013, **19**, 10895–10902.
- 20 S. Li, R. Liu, R. N. Biboum, B. Lepoittevin, G. Zhang, A. Dolbecq, P. Mialane and B. Keita, *Eur. J. Inorg. Chem.*, 2013, 1882–1889.
- 21 I. Creaser, M. C. Heckel, R. J. Neitz and M. T. Pope, *Inorg. Chem.*, 1993, **32**, 1573–1578.
- 22 C. H. Xu, B. H. Xu, Y. Gu, Z. G. Xiong, J. Sun and X. S. Zhao, *Energy Environ. Sci.*, 2013, **6**, 1388–1414.