Supporting Information

Ultrasensitive NO_2 gas sensor based on hierarchical Cu_2O/CuO mesocrystals nanoflower

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S1. Gas sensor electrode and device images

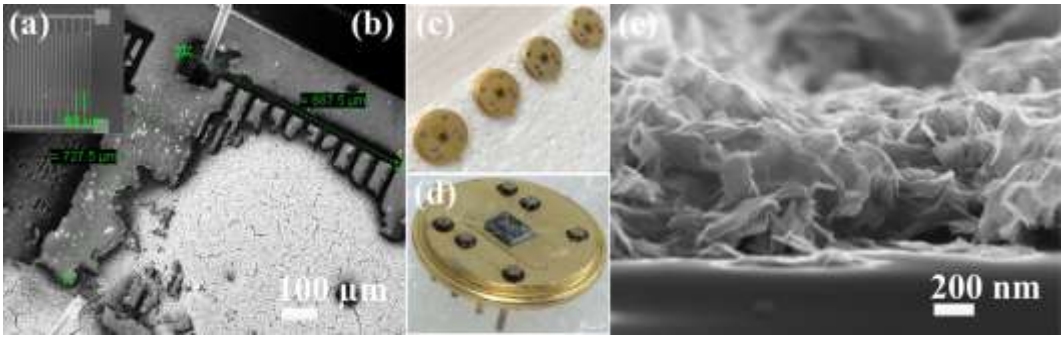

Fig. S1 SEM/digital images of the sensor device: the SEM images of the interdigital electrode unit (a) before and (b) after dropping sample, (c-d) the digital images of the electrode on metal base, (e) the cross-section SEM image of the sensor device.

S2. Gas sensing testing system

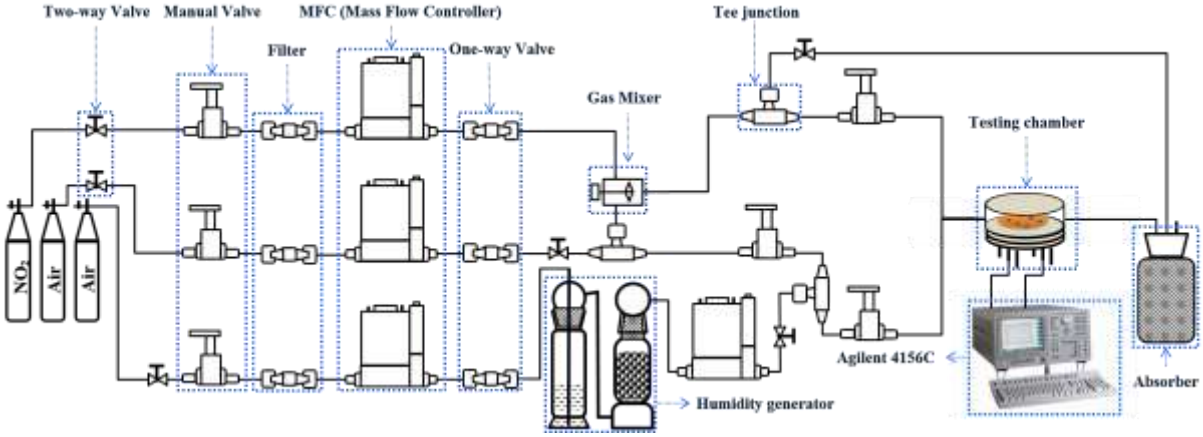

Fig. S2 Schematic diagram shows the gas sensor testing system.

S3. SEM characterizations of hierarchical Cu_2O/CuO mesocrystals

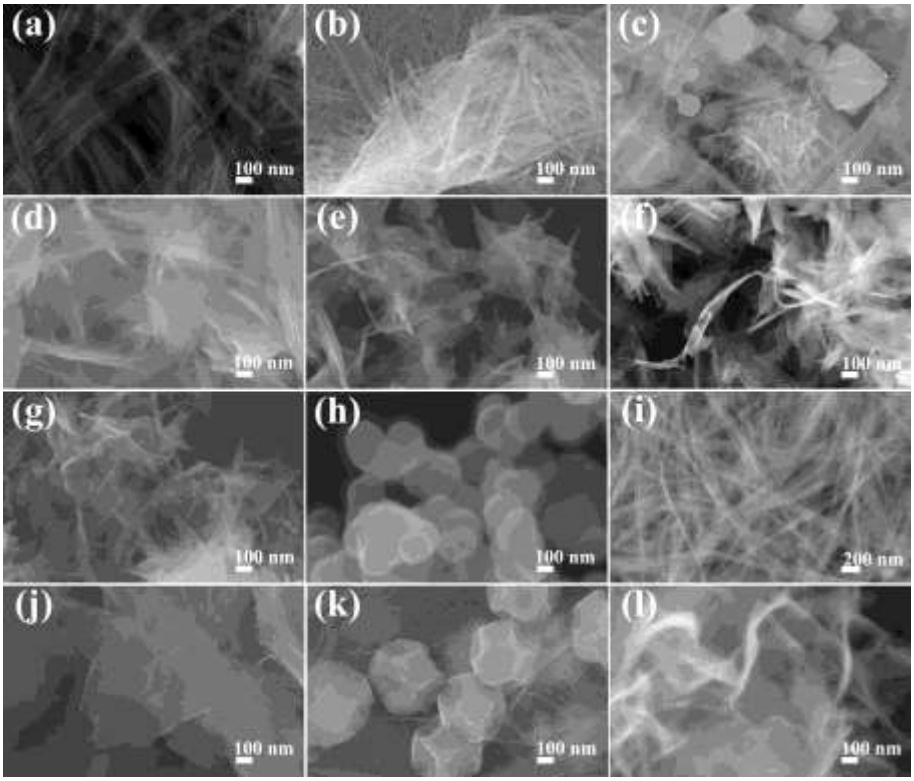

Fig. S3 (a-l) SEM images of lamellar Cu_2O-oleate complex intermediate.

Table S1 The corresponding reaction condition for the samples in Fig. S3

Sythesis condition	Temperature/°C	NaOH/M	$N_2H_4 \cdot H_2O$/M	Cu^{2+}/M	Time (h)
(a)	25	0.0175	0	0.001	10
(b)	25	0.0175	0.0008	0.001	10
(c)	25	0.0175	0.001	0.001	10
(d)	25	0.0175	0.002	0.001	10
(e)	25	0.0175	0.0035	0.001	10
(f)	25	0.0175	0.0075	0.001	8
(g)	25	0.0175	0.015	0.001	6
(h)	25	0	0.0035	0.001	10
(i)	25	0.0375	0.0035	0.001	10
(j)	25	0.125	0	0.001	20
(k)	10	0.0175	0.0035	0.001	10
(l)	25	0.25	-	Replaced by 0.5 g Cu_2O	12

S4. Morphology comparsion of comercial Cu_2O before and after reaction

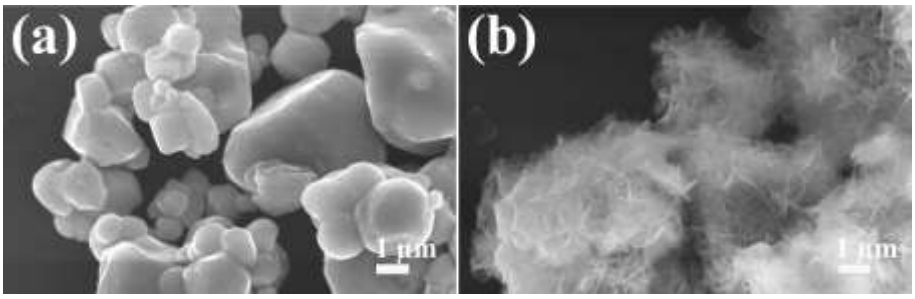

Fig. S4 SEM images of comercial Cu_2O before (a) and after (b) reaction.

S5. Morphology comparsion of Cu_2O/ CuO-10 composite with different copper salts

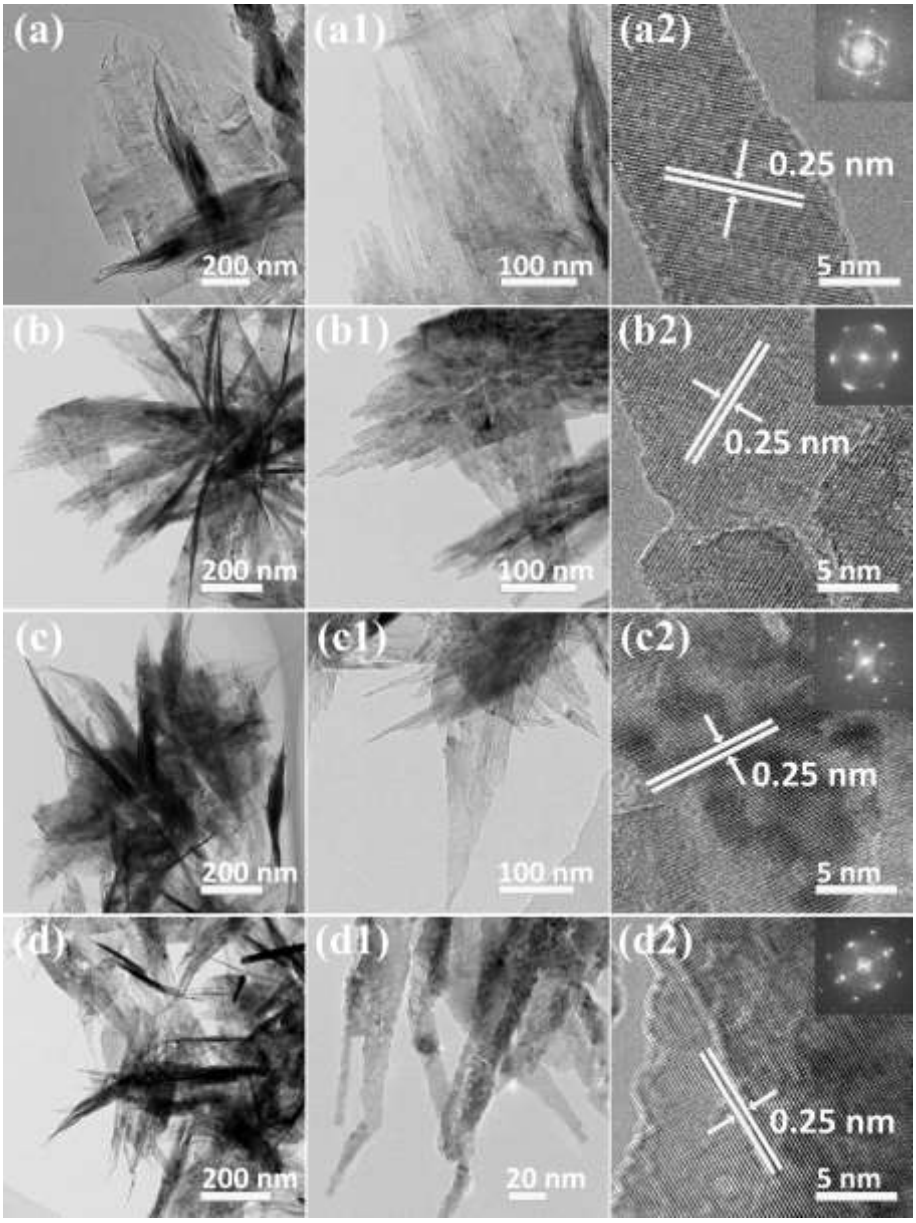

Fig. S5 Typical TEM images with different magnification and HRTEM images of Cu_2O/ CuO-10 composites obtained with different copper salts: (a-a2) $CuSO_4$, (b-b2) $CuCl_2$, (c-c2) $Cu(NO_3)_2$, (d-d2) $Cu(CH_3COO)_2$.

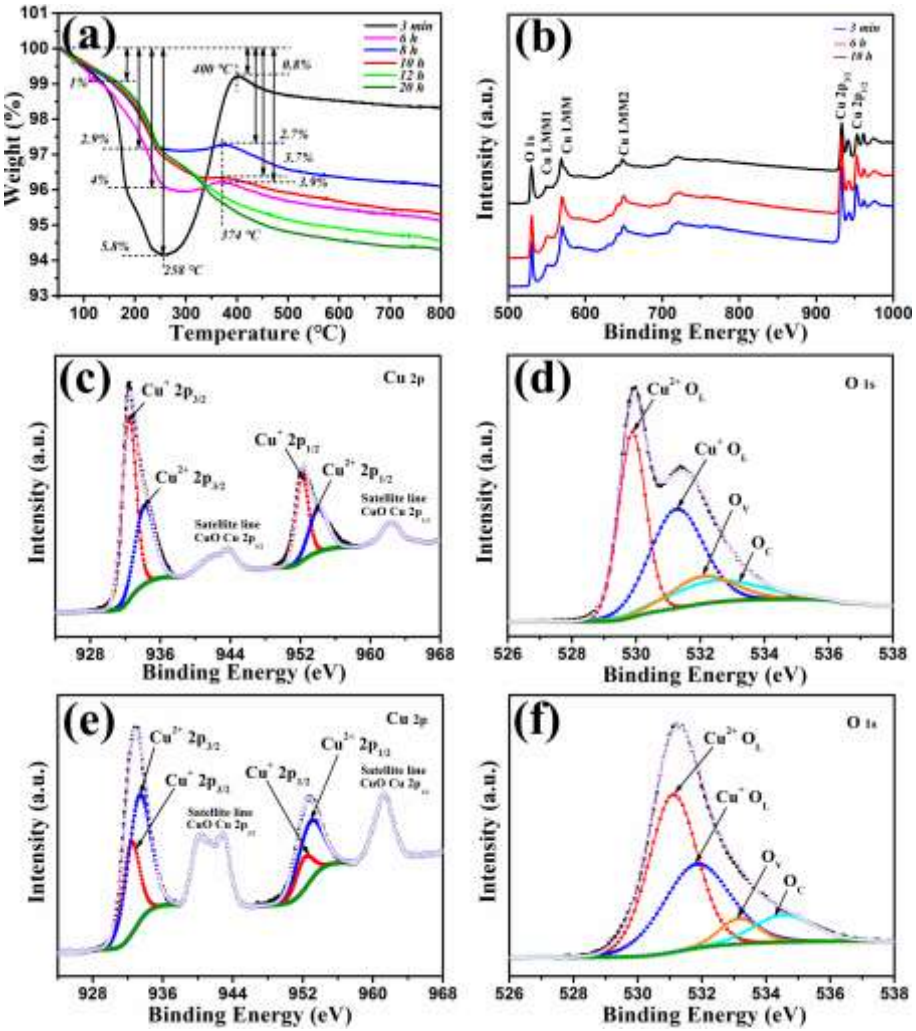

Fig. S6 (a) TGA curves of sample obtained at 3 min, 6 h, 8 h, 10 h and 20 h; (b) Complete XPS spectra of the samples at 3 min, 6 h and 10 h; (c-d) Cu 2p XPS and O1s XPS spectra of the sample at 3 min; (e-f) Cu 2p XPS and O1s XPS spectra of the sample at 10 h.

Table S2 Results of curve fitting of Cu 2p XPS spectra of the samples.

Sample	Cu $2p_{3/2}$	Cu^{+} $2p_{3/2}$	Cu^{2+} $2p_{3/2}$	Cu $2p_{1/2}$	Cu^{+} $2p_{1/2}$	Cu^{2+} $2p_{1/2}$
Cu_2O/CuO-0.05	932.5 eV	932.5 eV	934.2 eV	952.3 eV	952.3 eV	954.2 eV
Cu_2O/CuO-10	933.0 eV	932.6 eV	933.5 eV	952.8 eV	952.6 eV	953.3 eV

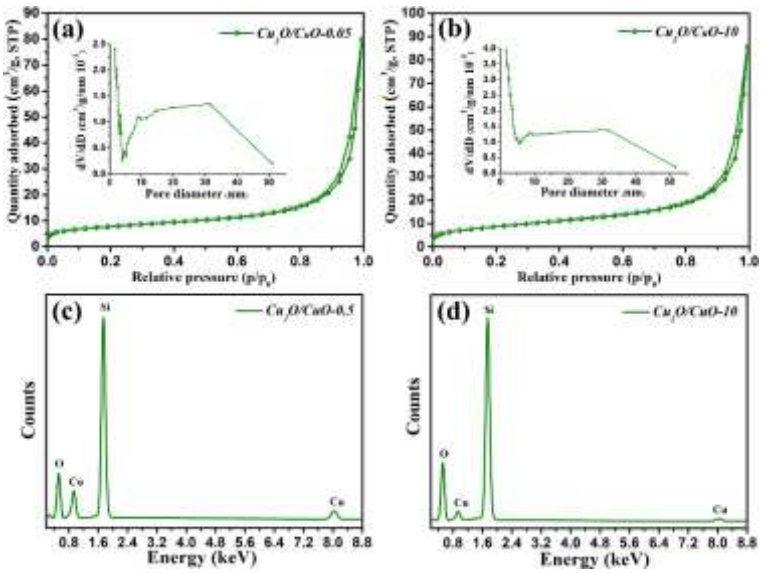

Fig. S7 N_2 adsorption-desorption isotherm and pore size distribution (inset) of sample obtained at 0.5 h (a) and 10 h (b). EDX spectrum of sample obtained at 0.5 h (c) and 10 h (d).

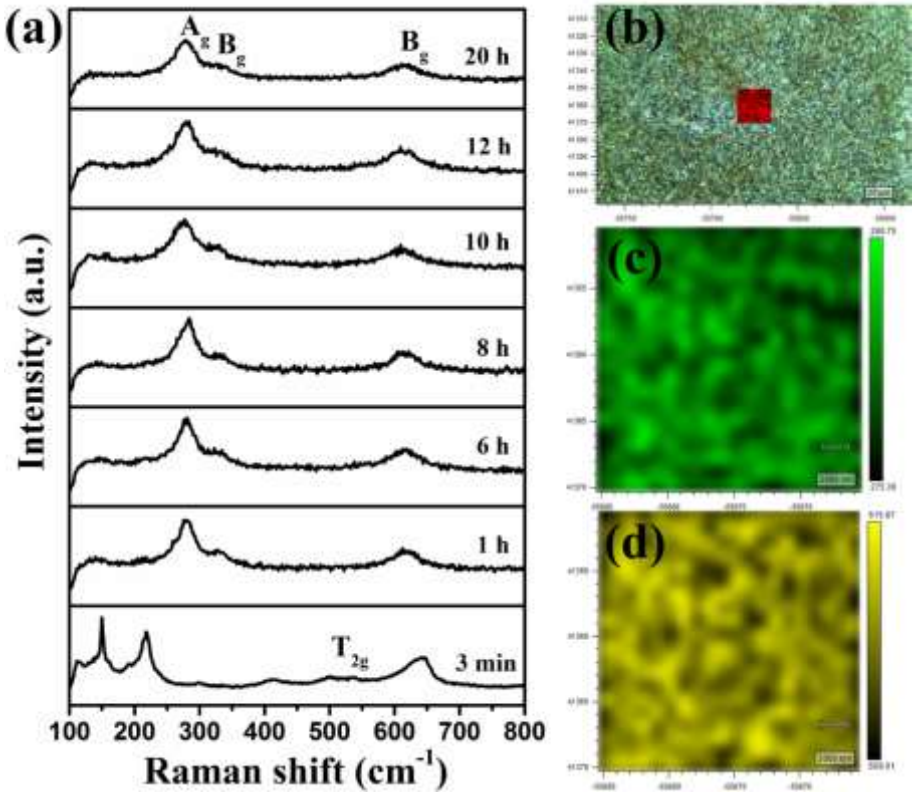

Fig. S8 (a) Raman spectra of sample obtained at 3 min, 1 h, 6 h, 8 h, 10 h, 12 h and 20 h; (b) Digital Photo of sample obtained at 10 h; (c-d) Raman mapping scanning of samples obtained at 10 h with 278 and 615 cm^{-1} as the characteristic peak positions.

S9. The stability of the Cu_2O/CuO-10 sensors and the sensing performance of devices with different sample concentration

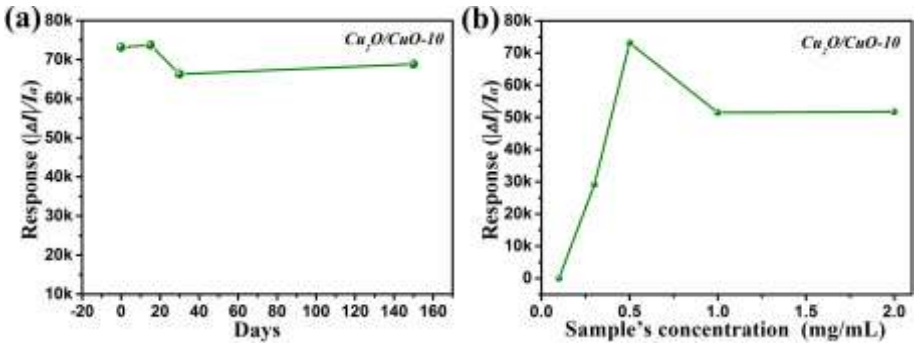

Fig. S9 The response of the fresh fabricated Cu_2O/CuO-10 sensors exposure to 10 ppm NO_2 within 100 s (a) in 150 days and (b) with different sample concentrations.

S10. Morphology comparsion of the prepared CuO/Cu_2O-10 sensor device with different sample concentrations

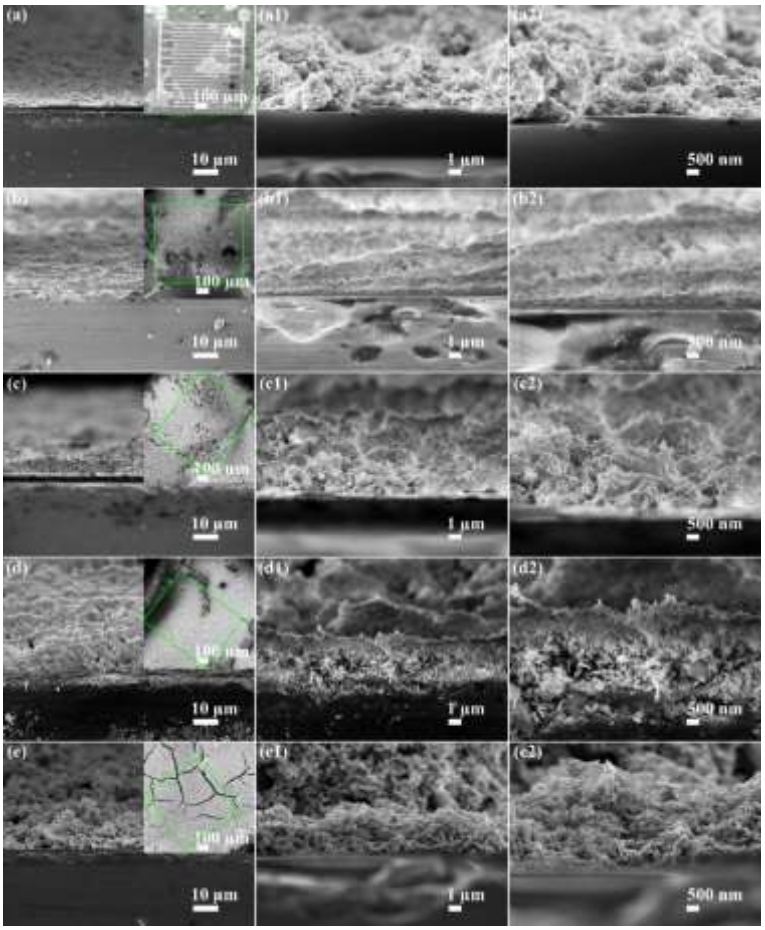

Fig. S10 The cross-section SEM images of the prepared CuO/Cu_2O-10 sensor device with different sample concentrations: (a-a2) 0.1 mg/mL, (b-b2) 0.3 mg/mL, (c-c2) 0.5 mg/mL, (d-d2) 1.0 mg/mL, (e-e2) 2.0 mg/mL. The insets are corresponding top view SEM images of the substrate.

S11. Morphology comparison of the prepared CuO/Cu_2O-10 composite before and after NO_2 sensing response

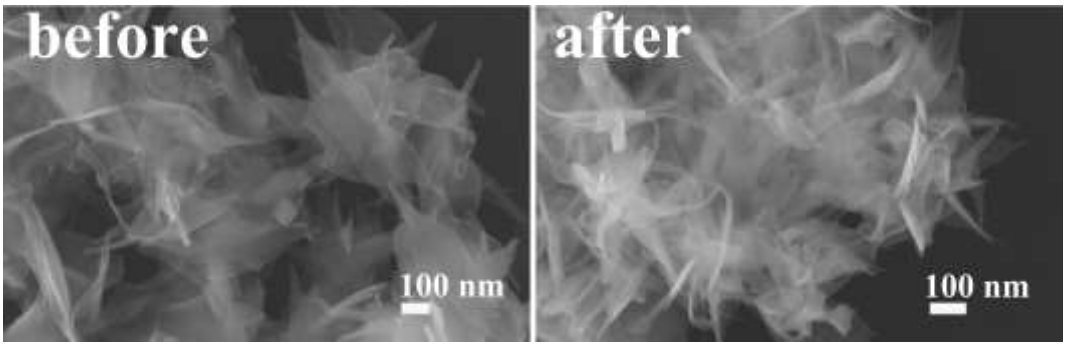

Fig. S11 SEM images of the prepared CuO/Cu_2O-10 composite before and after NO_2 sensing response.