Electronic Supplementary Material (ESI) for Nanoscale.

Spontaneous formation of Cu_2O–g-C_3N_4 core–shell nanowires for photocurrent and humidity responses

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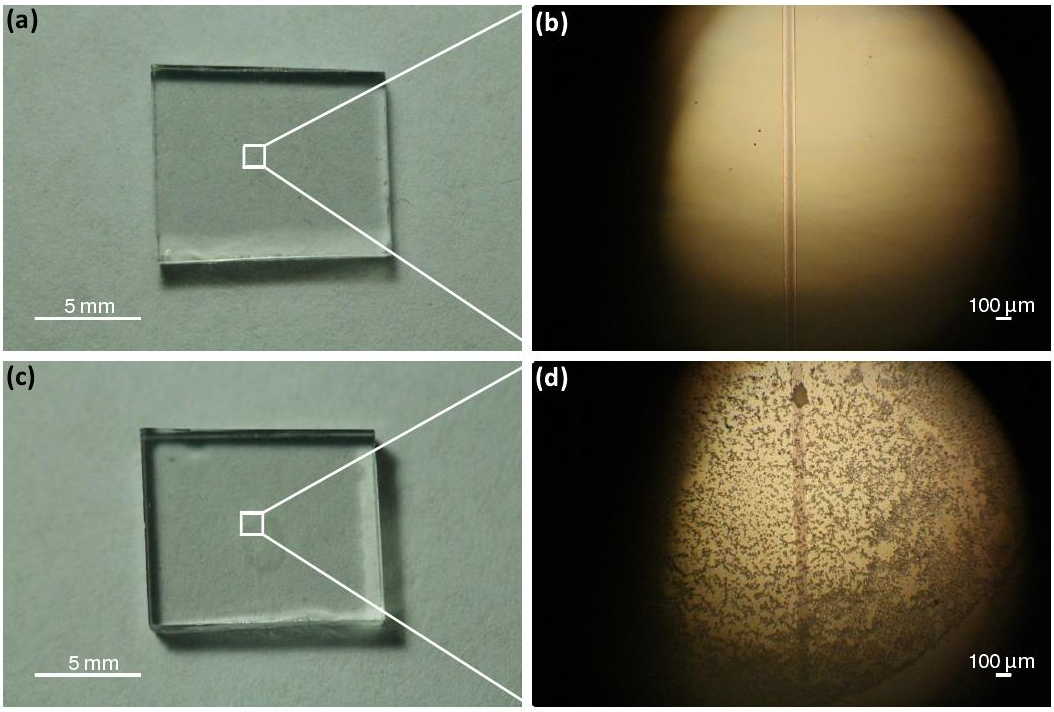

Fig. S1 (a)The photograph of the prepared FTO electrode. (b) The magnified optical microscope photograph of the white box area in (a). (c) The photograph of Cu_2O–g-C_3N_4 core–shell nanowires-coated FTO sensor. (d) The magnified optical microscope photograph of the white box area in (c). Scale bars: (a, c), 5 mm; (b, d), 100 μm.

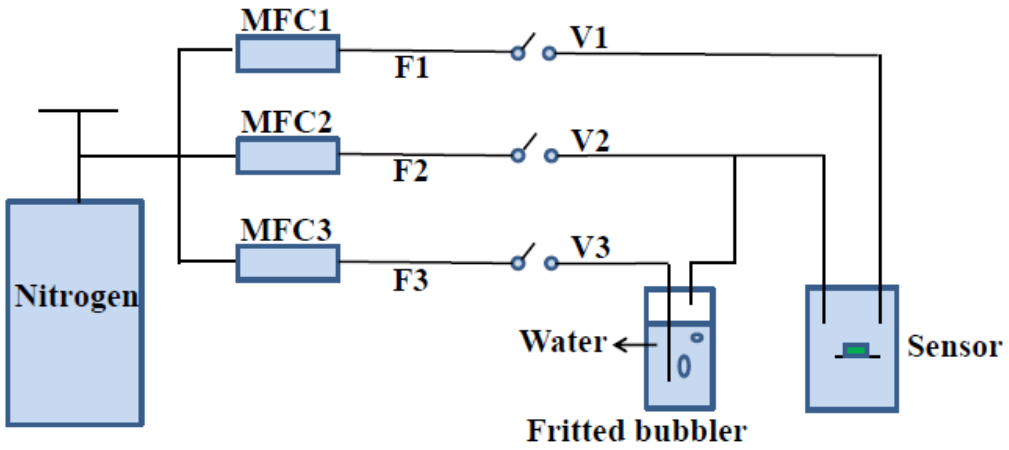

Fig. S2 Test arrangement. Flow F3 generates a constant saturated humidity, Flow F2 dilutes it and Flow F1 provides dry reference.

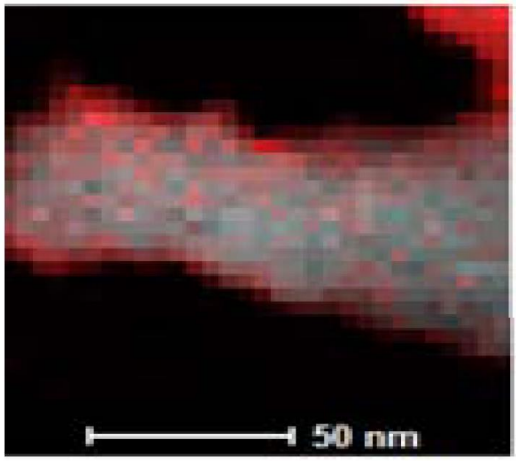

Fig. S3 The overlay chart of the elemental mapping images of C and Cu elements of the prepared Cu_2O–g-C_3N_4 core–shell nanowires. Scale bar: 50 nm.

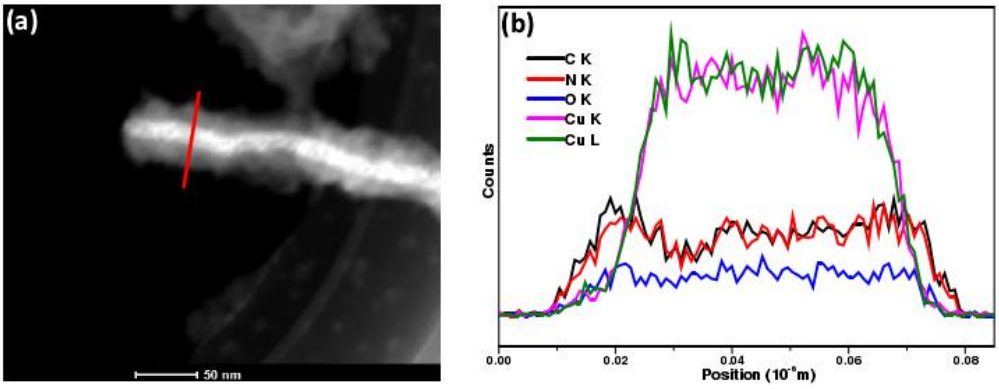

Fig. S4 (a) HAADF image of the prepared Cu_2O–g-C_3N_4 core–shell nanowires. The red line in (a) is the position of the elemental line-scanning. (b) Elemental line-scanning image of C, N, O and Cu elements, respectively. Scale bar: (a), 50 nm.

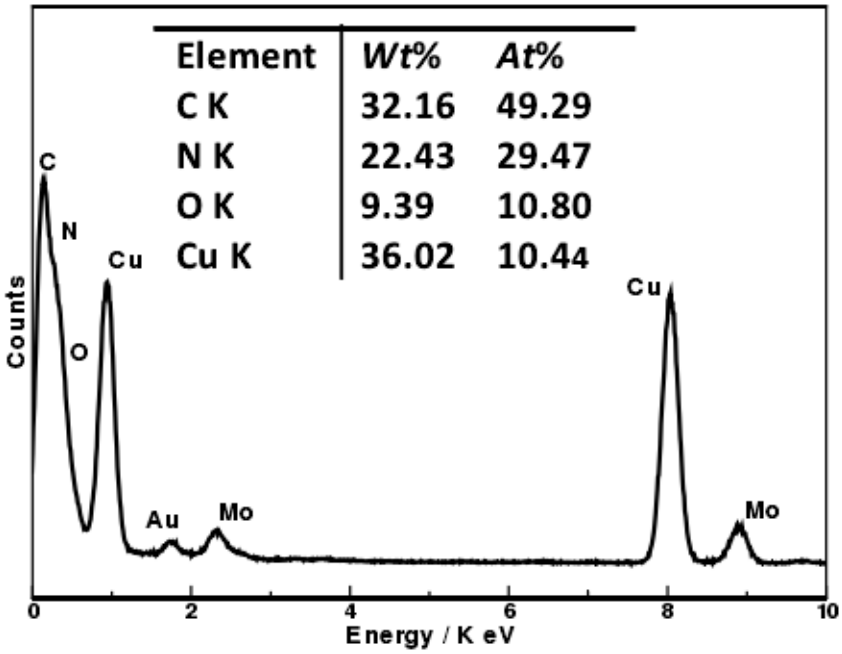

Fig. S5 EDS spectrum and the corresponding contents of C, N, O and Cu of Cu_2O–g-C_3N_4 core–shell nanowires. The peaks of Mo and Au are attributed to the Mo micro-grid substrate used.

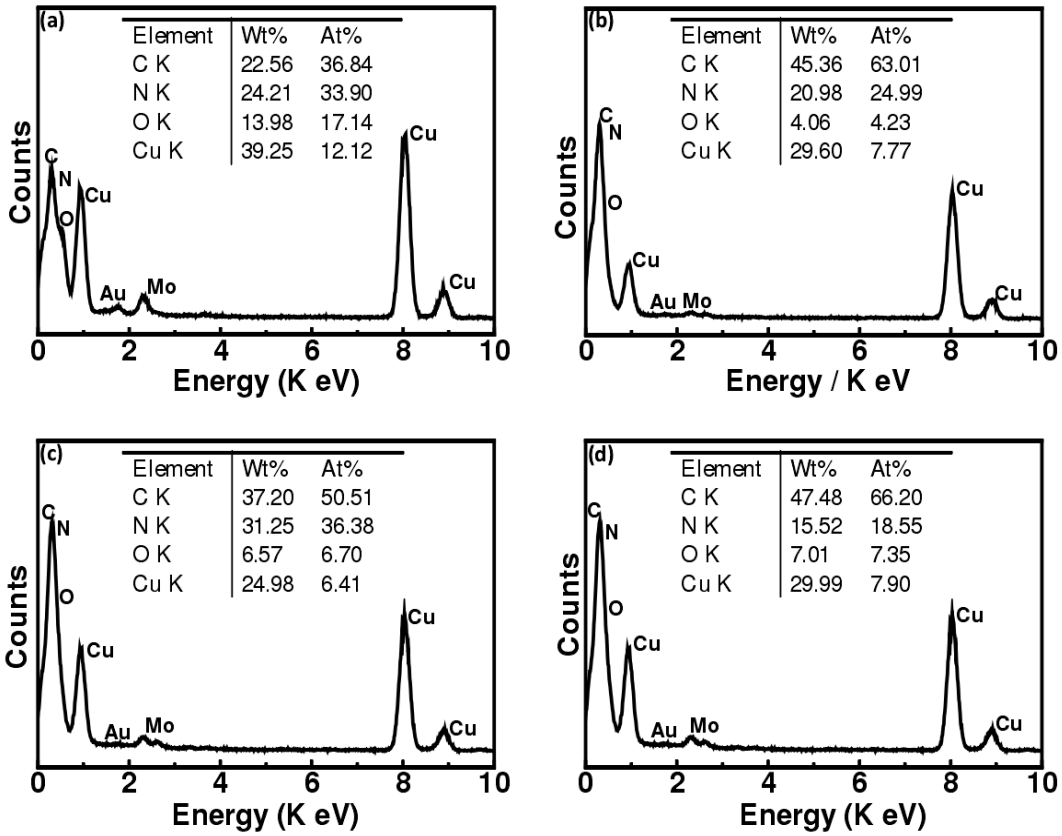

Fig. S6 EDS spectra and the corresponding contents of C, N, O and Cu of Cu_2O–g-C_3N_4 core–shell nanowires with different growth conditions. (a) 48 h and (b) 144 h with 1 mg $mL^{-1}$of O-functional g-C_3N_4 solution, (c) 96 h with 0.1 mg $mL^{-1}$of O-functional g-C_3N_4 solution, (d) 96 h with 0.3 mg $mL^{-1}$of O-functional g-C_3N_4 solution. The peaks of Mo and Au are attributed to the Mo micro-grid substrate used.

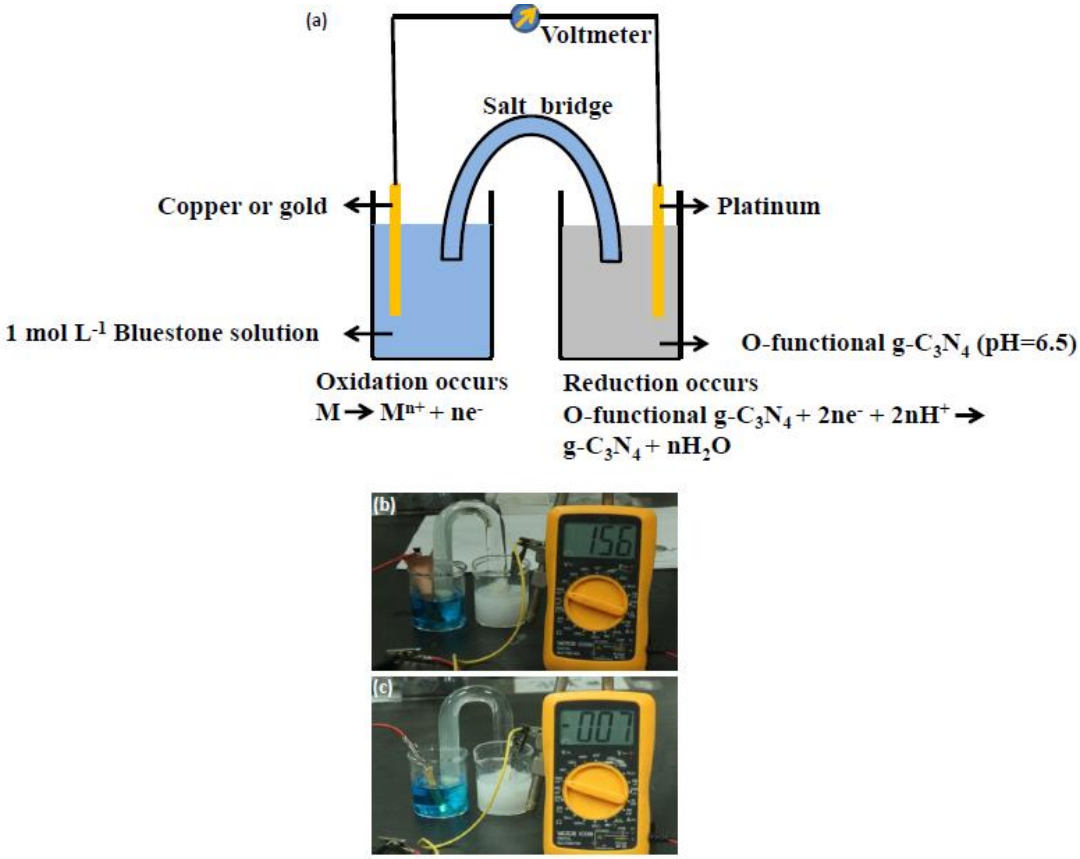

Fig. S7 (a) Schematic description of the designed galvanic cell. Cu and Au foils was used as the anode and inert platinum was used as the cathode. A salt bridge was used to allow the flow of current. In the anode compartment, the electrolyte was 1 mol L^{-1} bluestone solution. In the cathode compartment, the electrolyte was O-functional g-C_3N_4 solution with pH=6.5. Before measurements, the electrolytes were saturated with nitrogen. Oxidation occurred at the anode and provided electrons ($M \rightarrow M^{n+} + ne^-$). O-functional g-$C_3N_4$ would accept the electrons and be reduced at the cathode (n O-functional g-C_3N_4 + $2ne^-$ + $2nH^+ \rightarrow$ g-C_3N_4 + nH_2O). (b) The cell (-) $Cu|Cu^{2+}||$ O-functional g-C_3N_4| g-C_3N_4 (+) could generate a cell voltage of 156 mV. So, according to the relationship between the thermodynamic function and the cell voltage ($\Delta G = -nFE$), the redox reaction between O-functional g-C_3N_4 and copper was spontaneous. (c) The cell (-) $Au|Au^{3+}||$ O-functional g-C_3N_4| g-C_3N_4 (+) only generated a very small voltage (~ -7 mV) that might be caused by the concentration potential and liquid junction potential. So, gold could not be used to reduce O-functional g-C_3N_4.

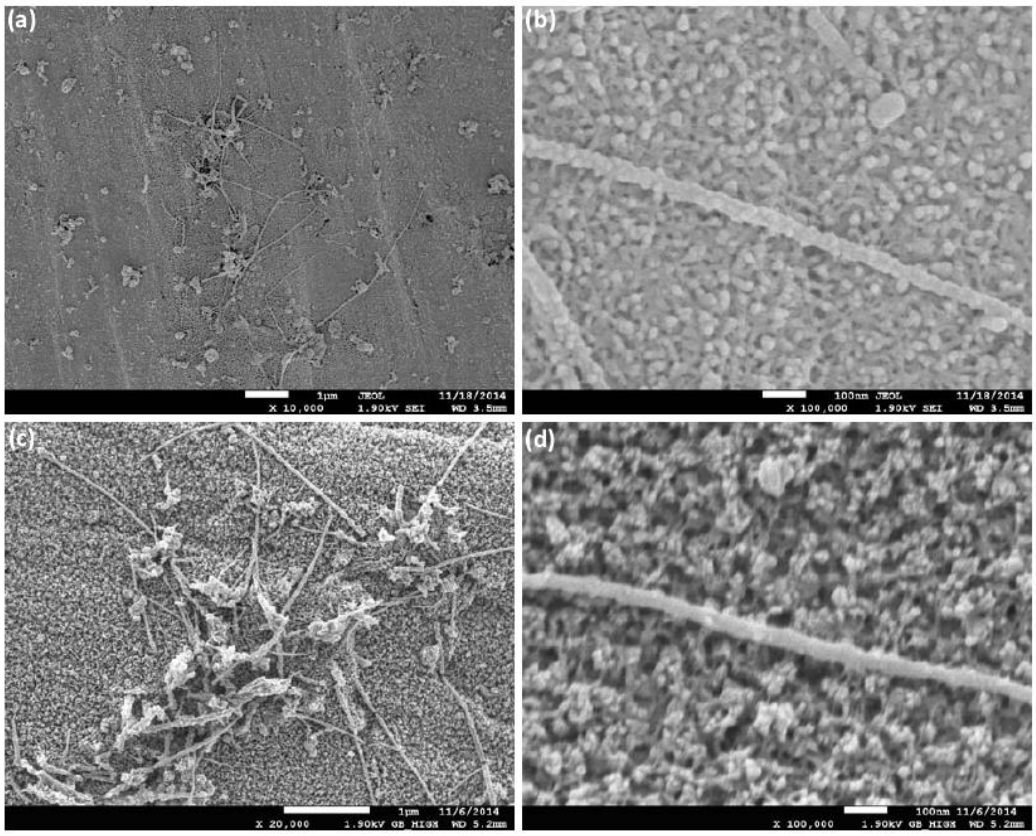

Fig. S8 The SEM images of Cu_2O−g-C_3N_4 core−shell nanowires kept still for 96 h with different concentrations of O-functional g-C_3N_4 solution (a, b) 0.1 mg mL^{-1}, (c, d) 0.3 mg mL^{-1}. Scale bars: (a, c), 1 μm; (b, d), 100 nm.

In addition, When the concentration is 0.1 mg mL^{-1}, Cu_2O−g-C_3N_4 core−shell nanowires has formed, but the amount was less. With increasing the concentration to 0.3 mg mL^{-1}, there is almost no change of the structure of Cu_2O−g-C_3N_4 core−shell nanowires but more amouts appeared.

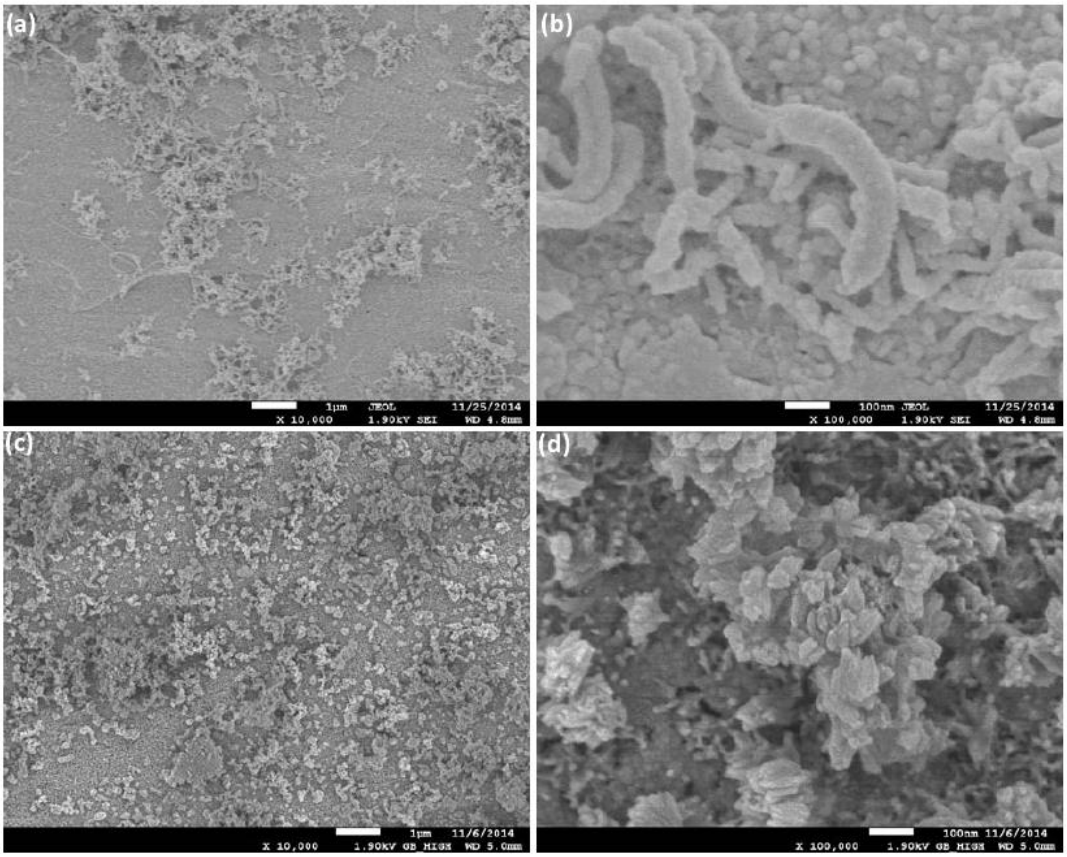

Fig. S9 The SEM images of Cu_2O−g-C_3N_4 core−shell nanowires kept still for 96 h in dark (a, b) and under illumination (c, d). Scale bars: (a, c), 1 μm; (b, d), 100 nm.

Given the excellent photocatalytic activity of g-C_3N_4 under visible light, the illumination contrast experiments were conducted at identical experimental conditions to explain further the reaction process. Compared with the long and thick nanowires prepared under normal indoor lighting, short and thin nanowires formed on the surface of Cu under totally dark condition, indicating the main drive force to contribute the reaction should be oxidation-reduction between the O-functional g-C_3N_4 and Cu, illumination only accelerating it. while the sample was irradiated under a 300 W Xe lamp, flower-like nanoclusters formed on the surface of Cu foil probably because the accelerating reaction between the O-functional g-C_3N_4 and Cu under illumination caused the disorder stack of g-C_3N_4.

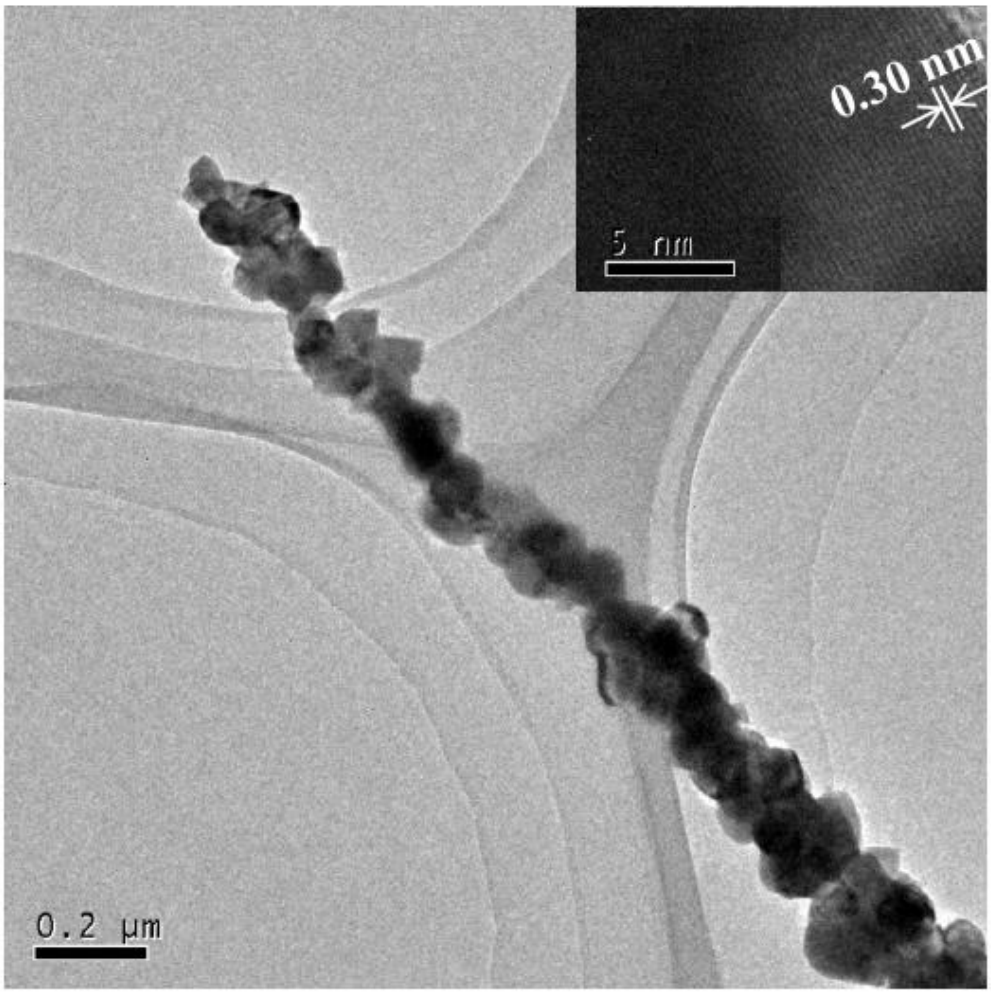

Fig. S10 The TEM of the contrast Cu_2O nanowires. The inset is the magnified image of of the Cu_2O nanowires.

In accordance with the solution-grown condition at room temperature for Cu_2O−g-C_3N_4 core − shell nanowires, a similar process was choosed for the preparation of the contrast Cu_2O nanowires.[1] The HRTEM image of the Cu_2O nanowires show interplanar spacing of 0.30 nm, consistent with the (110) lattice planes of cubic-phase Cu_2O, which is well matched with that in the XRD pattern (Figure 2g (ii)). Scale bars: 0.2 μm; The inset, 5 nm.

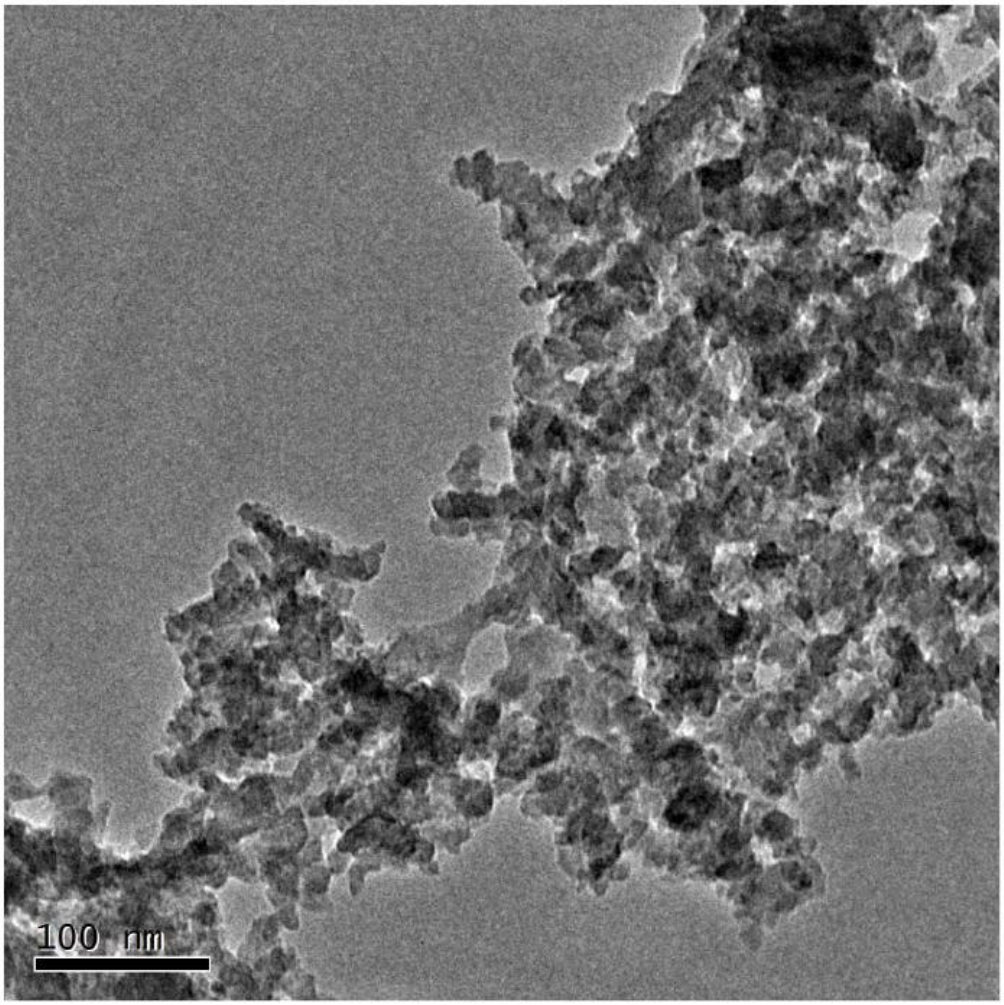

Fig. S11 The TEM image of the g-C_3N_4. Scale bar: 100 nm.

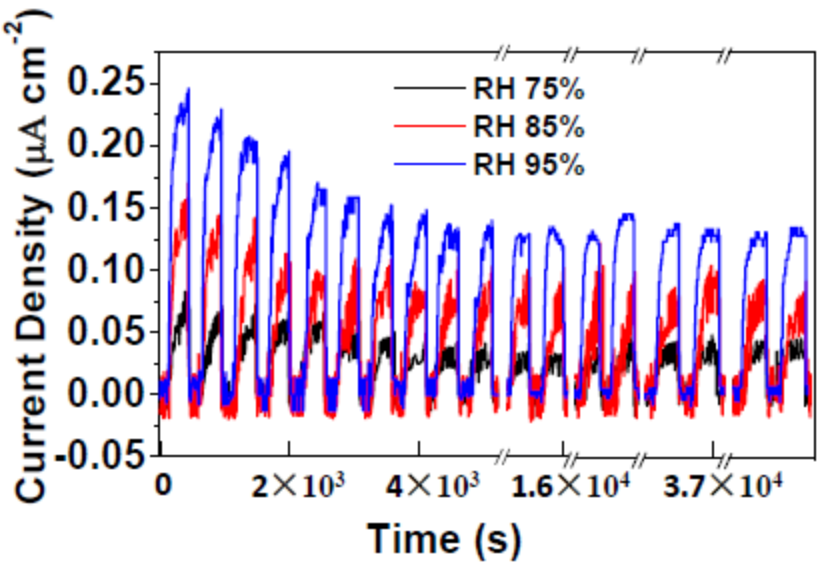

Fig. S12 Current response of Cu_2O−g-C_3N_4 core−shell nanowires-coated FTO sensors to dynamic switches between dry air (0%) and different (75%−95%) RH at 30 °C for 100 cycles. The first 10 cycles in the figure were the first 10 cycles of the 100 cycles, the eleventh (11th) and twelfth (12th) cycles correspond to the 29th and 30th cycles of the 100 cycles, 13th and 14th cycles to the 49th and 50th cycles, 15th (69th) ,16th (70th), 17th (99th) and 18th (100th).

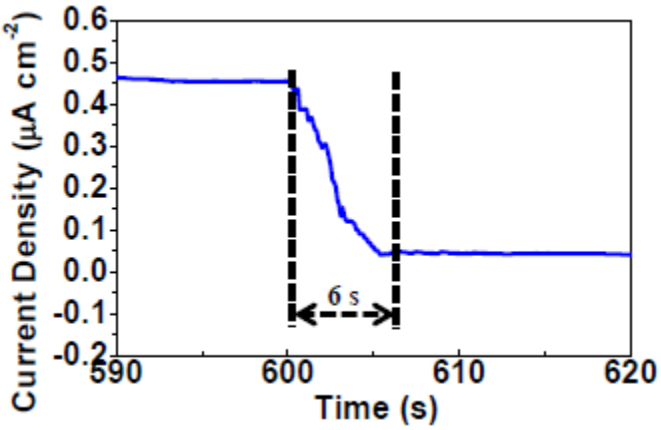

Fig. S13 The enlarged image of the recovery process in the Fig. 6e.

References

[s1] A. Kargar, S. S. Partokia, M. T. Niu, P. Allameh, M. Yang, S. May, J. S. Cheung, K. Sun, K. Xu and D. L. Wang, *Nanotechnology*, 2014, **25**, 1.