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Electronic Supplementary Information

Enhanced NO_2 sensing performance of reduced graphene oxide by *in-situ* anchoring carbon dots

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Preparation of GO

Typically, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was added to a mixture of graphite flakes (3.0 g) and $KMnO_4$ (18.0 g). The reaction was then heated to 50 °C and stirred for 12 h. The reaction was cooled to room temperature and poured onto ice (400 mL) with 30 % H_2O_2 (3.0 mL). After that, the mixture was centrifuged (5000 rpm for 30 min) to remove the residual of graphite flakes. Then the obtained solution was centrifuged (5000 rpm for 4 h), and the supernatant was decanted away. The remaining solid material was then redispersed in 200 mL of water and separated by centrifugation and washed several times with 5 % HCl solution. The product was then washed several times with distilled water and dried overnight in an oven at 60 °C.[1]

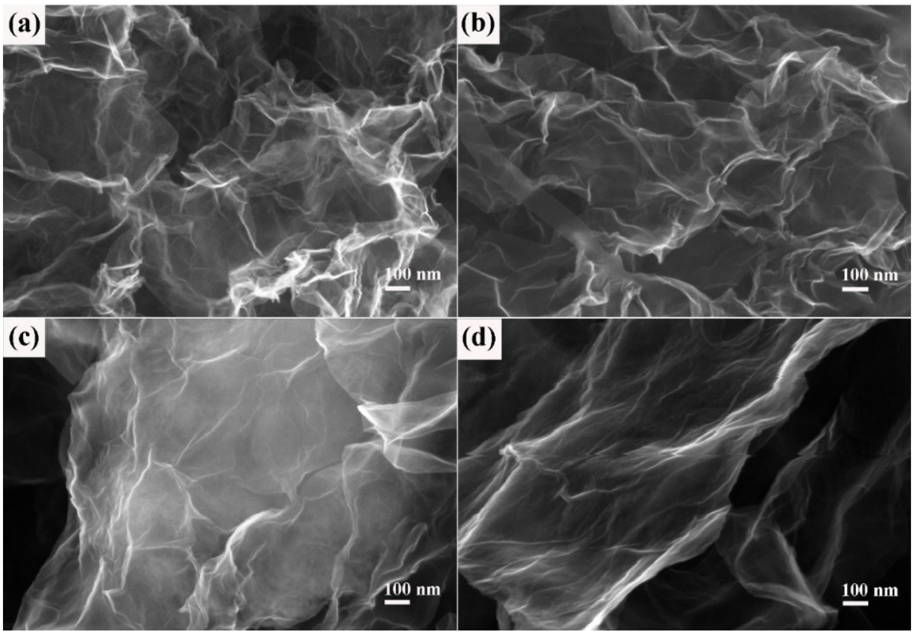

Fig. S1 SEM images of the GO nanosheet (a), rGO(300/1-air) nanosheet (b), rGO-CDs hybrids (c) and rGO-CDs(300/1-air) hybrids (b).

XRD pattern and FTIR spectra of GO:

As shown in Fig. S2a, the GO exhibit a sharp peak (002) at 2θ =11.6° corresponding to the presence of various types of atomic-level structural defects (sp^3 bonding) and nanoholes, various oxygen functionalities (e.g., OH, CO_2H), and intercalated water molecules attached to both sides of the GO.[2, 3] In Fig. S2b, the wide and strong band of GO at 3400 cm^{-1} indicated the existence of hydroxyl groups, while the strong band at ~2850 cm^{-1} and ~1750 cm^{-1} corresponded to the C-H and C=O groups. The band at ~1620 cm^{-1} was for the aromatic C=C groups, while the peak at ~1072 cm^{-1} was for the C-O groups and ~1250 cm^{-1} for the C-OH stretching.[2] The other characteristic peaks at ~1380 and ~1067 cm^{-1} were assigned to C-O-C asymmetric and symmetric vibrations, respectively.

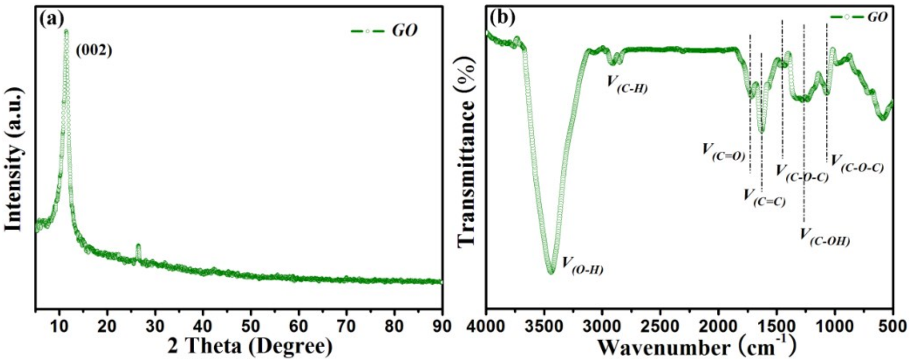

Fig. S2 (a) XRD pattern of GO. (b) FTIR spectra of GO.

Sensing response of rGO-CDs hybrids synthesized by various temperature, weight of citric acid, volume of ethylenediamine and time, respectively. The synthesis experiments followed the principle of single variable.

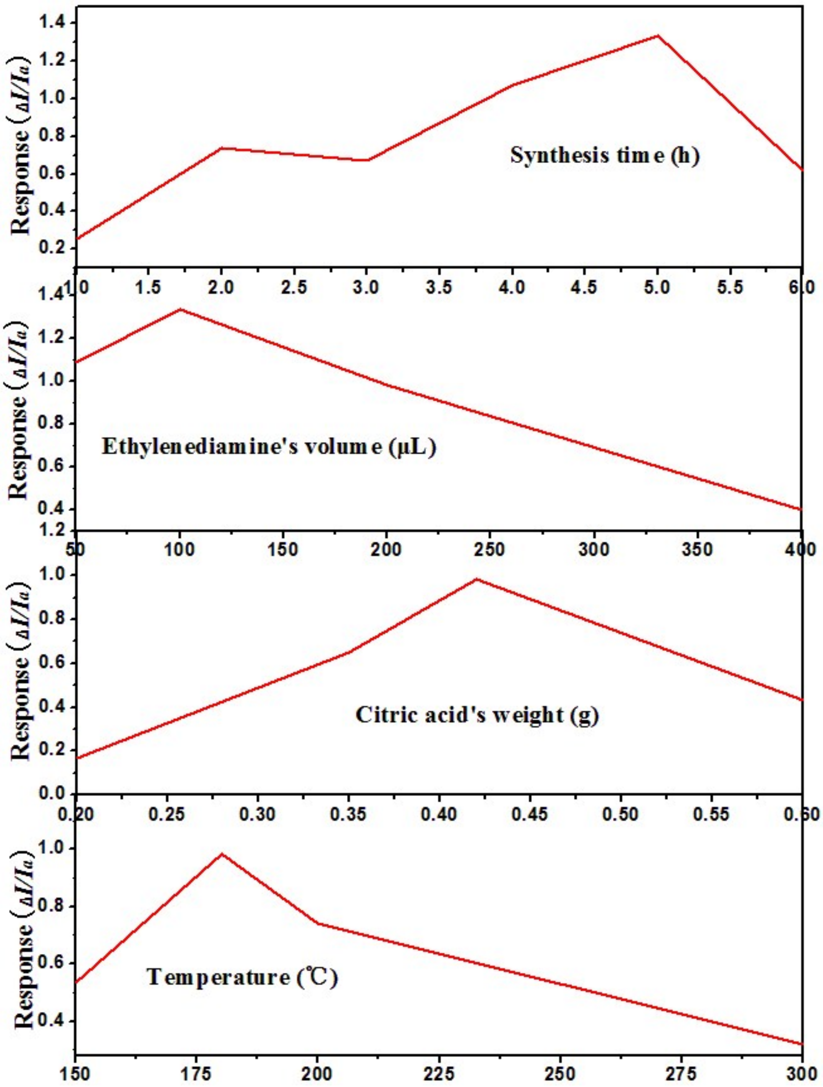

Fig. S3 Response of the rGO-CDs synthesis by different temperature, weight of citric acid, volume of ethylenediamine and time upon exposure to 50 ppm NO_2 gas, respectively.

As shown in Fig. S4, with 0.42 g citric acid and 5 mL 0.45 mg/mL GO aqueous solution, various weight of urea was hydrothermal treated at 180 ℃ for 5 h. The obtained products were annealed at 300 ℃ for 1 h and then measured their sensing characteristics of 50 ppm NO_2 gas at room temperature.

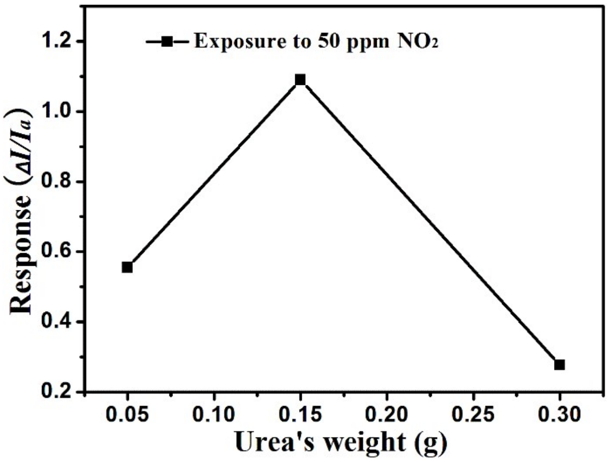

Fig. S4 Response of the rGO-CDs synthesis by different weight of urea.

Raman spectra of GO, rGO, rGO(300/1-air), rGO-CDs, rGO-CDs(300/1-air), rGO-CDs(300/1-N_2) and rGO-CDs(300/2-air) in Fig. S5a were tested at room temperature. TGA curves of rGO under air flow, rGO-CDs under air flow and N_2 flow were shown in Fig. S5c. The rGO-CDs of different annealing conditions were exposure to 50 ppm of NO_2 gas to check the sensing performance. The results were illustrated in Fig. S5d.

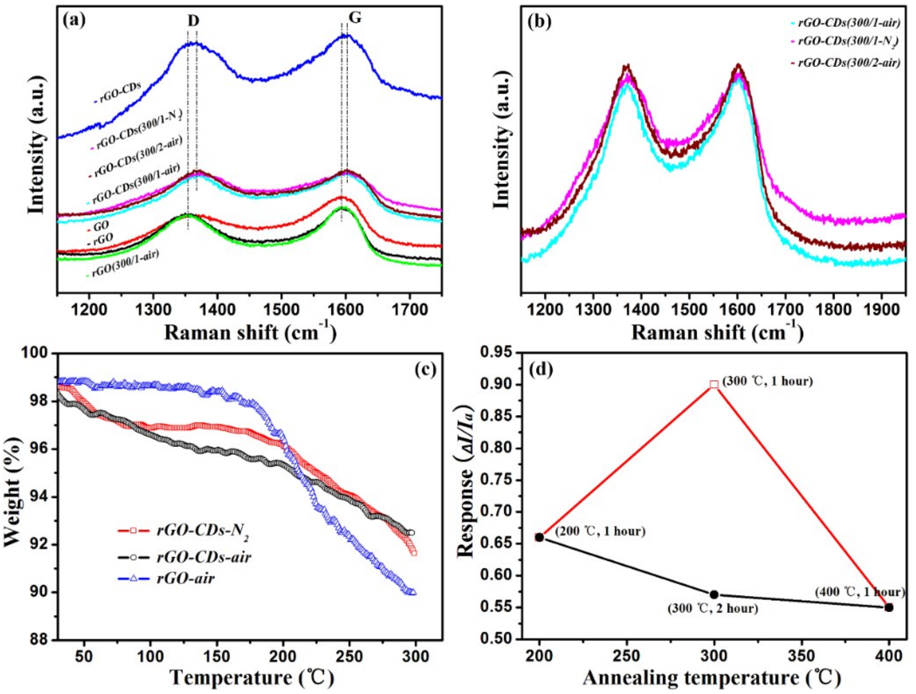

Fig. S5 (a) Raman spectra of GO, rGO, rGO(300/1-air), rGO-CDs, rGO-CDs(300/1-air), rGO-CDs(300/1-N_2) and rGO-CDs(300/2-air), respectively. (b) Partial enlarged Raman spectra of rGO-CDs(300/1-air), rGO-CDs(300/1-N_2) and rGO-CDs(300/2-air), respectively. (c) TGA analyses of rGO under air flow, rGO-CDs under air flow and N_2 flow. (d) Response of the rGO-CDs annealed by different temperature and time upon exposure to 50 ppm of NO_2 gas.

Micrographs of rGO-CDs(300/1-air) and rGO-CDs(300/1-N_2) hybrids:

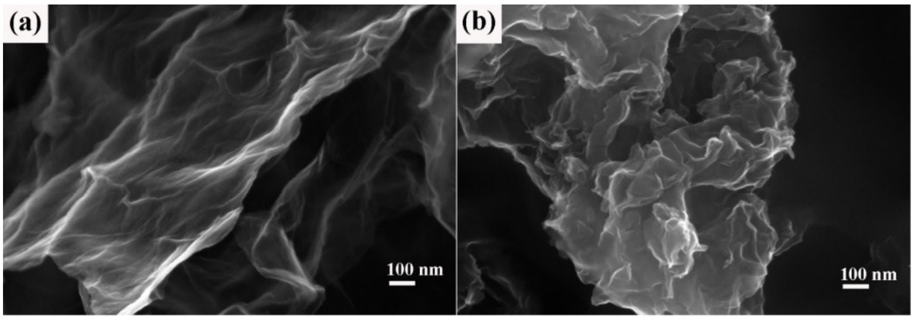

Fig. S6 SEM images of the rGO-CDs(300/1-air) (a) and rGO-CDs(300/1-N_2) hybrids (b).

Fig. S6 shows the SEM images of the rGO-CDs(300/1-air) and rGO-CDs(300/1-N_2), from which we can find both of the surface of hybrids are rough, beyond that no difference can be find between them.

Micrographs of different rGO-CDs(300/1-air) ethanol solutions deposited on the interdigital electrode:

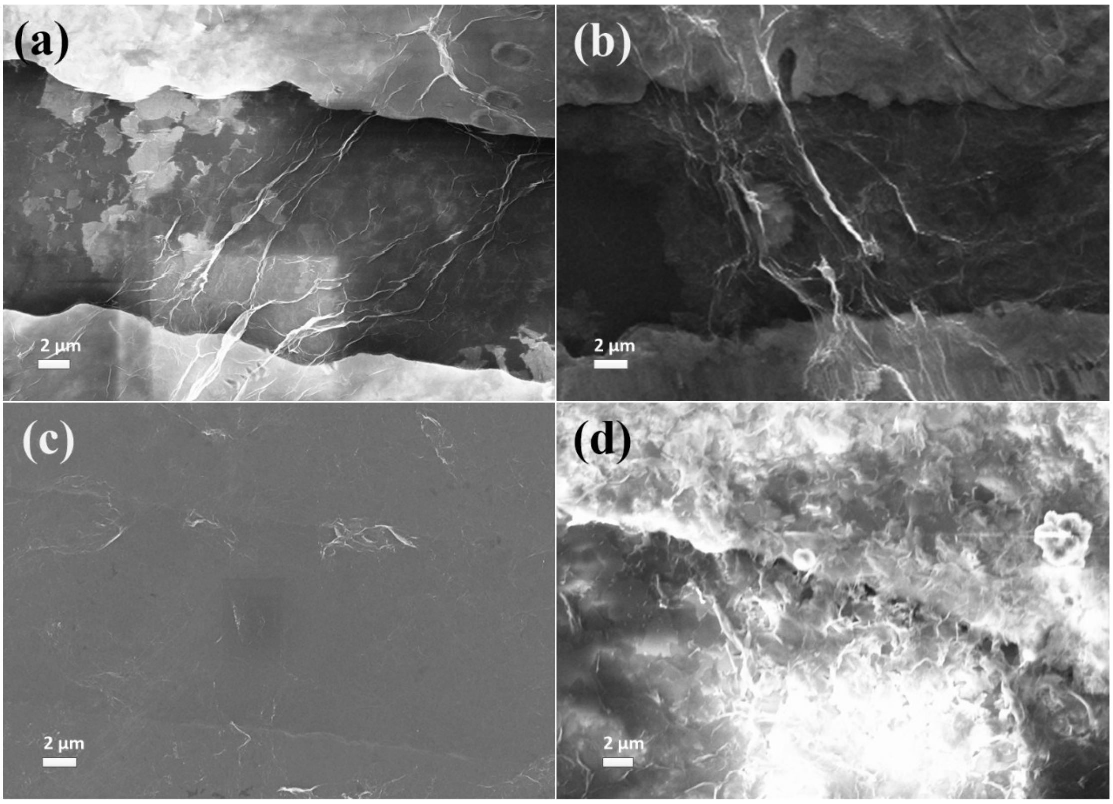

Fig. S7 The SEM images of the interdigital electrode after deposited with 2.0 μL of (a) 0.5 mg mL^{-1}, (b) 1.0 mg mL^{-1}, (c) 2.0 mg mL^{-1} and (d) 5.0 mg mL^{-1} rGO-CDs(300/1-air) ethanol solution.

Table S1 Performance Comparison of the NO_2 Sensors synthesized by different reductants

Citric acid	Reductant	GO (0.45 mg/mL)	Synthetic conditions	Sensitivity (exposure to 50 ppm NO_2)
0.42 g	Ethanediamine (100 μL)	5 mL	180°C/5 h	136.2%
0.42 g	Urea (0.15 g)	5 mL	180°C/5 h	108.9%
0.42 g	Hexamine (0.15 g)	5 mL	180°C/5 h	72.7%
0.42 g	Vitamin C (0.15 g)	5 mL	180°C/5 h	10.9%
0.42 g	Thiourea (0.15 g)	5 mL	180°C/5 h	4.1%
0.42 g	Thioacetamide (0.15 g)	5 mL	180°C/5 h	7.0%

Table S2 Performance Comparison of the NO_2 Sensors by different synthetic methods

Composition of the reactants	Synthetic method	Synthetic conditions	Sensitivity (exposure to 50 ppm NO_2 100 s)
Citric acid + Ethanediamine + GO	Hydrothermal	180°C/5 h	136.2%
CDs + GO	Hydrothermal	180°C/5 h	98.5%
CDs + GO	Reflux	180°C/5 h	85%

Table S3 Performance Comparison of the NO_2 Sensors synthesized by different ingredients

Citric acid	Ethanediamine	GO (0.45 mg/mL)	Synthetic conditions	Sensitivity (exposure to 50 ppm NO_2)
0.42 g	-	5 mL	180°C/5 h	39.3%
-	200 μL	5 mL	180°C/5 h	16.1%
-	-	5 mL	180°C/5 h	42.0%
0.42 g	200 μL	5 mL	180°C/5 h	98.4%
0.42 g	200 μL	10 mL	180°C/5 h	53.3%
0.42 g	200 μL	-	180°C/5 h	-

"-" equals none.

Notes and references

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