Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

One-step green synthesis of Cu_2O/CuO@rGO composites for ppt level detection of NO_2 at room temperature

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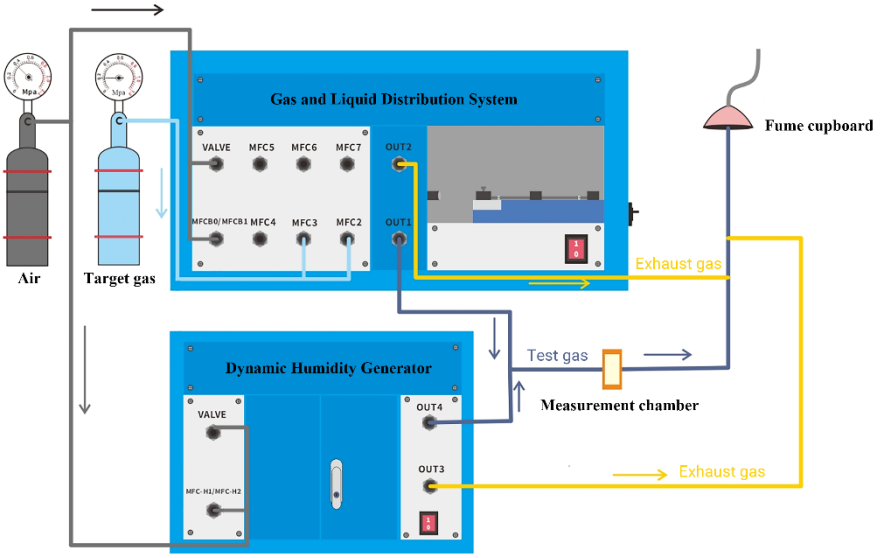

Fig. S1 Schematic diagram of dynamic gas sensitivity test system.

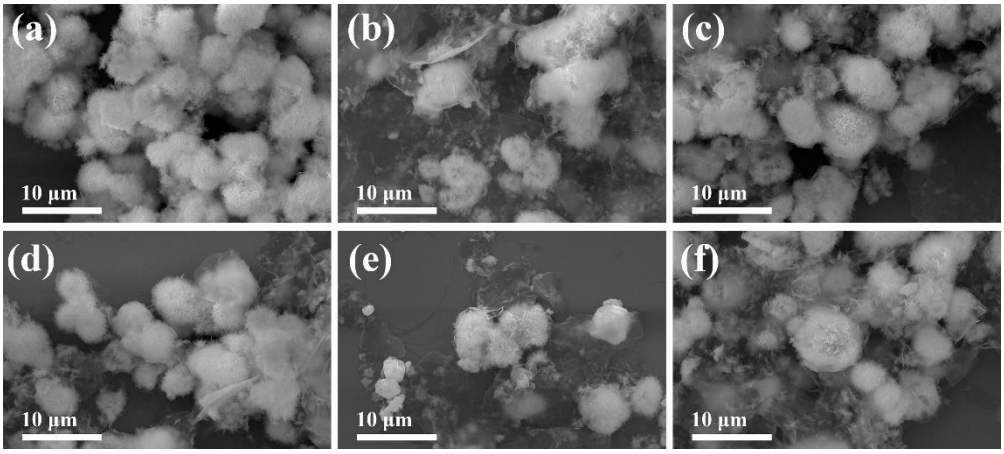

Fig. S2 FE-SEM images of (a) 550Cu_2O/CuO-5; (b) 150Cu_2O/CuO@rGO-5; (c) 300Cu_2O/CuO@rGO-5; (d) 450Cu_2O/CuO@rGO-5; (e) 550Cu_2O/CuO@rGO-5 and (f) 650Cu_2O/CuO@rGO-5.

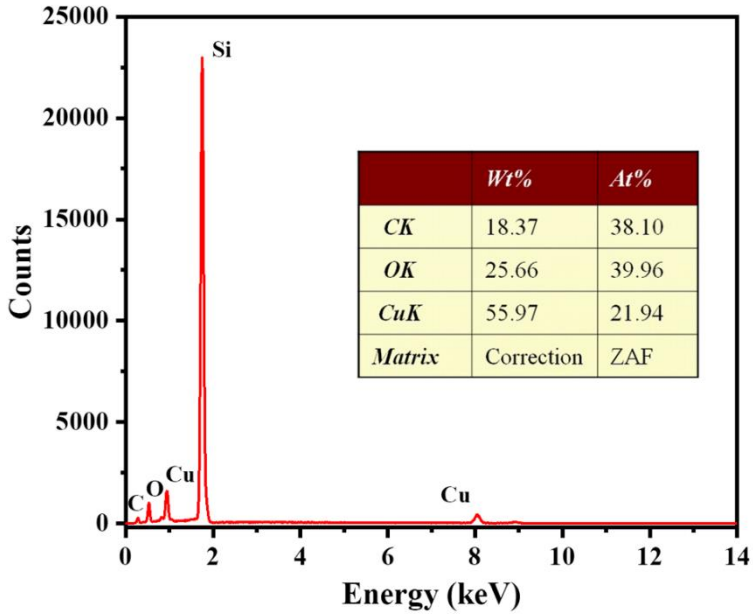

Fig. S3. EDX analysis of the 550Cu_2O/CuO@rGO-5.

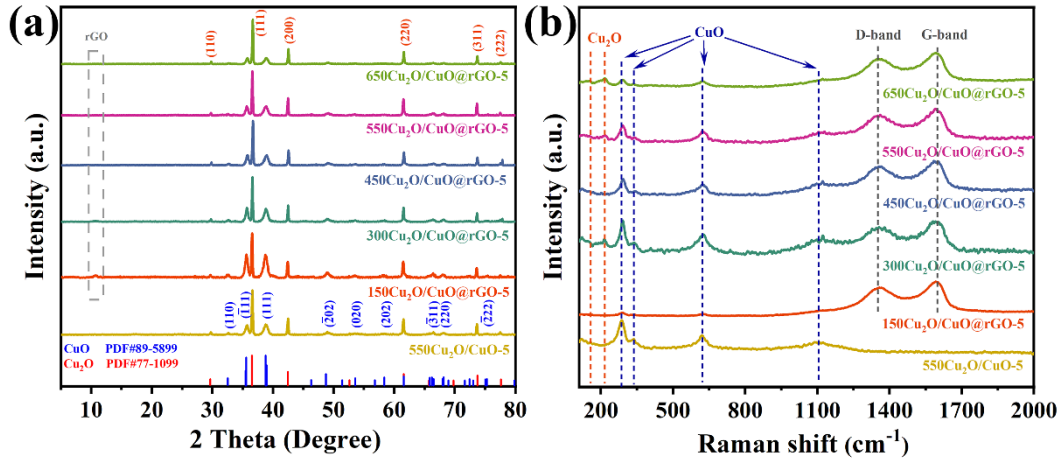

Fig. S4. (a) XRD and (b) Raman spectra of Cu_2O/CuO@rGO-5 composites with different Cu_2O additions.

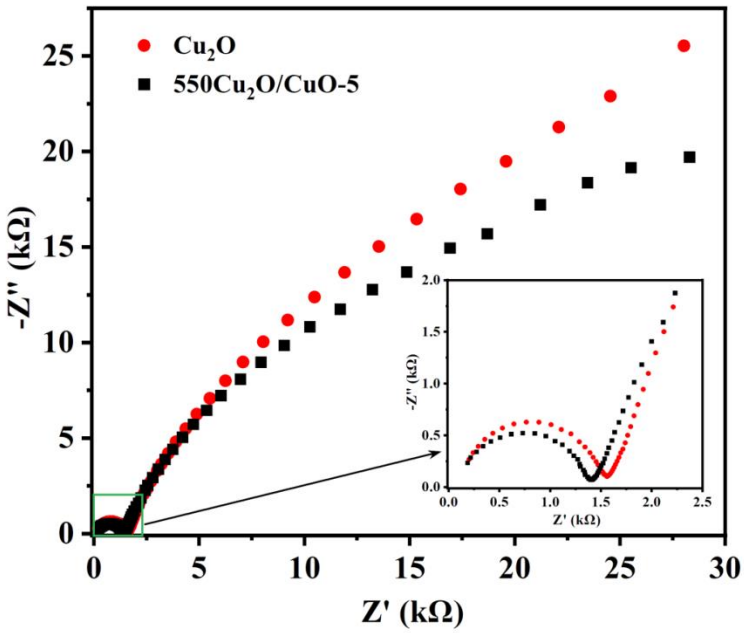

Fig. S5. Electrochemical impedance spectroscopy (Nyquist diagram) of pure Cu_2O and $550Cu_2O/CuO$-5 materials.

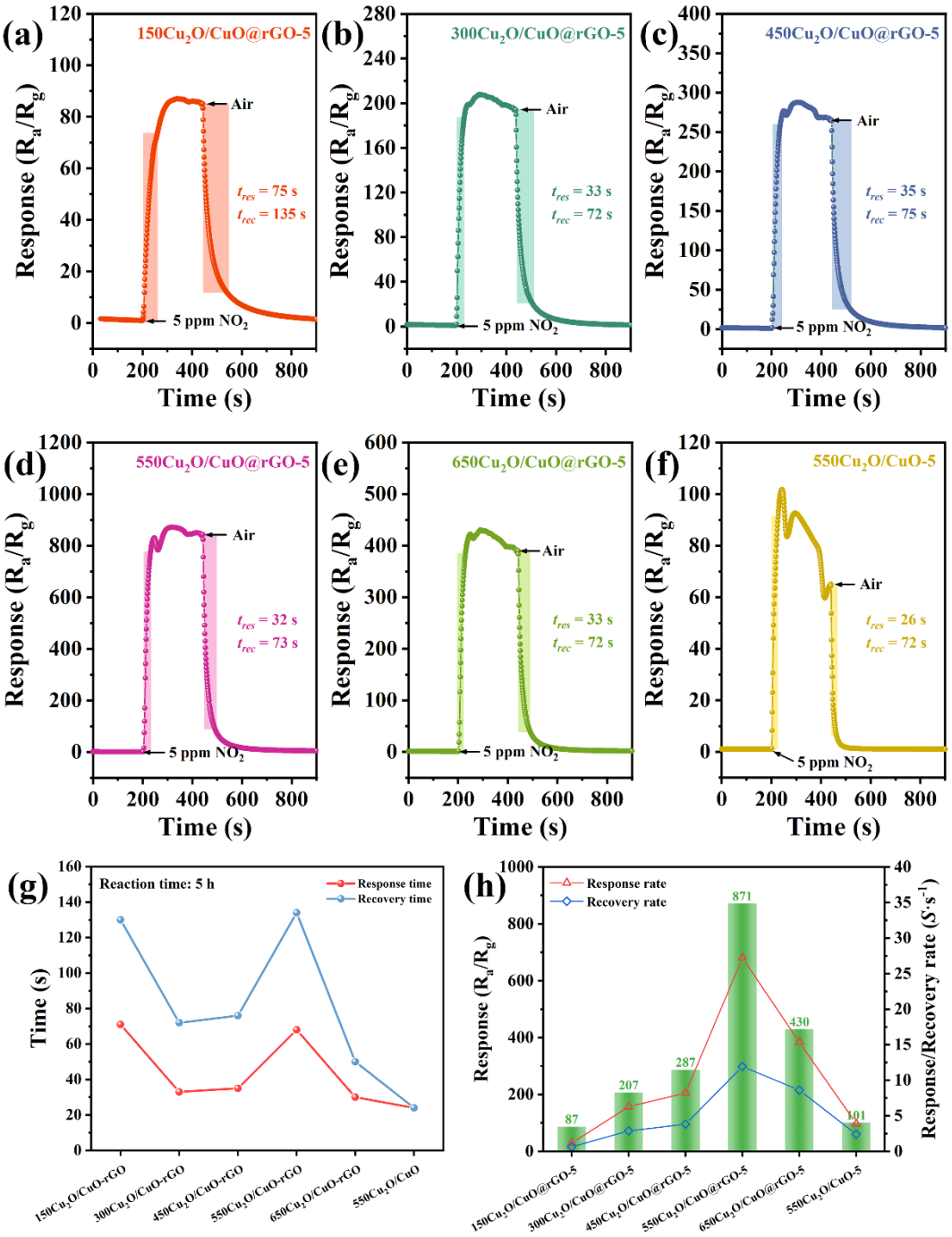

Fig. S6. Dynamic response-recovery curve of (a-e) Cu_2O/CuO@rGO-5 sensors with different Cu_2O additions and (f) 550Cu_2O/CuO sensor to 5 ppm NO_2 at RT; (g) response/recovery time of Cu_2O/CuO@rGO-5 sensors with different Cu_2O additions and 550Cu_2O/CuO sensor with different reaction time to 5 ppm NO_2 at RT; (h) response and response/recovery rate of Cu_2O/CuO@rGO-5 sensors with different Cu_2O additions and 550Cu_2O/CuO sensor with different reaction time to 5 ppm NO_2 at RT.

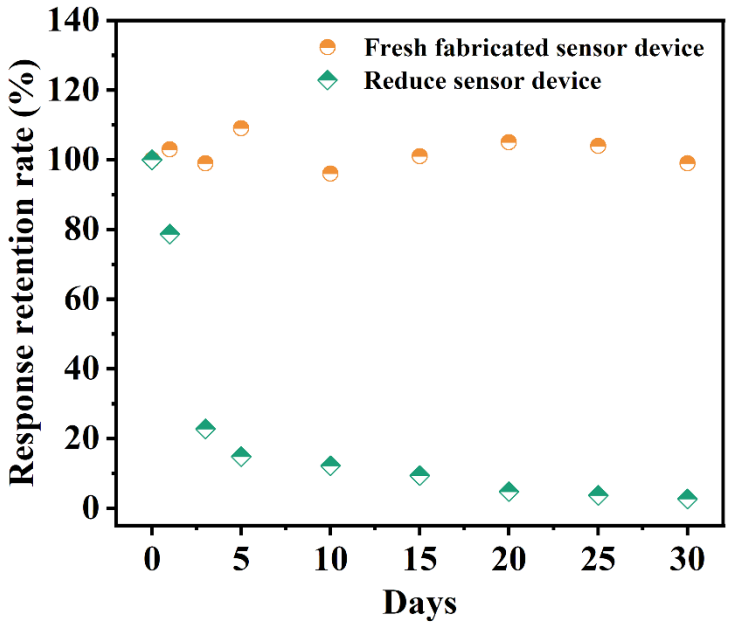

Fig. S7. The stability evaluation of the as-prepared 550Cu_2O/CuO@rGO-5 sensor within one month.

The evolution mechanism of the Cu_2O/CuO materials

The chemical equation of CuO obtained from Cu_2O is shown in Eq. 1-2. The excess OH^- in the solution together with O_2 etch the surface of Cu_2O and form $[Cu(OH)_4]^{2-}$ (Eq. 1). However, because $[Cu(OH)_4]^{2-}$ is unstable, it will decompose into CuO and H_2O (Eq. 2). At the same time, it self-assembles around the Cu_2O to form urchin-like Cu_2O/CuO spheres. Similarly, we have added the relevant description in the revised version.

$$Cu_2O + 1/2O_2 + 2H_2O + 4OH^- \rightarrow 2[Cu(OH)4]^{2-} \quad (1)$$

$$[Cu(OH)_4]^{2-} \rightarrow CuO + 2OH^- + H_2O \quad (2)$$

LOD

The sensor noise can be calculated by the change of the relative response of the sensor in the baseline. Ten consecutive data collected before exposure to NO_2 gas were averaged, and the standard deviation (S) calculated using the root mean square deviation (RMSD)[1] formula was 0.00022.

$$RMS_{noise} = \sqrt{\frac{S^2}{N}} \#(3)$$

where N is the number of data points. The RMS_{noise} is calculated according to the above Eq. 3 to be 0.000156. According to the definition of detection limit (three times the standard deviation of noise). The slope is 0.00227 from Fig. 8d, so that

$$LOD = 3 \times \frac{RMS_{noise}}{slope} = 0.0906 \text{ ppb} = 90.6 \text{ ppt} \#(4)$$

Table S1. The peak intensity ratio between Cu_2O and CuO and between D band and G band in Cu_2O/CuO@rGO-5 composites varies with the amount of Cu_2O added.

Sample at different Cu_2O addition amount (mg)	**GO**	**150**	**300**	**450**	**550**	**650**
$I_{Cu_2O\ (111)}/I_{CuO\ (111)}$	—	1:0.518	1:0.293	1:0.231	1:0.233	1:0.211
I_D/I_G	1.28	1.16	0.99	0.99	0.98	0.92

Table S2. NO_2 response of Cu_xO-based and rGO-based sensors in different work and the gas sensor in this work.

Material	Synthesis method/ temperature	Work Temperature	Response	τ_{res}/τ_{rec}	LOD
Cu_2O-CuO [2]	One -step/180 ℃	187 ℃	10.2 (1 ppm)	35/47*	—
CuO-Co_3O_4 [3]	Multi-step/450 ℃	160 ℃	37.86% (10 ppm)	158/738*	—
CuO/ZnO [4]	Multi-step/400 ℃	RT (30 ℃)	337% (5 ppm)	18/32	155 ppb
$BiVO_4$/Cu_2O/rGO [5]	Multi-step/180 ℃	60 ℃	8.1 (1 ppm)	51.3/87.5*	100 ppb
Cu_2O/rGO [6]	Multi-step/200 ℃	RT	67.80% (2 ppm)	~440/490	82 ppb
CuO/rGO [7]	Multi-step/80 ℃	RT (23 ℃)	400.80% (5 ppm)	6.8/55.1*	50 ppb
CuO/rGO [8]	One-step/25 ℃	RT	74395.2 (50 ppm)	30/270	100 ppb
CuO/rGO [9]	One-step/180 ℃	RT	30% (50 ppm)	Irreversible	150 ppb
rGO/Cu_2O [10]	Multi-step/100 ℃	RT	5.2 (1 ppm)	29.2/76.8	32 ppb
550Cu_2O/CuO@rGO-5 [This work]	One-step/25 ℃	**RT (25 ℃)**	**871 (5 ppm)**	**35/73**	**90.6 ppt**

* Representing that τ_{res}/τ_{rec} is defined in the literature as 90% of the change in resistance value.

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