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Electronic Supplementary Information

Nitrogen doped holey graphene as efficient metal-free multifunctional electrochemical catalysts for hydrazine oxidation and oxygen reduction

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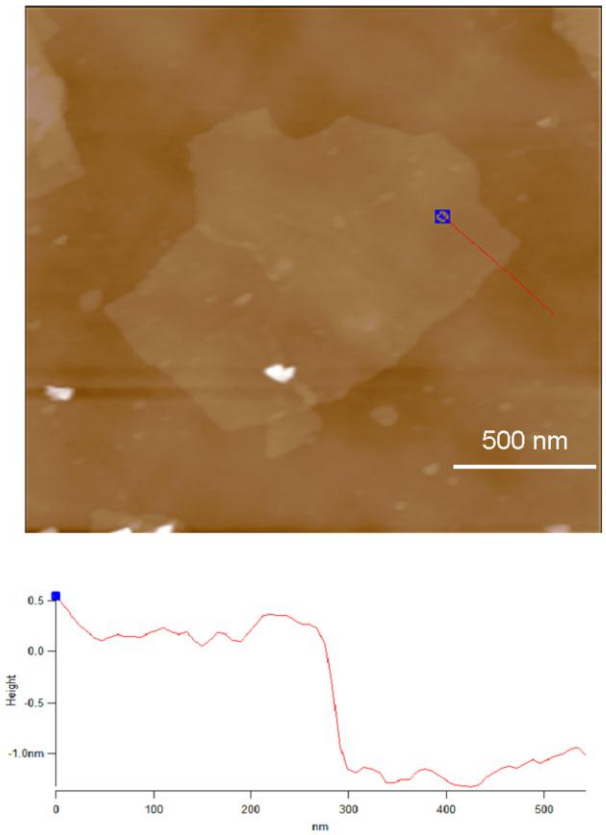

Fig. S1 AFM image and its corresponding height profile (along red line) of GO sheets deposited on Si wafer.

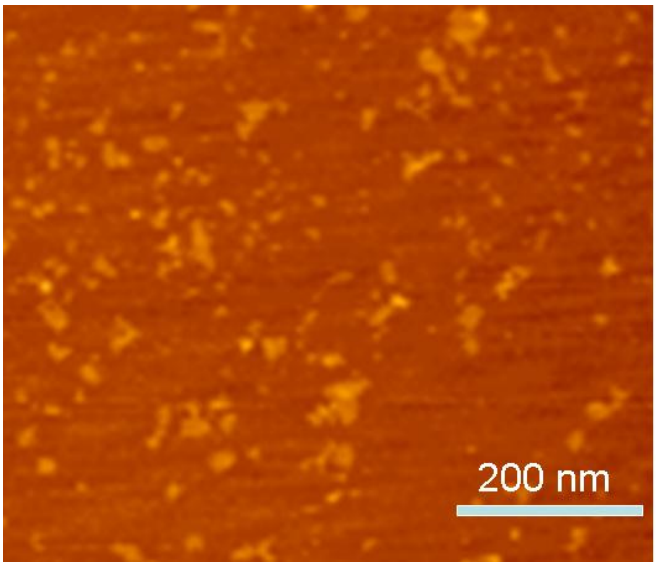

Fig. S2 AFM image of GO sheets after bath sonication for 60 min in HNO_3.

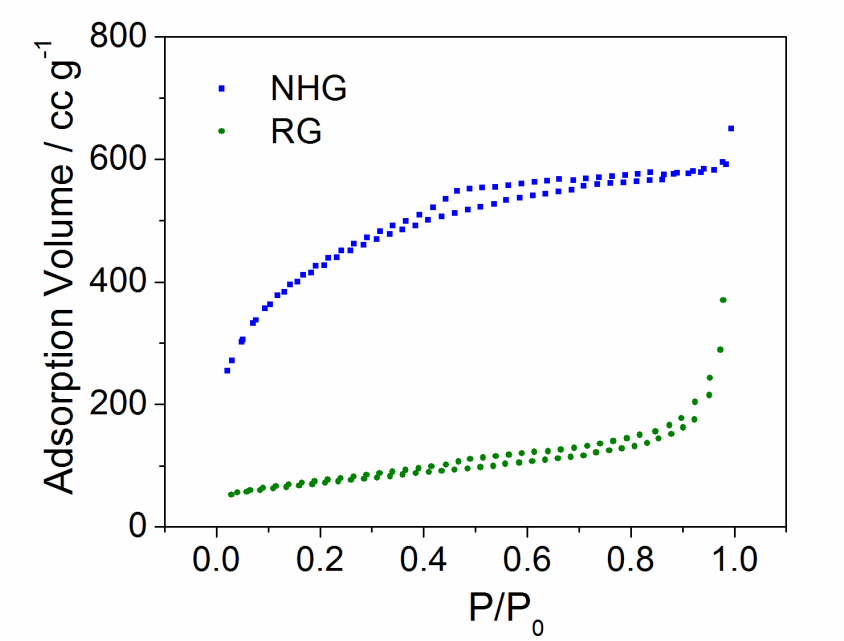

Fig. S3. Nitrogen adsorption/desorption isotherms of NHG and RG.

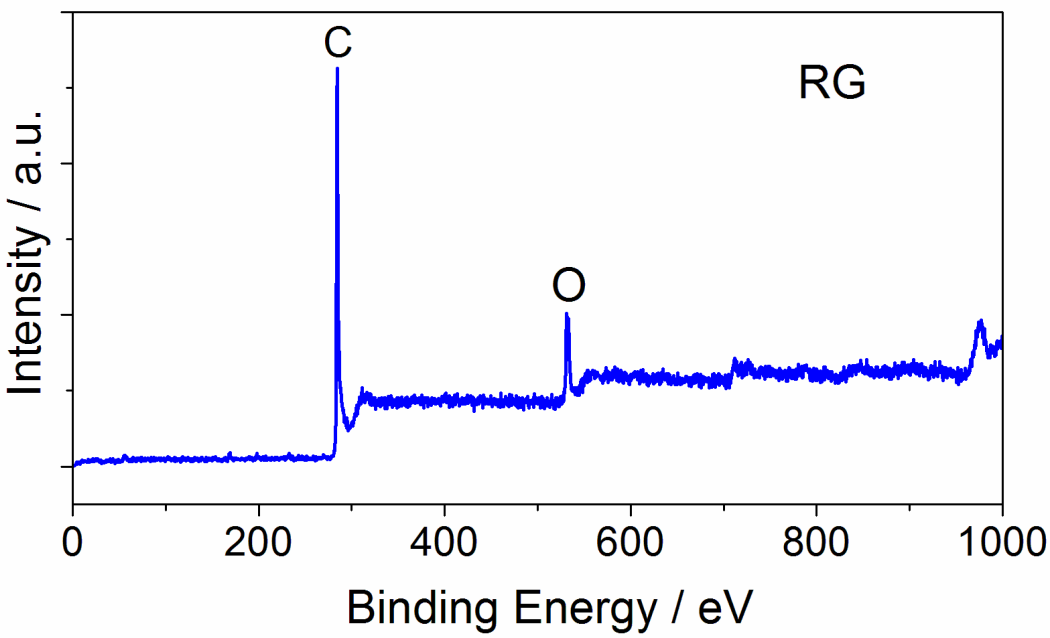

Fig. S4 XPS spectrum of RG.

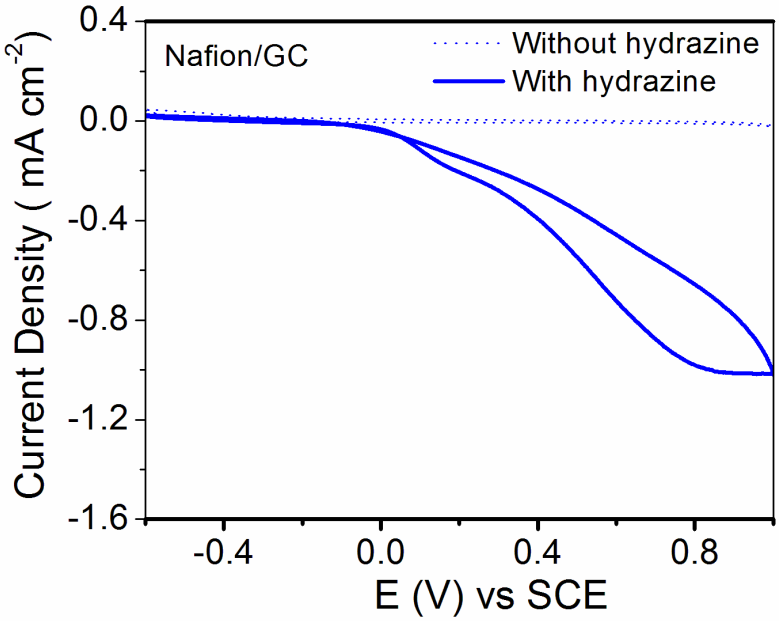

Fig. S5 CV curve obtained on a Nafion-coated GC (Nafion/GC) electrode in a nitrogen-saturated 0.1 M pH 7.4 PBS solution in the absence (dash lines) and in the presence (solid lines) of 10 mM hydrazine at a scan rate of 20 mV/s

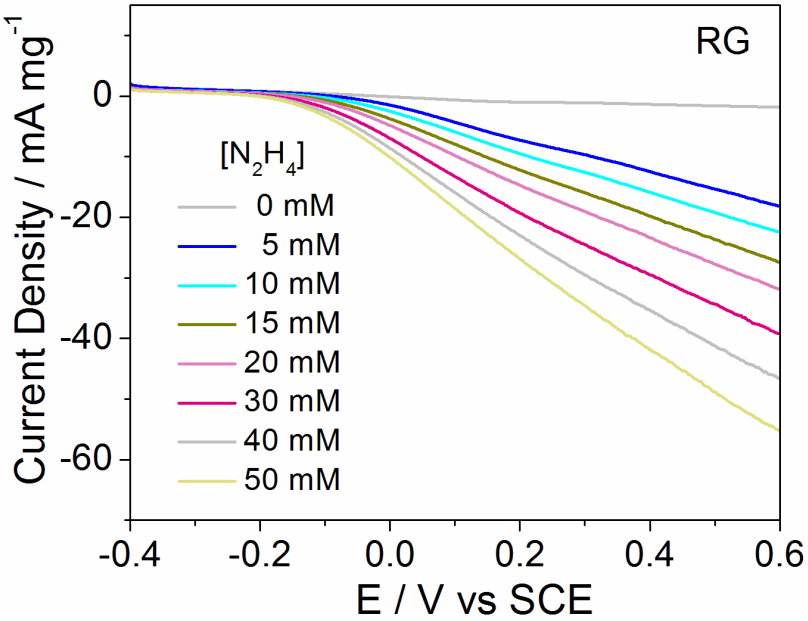

Fig. S6 RDE curves at 20 mV/s of the RG/GC electrode at 900 rpm in a nitrogen-saturate 0.1 M PBS solution at pH=7.4 as a function of the concentration of hydrazine from 0 to 50 mM.

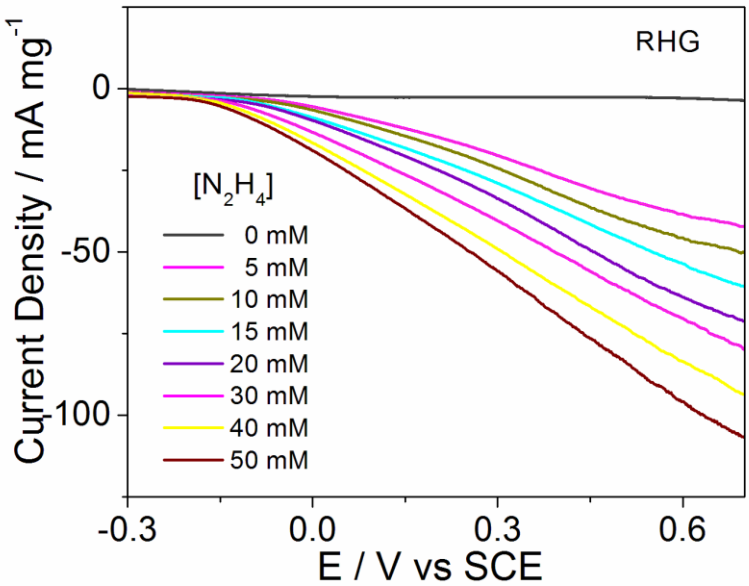

Fig. S7 RDE curves at 20 mV/s of the RHG/GC electrode at 900 rpm in a nitrogen-saturate 0.1 M PBS solution at pH=7.4 as a function of the concentration of hydrazine from 0 to 50 mM.

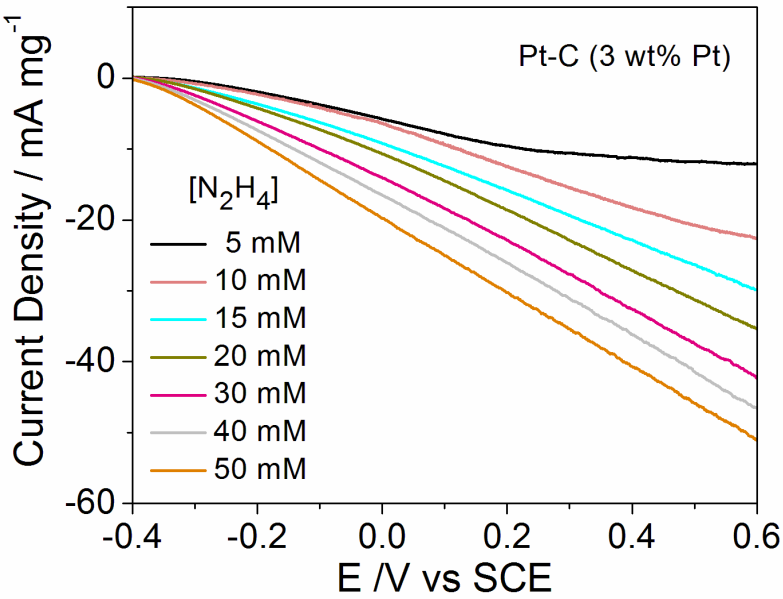

Fig. S8 RDE curves at 20 mV/s of the Pt-C (3 wt% Pt)/GC electrode at 900 rpm in a nitrogen-saturated 0.1 M PBS solution at pH=7.4 as a function of the concentration of hydrazine from 5 to 50 mM.

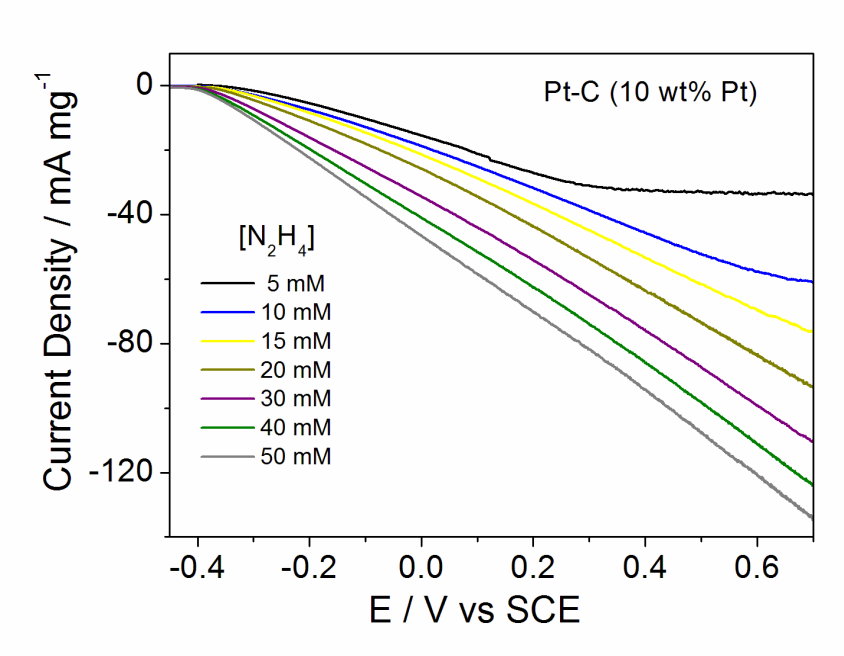

Fig. S9 RDE curves at 20 mV/s of the Pt-C (10 wt% Pt)/GC electrode at 900 rpm in a nitrogen-saturated 0.1 M PBS solution at pH=7.4 as a function of the concentration of hydrazine from 5 to 50 mM.

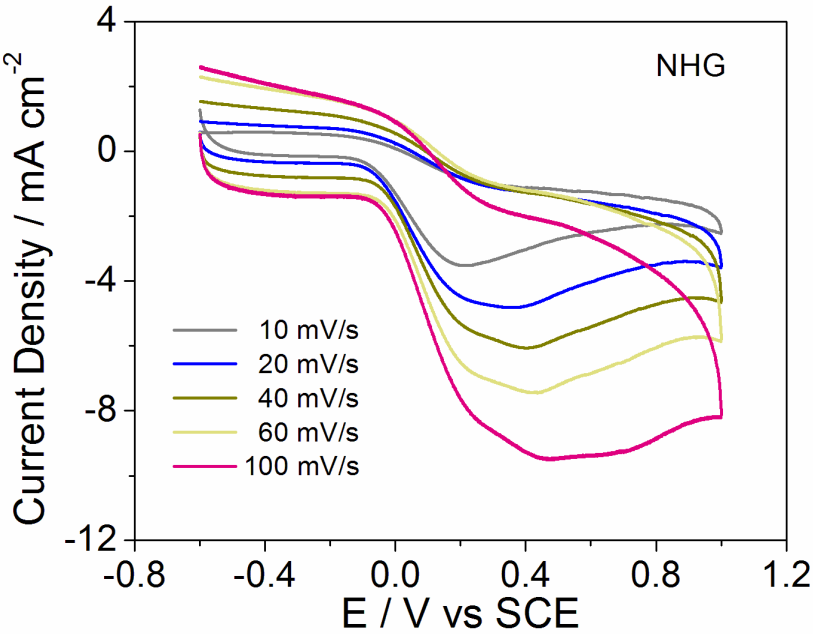

Fig. S10 CV curves of the NHG/GC electrode in a nitrogen-saturated 0.1 M PBS solution (pH=7.4) containing 10 mM hydrazine as a function of scan rate.

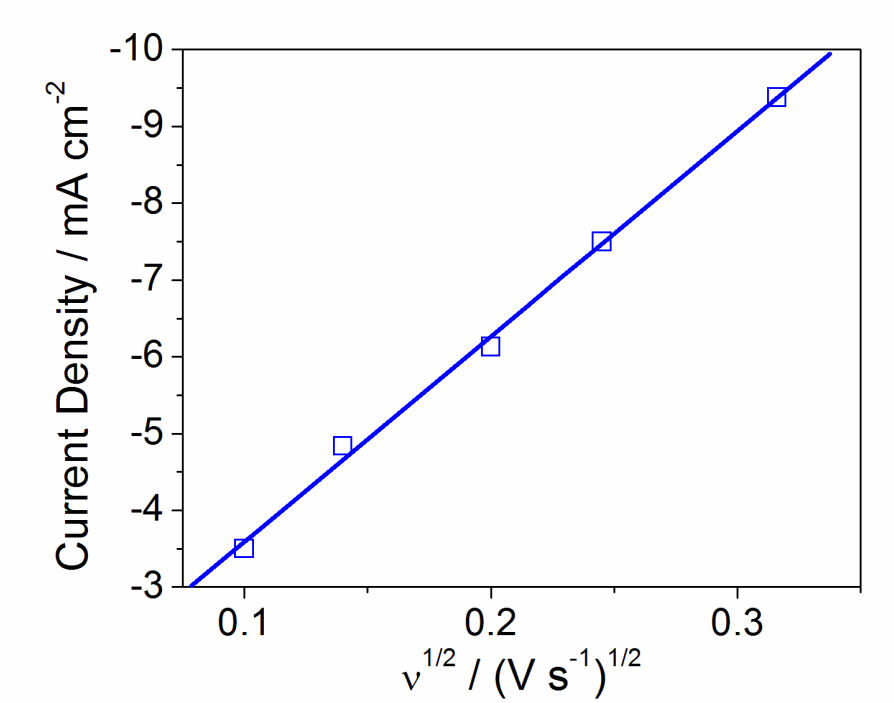

Fig. S11 Plot of catalytic oxidation peak current density of hydrazine on the NHG/GC electrode versus square root of scan rates.

To better understand the mechanism of hydrazine oxidation on the NHG/GC electrode, the effect of CV scan rate was studied in the range of 10–100 mV/s in 0.1 M PBS solution containing 10 mM hydrazine. As shown in Fig. S10, the peak current density increases, and the peak potential shifts positively with the increase of scan rate. It confirms the irreversible nature of hydrazine oxidation.[1] The peak current density varies linearly with the square root of scan rate (see Fig. S11), indicating a typical diffusion-controlled reaction kinetics.[3] The number of total electrons (n) involved in hydrazine oxidation can be obtained according to the following equation: [2]

$$I_P = 3.01\times10^5\, n[(1-\alpha)n_\alpha]^{1/2} A C_h D^{1/2} v^{1/2} \qquad (1)$$

where I_p, n, α, A, C_h, and D are peak current, electron transfer number, electron transfer coefficient, electrode surface area, hydrazine concentration, and hydrazine diffusion efficient,

respectively. The value of n is estimated to be ~3.9, from the slope of the plot of I_p vs $\nu^{1/2}$, considering $(1-\alpha)n_\alpha = 0.48$,[1, 2] $C_h = 10$ mM, $D = 1.8\times10^{-5}$ cm^2 S^{-1} (D is obtained from chronoamperometry results, see Fig. S12-S13). This suggests that the hydrazine oxidation on the NHG/GC electrode is a four-electron transfer process. We propose the overall reaction of the hydrazine oxidation catalyzed by NHG as following: [3, 4]

$$N_2H_4 \rightarrow N_2 + 4\,H^+ + 4\,e^- \qquad (2)$$

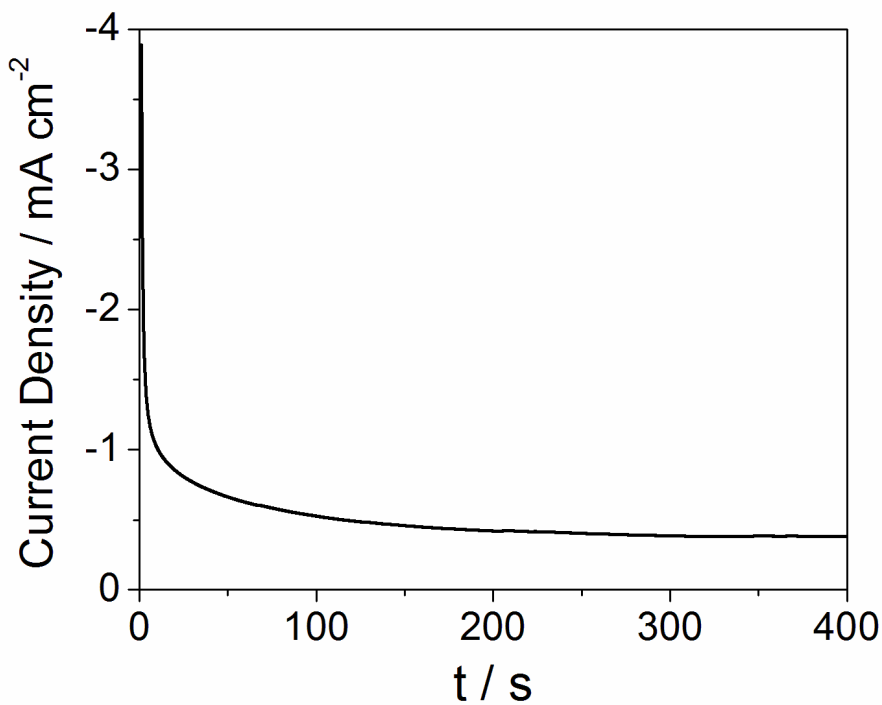

Fig. S12 Amperometric curve of the NHG/GC electrode at peak potential in a 0.1 M PBS solution at pH=7.4 in the presence of 5 mM hydrazine.

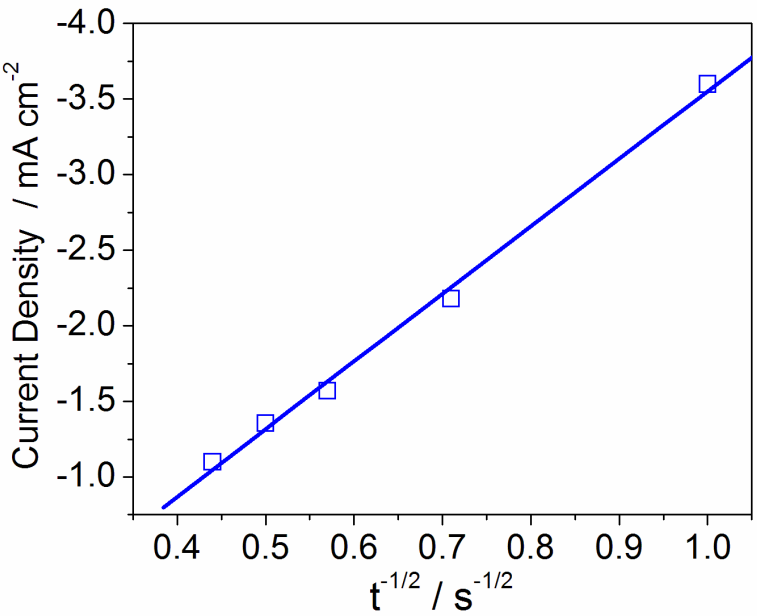

Fig. S13 Cottrell plot drawn using data obtained from chronoamperogram (Fig. S12)**.**

Chronoamperometry was used to determine the diffusion coefficient (D) of hydrazine by setting the working electrode potential at 0.35 V. The diffusion coefficient of hydrazine was obtained according to the Cottrell equation:[5]

$$I = nFAC_h D^{1/2} \pi^{-1/2} t^{-1/2}$$

Where D is diffusion coefficient ($cm^2\ s^{-1}$), A is effective electrode area (cm^2), and C_h (M) is the hydrazine concentration. Considering n = 4 (electron transfer number), F = 96485 C mol^{-1}, and C_h = 0.005 M, The D value can be obtained from the slope (-4.5) of the linear plot shown in Figure S13 to be about 1.8×10^{-5} $cm^2\ s^{-1}$, which is comparable to the reported value in the literature.[1]

References

[1] Y. Wang, Y. Wan, D. Zhang, *Electrochem. Comm.* **2010**, *12*, 187-190.

[2] J. Li, X. Q. Lin, *Sens. Actuators B* **2007**, *126*, 527-535.

[3] M. M. Ardakani, P. E. Karami, P. Rahimi, H. R. Zare, H. Naeimi, *Electrochim. Acta* **2007**, *52*, 6118-6124.

[4] B. Dong, B. He, J. Huang, G. Gao, Z. Yang, H. Li, *J. Power Sources* **2008**, *175*, 266-271.

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