

Electronic Supplementary Information for One-Step Potentiodynamic Synthesis of Poly(1,5-diaminoanthraquinone)/Reduced Graphene Oxide Nanohybrid with Improved Electrocatalytic Activity

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Preparation of Graphene Oxide

Typical synthesis process of GO was as follows.^{1,2} graphite powder (10 g, 600 mesh), K₂S₂O₈ (5 g) and P₂O₅ (5 g) were added to an 80 °C solution of 100 mL concentrated H₂SO₄, keeping stirring for 6 h. Then the mixture was cooled in room temperature for 12 h, followed by washed with distilled water until it became neutral and dried. The pre-oxidized graphite (10 g) was placed in a flask. Concentrated H₂SO₄ (230 mL) was added slowly with stirring in an ice-water bath while the temperature was controlled not to exceed 20 °C. Then, KMnO₄ (30 g) was added gradually and keep stirring for 2 h. The solution was then stirred at 35 ± 3 °C for 2 h. 460 mL of distilled water was slowly added to cause an increase in temperature to 85 °C, and the solution was kept at the temperature for 30 min. 1.4 L of distilled water and 25 mL of 30 wt% H₂O₂ were added, the color of the mixture was bright yellow. After placed for 24 h, the product was filtered and washed with 5wt% HCl aqueous solution until there was no SO₄²⁻. The product was then centrifuged and the precipitate was directly dried on the glass with a thin layer or the precipitate was directly dispersed in the aqueous solution by using a supersonic cleaner for next experimental step.

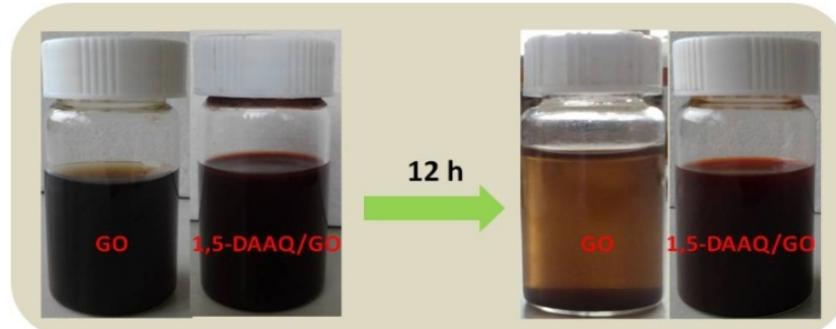


Fig. S1 Photograph of the dispersion of GO and 1,5-DAAQ/GO in ethanol.

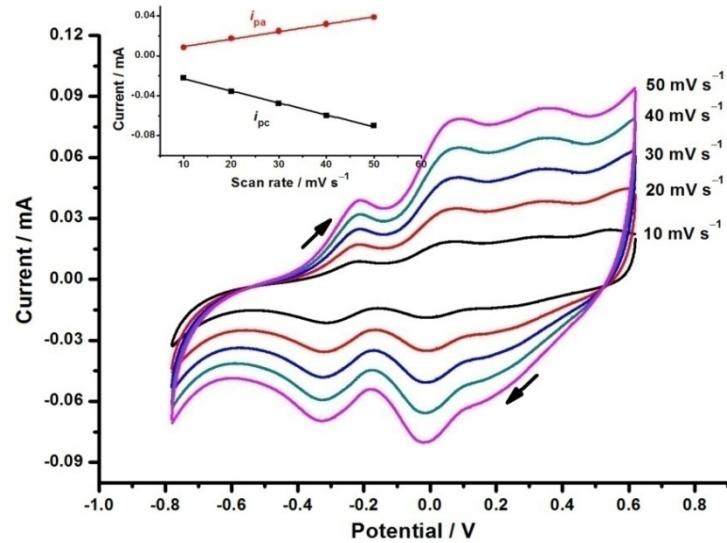


Fig. S2 CVs of P(1,5-DAAQ)/RGO-GCE in N_2 -saturated 1.0 M H_2SO_4 solution at various scan rates. The inset shows the plot of peak current (i_{pa} and i_{pc}) vs. scan rate.

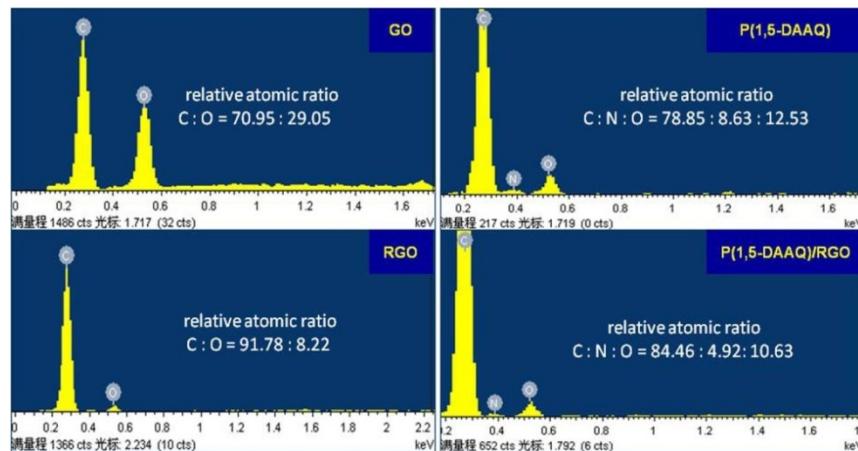


Fig. S3 EDS patterns of GO, P(1,5-DAAQ), RGO and P(1,5-DAAQ)/RGO nanohybrid film, and the corresponding relative atomic ratio.

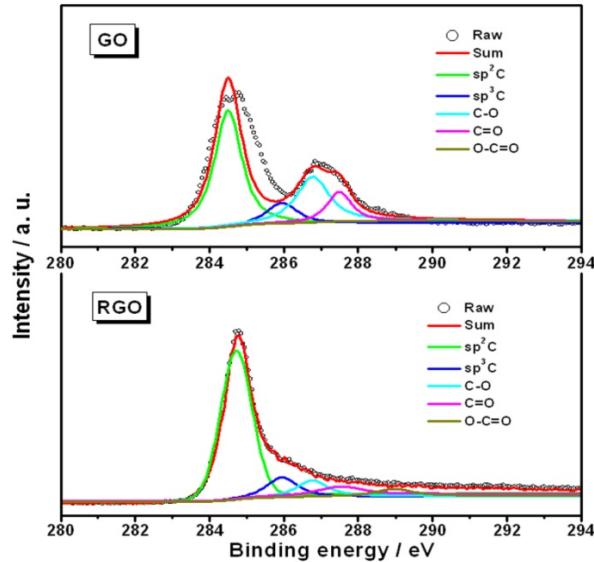


Fig. S4 Deconvoluted C 1s XPS spectra of GO and RGO.

The core level high resolution C 1s XPS spectra of GO and RGO were shown in Fig. S4. From the C 1s XPS spectrum of GO, five different peaks centered at 284.5, 285.6, 286.8, 287.5, and 289.2 eV were observed, which are assigned to sp^2 C, sp^3 C, C–O (hydroxyl and epoxy), C=O (carbonyl) and O–C=O (carboxyl) oxygen-containing functional groups, respectively. These results agree well with those of previous studies.³⁻⁵ After the electro-reduction of GO, the spectrum of RGO shows that the intensities of C 1s peaks of the carbons binding to oxygen and the peak of sp^3 C decrease, while the peak of sp^2 C increases accordingly, revealing that most of the oxygen-containing functional groups are removed and the efficient reduction of GO.

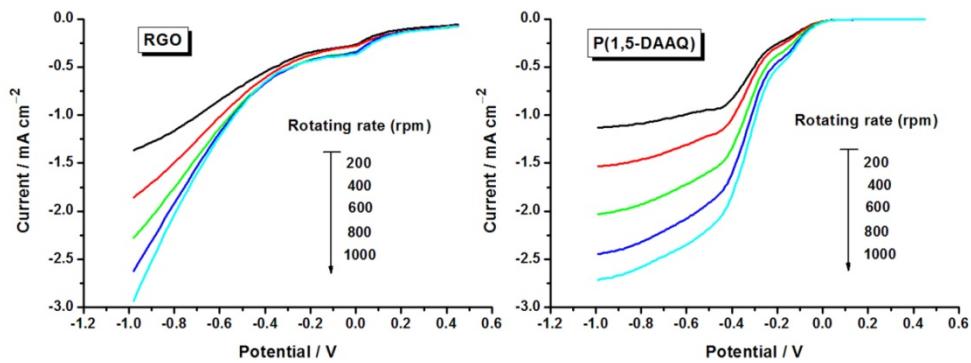


Fig. S5 RDE linear sweep voltammograms of RGO and P(1,5-DAAQ) in O_2 -saturated 1.0 M H_2SO_4 solution with various rotation rates at a scan rate of 10 mV s^{-1} .

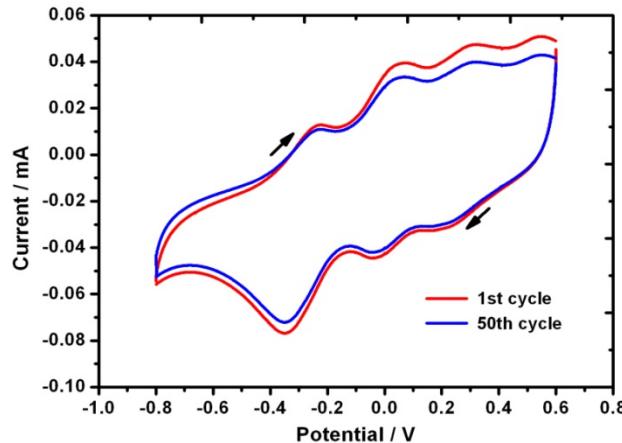


Fig. S6 The 1st and 50th CV curves of the P(1,5-DAAQ)/RGO-GCE in O₂-saturated 1.0 M H₂SO₄ solution at scan rate of 20 mV s⁻¹.

Table S1 Main IR bands (cm⁻¹) and their possible assignments of P(1,5-DAAQ)/RGO nanohybrid film and 1,5-DAAQ monomer.

Possible assignments	1,5-DAAQ monomer	P(1,5-DAAQ)/RGO
C=O (quinone)	1608	1608
C=C _{aromatic}	-	1580, 1504
C=N stretch (imino group)	-	1658
N–H deformation	1545 (primary amine)	1504 (secondary amine)
C–N stretching	-	
primary amino group	1275	1290
secondary amino group	-	1225
C–N–C stretching	1332	1327
N–H stretching		
–NH ₂ (asymmetric)	3423	-
–NH ₂ (symmetric)	3315	3448
–NH ₂ bending	494	494 (very weak)
C–H out-of-plane bending		
of 2H	856	837
of 3H	705-810	710-750

Notes and references

- 1 F. Lima, G. V. Fortunato, and G. Maia, *RSC Adv.*, 2013, **3**, 9550;
- 2 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.
- 3 Z. J. Fan, W. Kai, J. Yan, T. Wei, L. J. Zhi, J. Feng, Y. M. Ren, L. P. Song, and F. Wei, *ACS Nano*, 2011, **5**, 191.
- 4 H. R. Byon, J. Suntivich, and S. H. Yang, *Chem. Mater.*, 2011, **23**, 3421.
- 5 K. R. Lee, K. U. Lee, J. W. Lee, B. T. Ahn, and S. I. Woo, *Electrochim. Commun.*, 2010, **12**, 1052.