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Supporting Information

Synthesis of graphene-like CuB_{23} nanosheets with fast and stable response to H_2S at ppb level detection

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Summary: 17 Pages; 12 Figures; 1 Table

Table of Contents

1. Experimental

1.1. Preparation of graphene-like CuB_{23}

The self-designed SPT reactor used for the preparation of graphene-like CuB_{23} was present in our previous study.[51] The pulsed direct current voltage was 200 V (duty: 90%, frequency: 12 kHz). The electrodes were tungsten wire (diameter: 2 mm) and the gap between the cathode and anode was 1 mm.

In a typical synthesis, 40 mL of 25% $NH_3 \cdot H_2O$ solution was mixed with 10mL of copper chloride (0.0085 mol) to form a $Cu(NH_3)_6^{2+}$ complex. Then 32 mL of 1.0 M KBH_4 aqueous solution, and 0.010 M PVA (Mw = 10000) was added at 298 K under an argon atmosphere. The SPT was carried out for 15 min. The obtained product was washed with deionized water, followed by three washings with alcohol. Finally, the sample was dried at 60 °C. The commercial CuB_{23} samples were provided by the Changzhen High Technology Limited Company.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded using an X′Pert X-ray powder diffractometer equipped with a CuKα radiation source (λ = 0.15406 nm). The Cu and B contents in the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Irris, Advantage). The Brunauer–Emmett–Teller (BET) specific surface area of the sample was made using a N_2 adsorption–desorption technique. Before the measurements, the sample was degassed at 473 K for 3 h. Scanning transmission electron microscopy (STEM) images and selected-area electron diffraction patterns (SAED) of the samples were carried out with a JEOL-2100F microscope. Samples for STEM analysis were fabricated by depositing a single drop of diluted nanoparticle dispersion in ethanol on an amorphous, carbon-coated, nickel grid. The surface electronic states of the samples were determined using X-ray photoelectron spectroscopy (XPS; Perkin–Elmer PHI 5000C ESCA, using AlKα radiation). Samples were fixed in a homemade in situ XPS reactor cell.[44,45,49] After the samples were dried under an argon atmosphere, they were transferred to an analysis chamber, and their XPS spectra were recorded. All binding

energies were referenced to the C1s peak (binding energy of 284.6 eV) of the surface adventitious carbon. Infrared spectra were acquired using a Bruker FTIR spectrometer (EQUINOX55). The emission spectra of SPT, temperature distribution and electron concentration variation in the envelope were obtained by AvaSpec-3648 optical fiber apparatus controlled with a Matlab software. The AFM image of the sample deposited on the silicon wafer substrate was obtained by atomic force microscope (Veeco D3100, USA) under the conditions of relative humidity of 63% at 20 °C with a tapping mode at a 1-3Hz scan rate and a 512×512 pixel resolution.

2.3. Manufacture and Testing of Gas Sensor

The gas sensing test was performed in an HW-30A measuring system (Hanwei Electronics Co. Ltd.) controlled with a Lab-VIEW software at room temperature under 60% relative humidity (RH). For measuring, the sample was mixed with terpineol to form a paste and then coated onto a commercial Interdigitated Electrode (IDE) to fabricate a capacitive sensor. The IDE has a silicon wafer depositing layers of 2 μm electrical isolation oxide and 10 nm Ti and 300 nm Au, and is patterned with conventional photolithography process. A pair of Au wires was annealed to perform the electrical measurements. During assessing, argon is used as a carrier gas to dilute the H_2S to desired concentration. There concentrations of H_2S and argon are monitored by mass flow controllers. Moreover, we have also investigated the water-sensing response of graphene-like CuB_{23} nanosheets exposing to different RH water vapor. The H_2S gas sensing performances of our sample under 30%RH and 80%RH were also evaluated. The detection limits in both ppm and ppb levels of H_2S were calculated based on the root-mean-square deviation method.

Table S1 Specific surface areas of different CuB_{23} samples

Samples	Specific surface areas / m^2g^{-1}
CuB_{23} nanotubes [24]	84.7
CuB_{23}/graphene [25]	133.2
commercial CuB_{23}	28.2
Graphene-like CuB_{23} nanosheets in this work	674.9
CuB_{23} NPs prepared by SPT for 1 min in this work	32.4
CuB_{23} NPs prepared by SPT for 5 min in this work	50.8
CuB_{23} NPs prepared by SPT for 10 min in this work	73.3

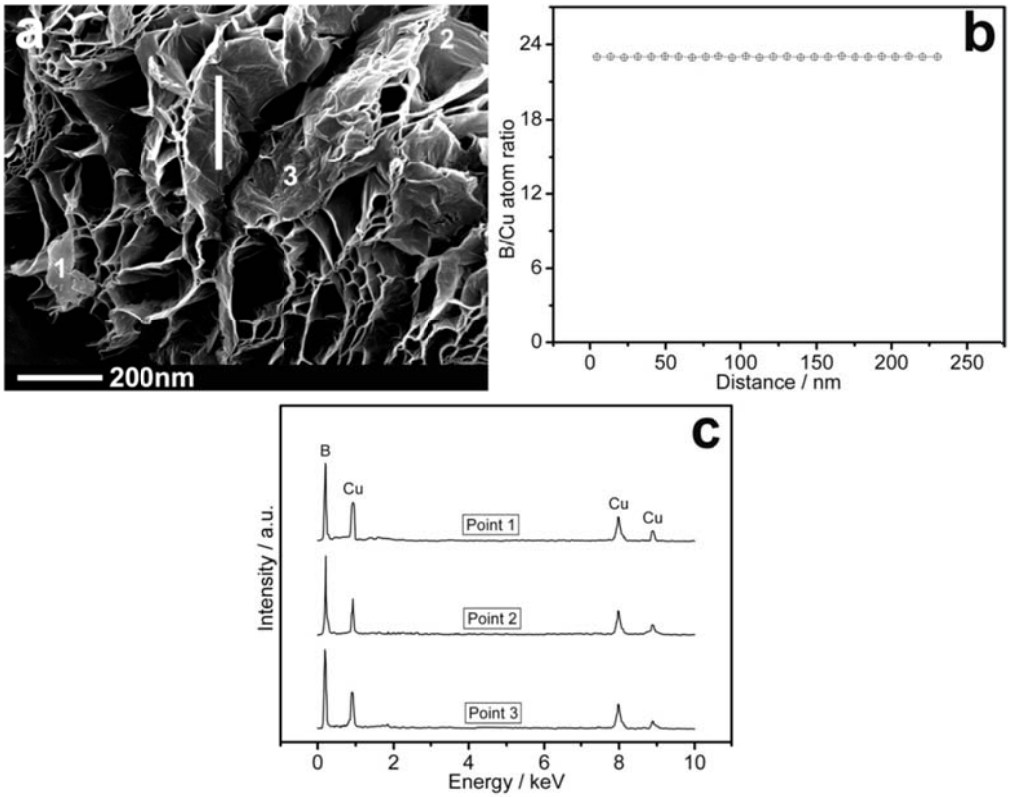

Fig.S1 (a) The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); (b) B/Cu atomic ratio recorded along the white cross-sectional compositional line shown in (a); (c) the Energy-dispersive X-ray spectroscopy (EDAX) at points 1-3 in (a) of the as-prepared graphene-like amorphous CuB_{23} alloy nanosheets

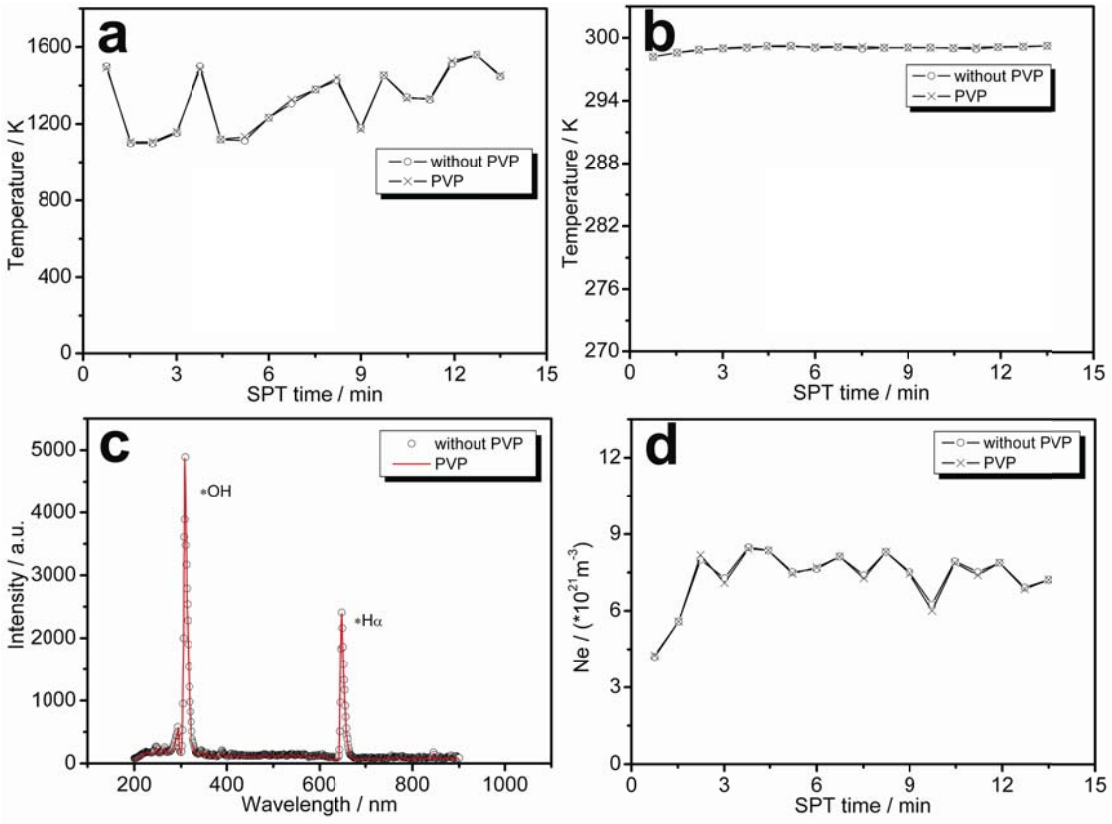

Fig.S2 (a) Electron temperature variation with discharge time; (b) Solution temperature variation with discharge time; (c) The emission spectra of SPT; (d) Electron concentration variation with SPT time with the addition of 0.010 M PVP or not

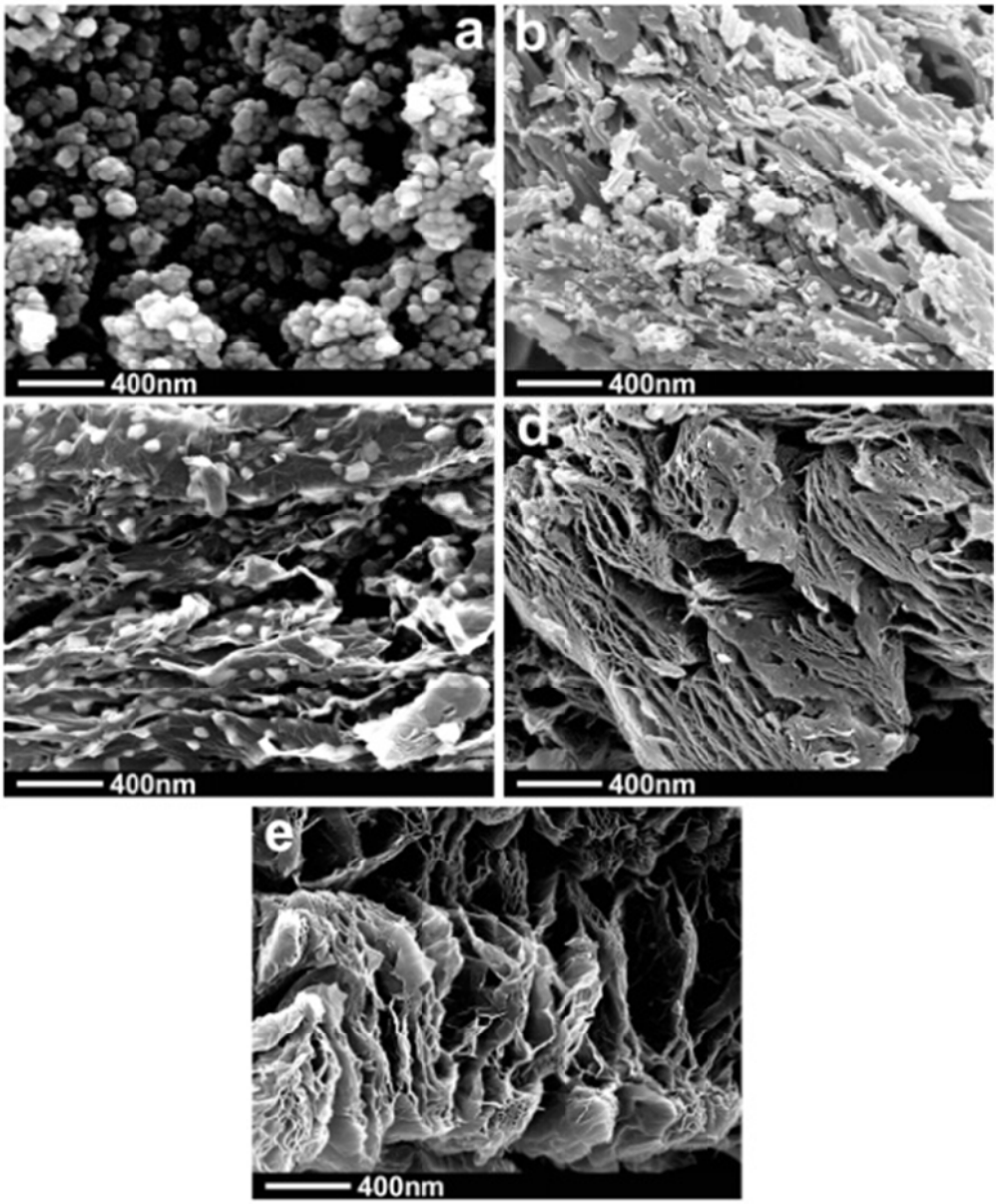

Fig.S3 STEM images of the graphene-like amorphous CuB_{23} alloy nanosheets prepared by SPT with different concentrations of PVP (a) 0; (b) 0.002; (c) 0.005; (d) 0.010 M; (e) 0.015 M

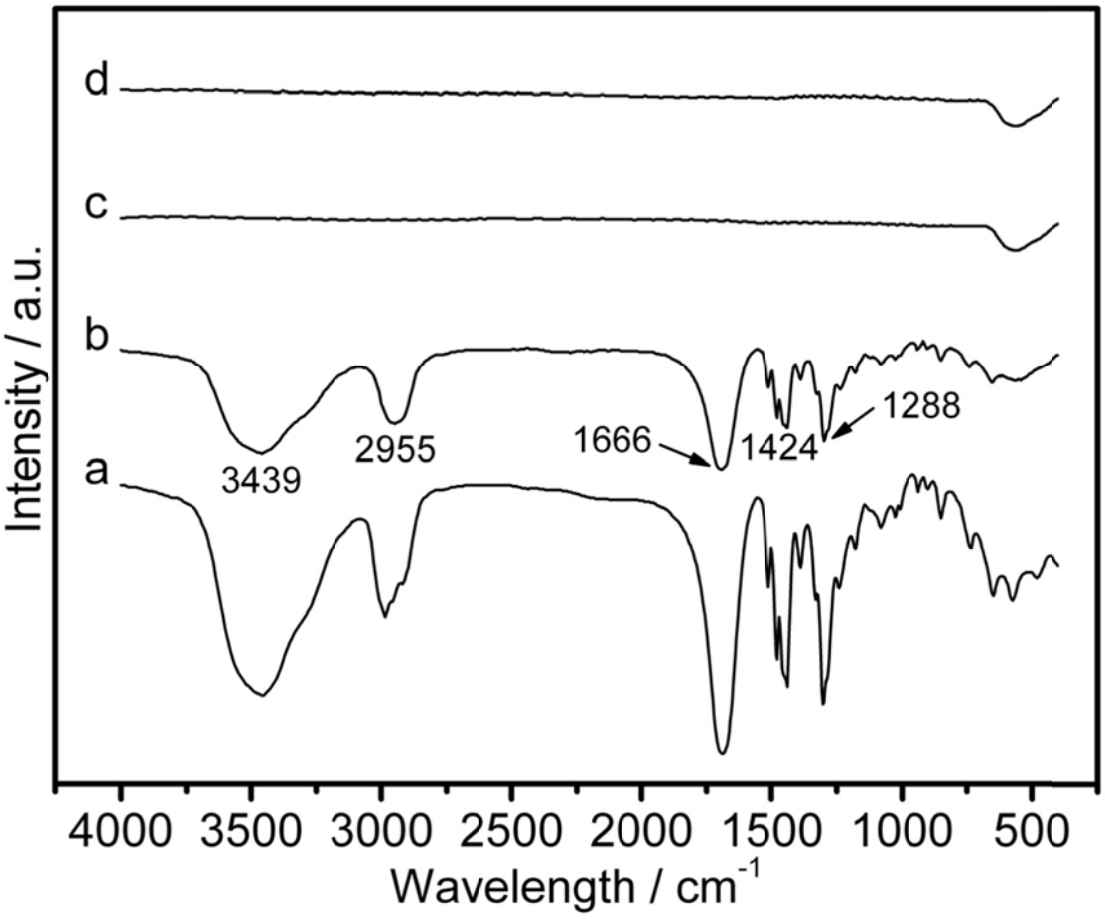

Fig.S4 FT-IR spectra of (a) PVP; (b) the as-prepared graphene-like amorphous CuB_{23} alloy nanosheets only washed with water; (c) the as-prepared graphene-like amorphous CuB_{23} alloy nanosheets washed with ethanol; and (d) commercial CuB_{23} NPs

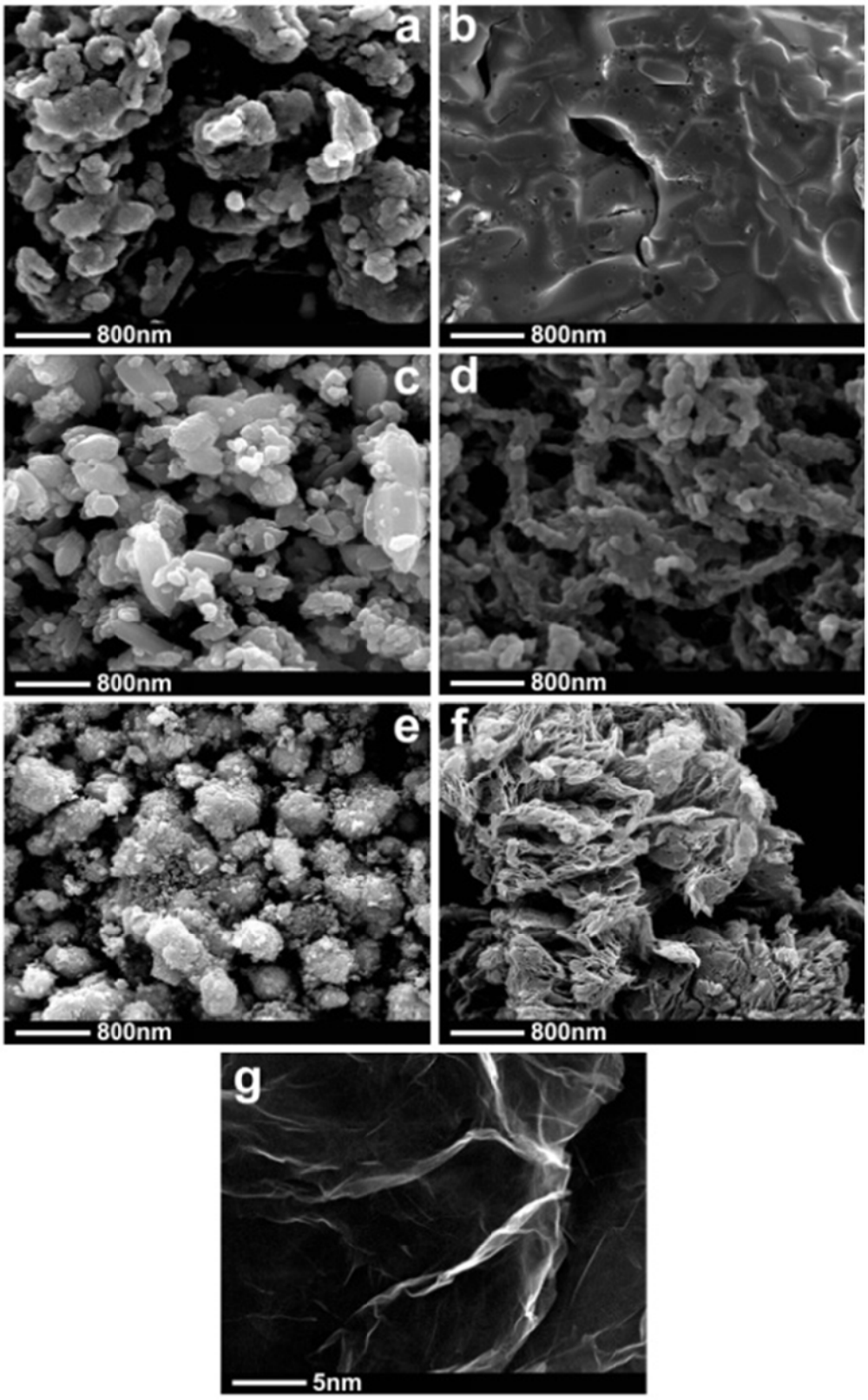

Fig.S5 STEM images of the graphene-like amorphous CuB_{23} alloy nanosheets prepared by SPT with (a) CTAB; (b) PVA; (c) P123; (d) ethylenediamine; (e) SDBS; (f, g) either of (a)-(e) after additional of PVP at different magnifications

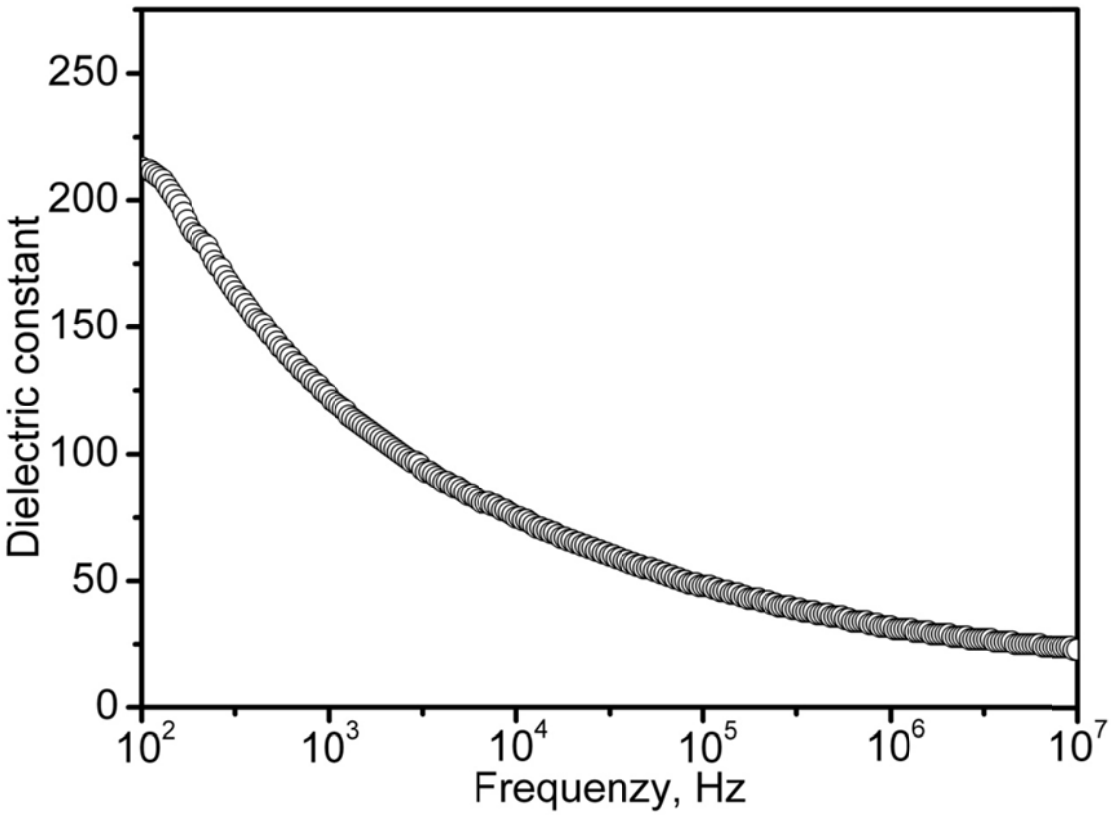

Fig.S6 Measured dielectric constant of the graphene-like amorphous CuB_{23} alloy nanosheets from 10^2 Hz to 10^7 Hz

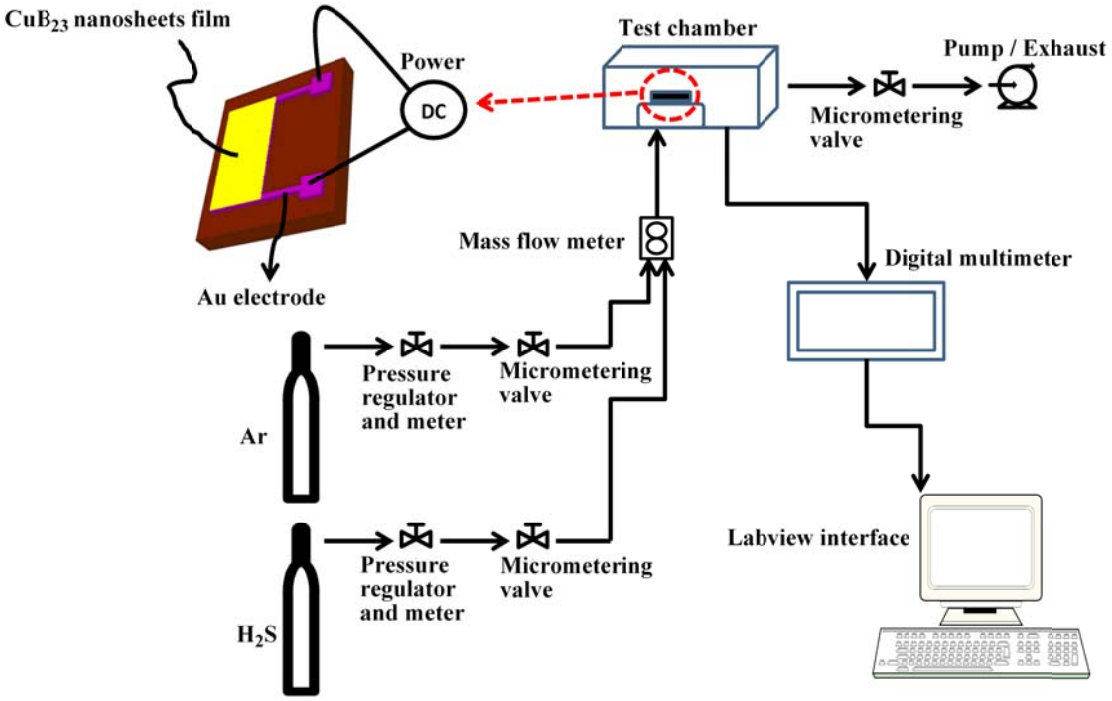

Fig.S7 Schematic diagram of the sensor measurement system with magnified sensor device configuration in our work

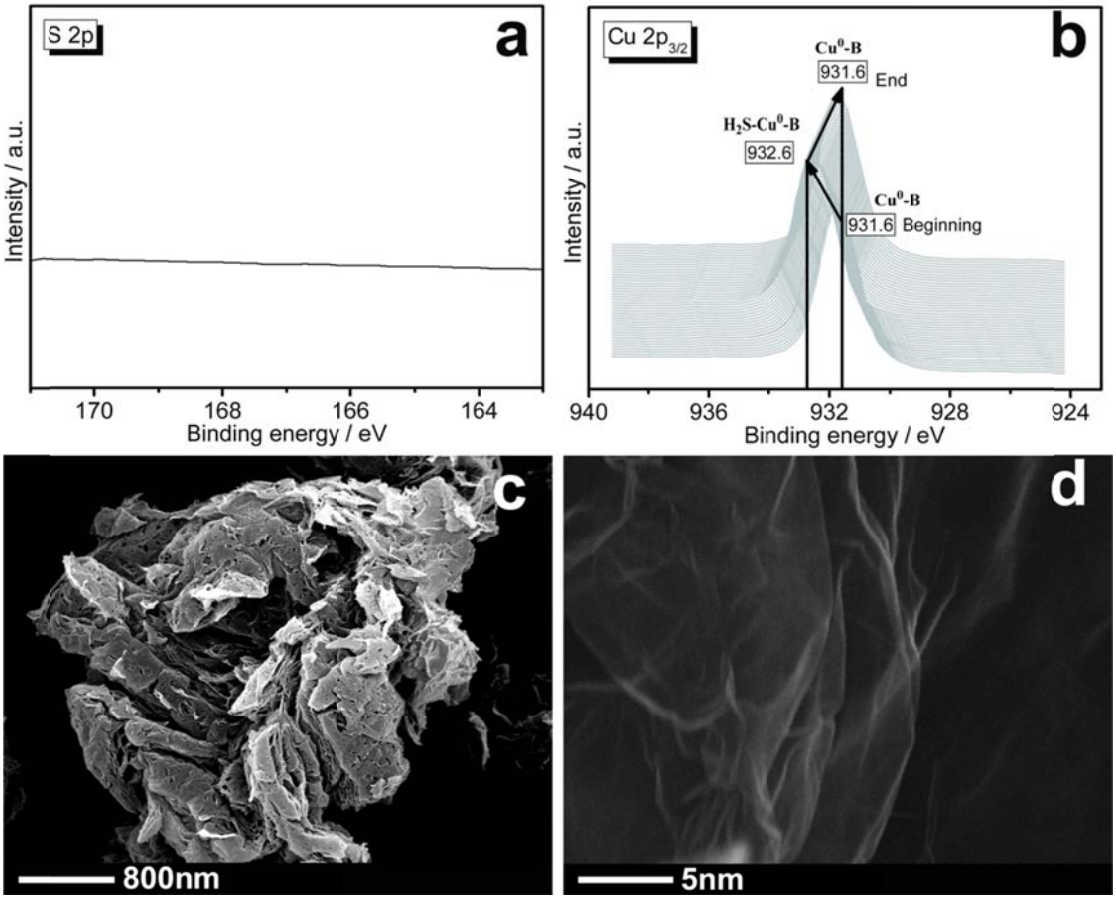

Fig.S8 (a) S 2p XPS spectrum of the graphene-like amorphous CuB_{23} alloy nanosheets after exposure to H_2S; (b) In-situ Cu $2p_{3/2}$ spectra of the graphene-like amorphous CuB_{23} alloy nanosheets during detection of H_2S; (c, d) STEM images of the recycled the graphene-like amorphous CuB_{23} alloy nanosheets after 6 months testing at different magnifications

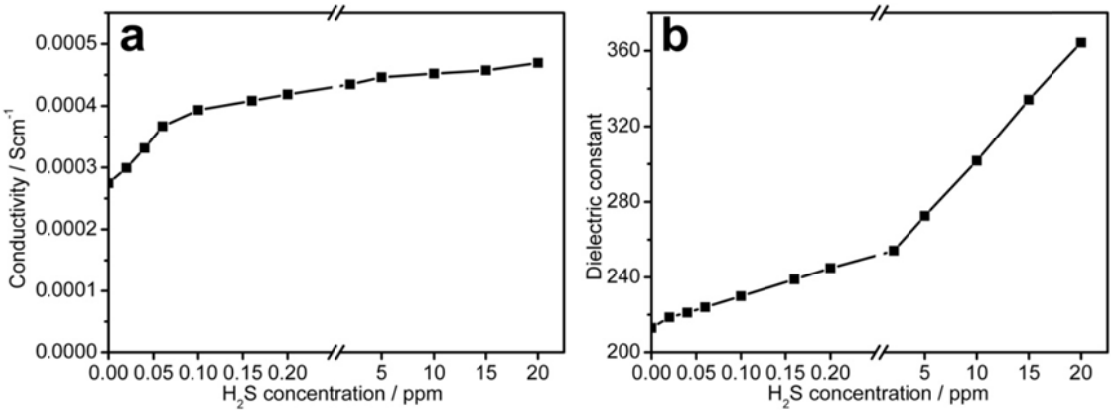

Fig.9 Variation of (a) conductivity and (b) dielectric constant (at 100 Hz) of the graphene-like amorphous CuB_{23} alloy nanosheets at different H_2S gas concentrations from 20 ppb to 20 ppm

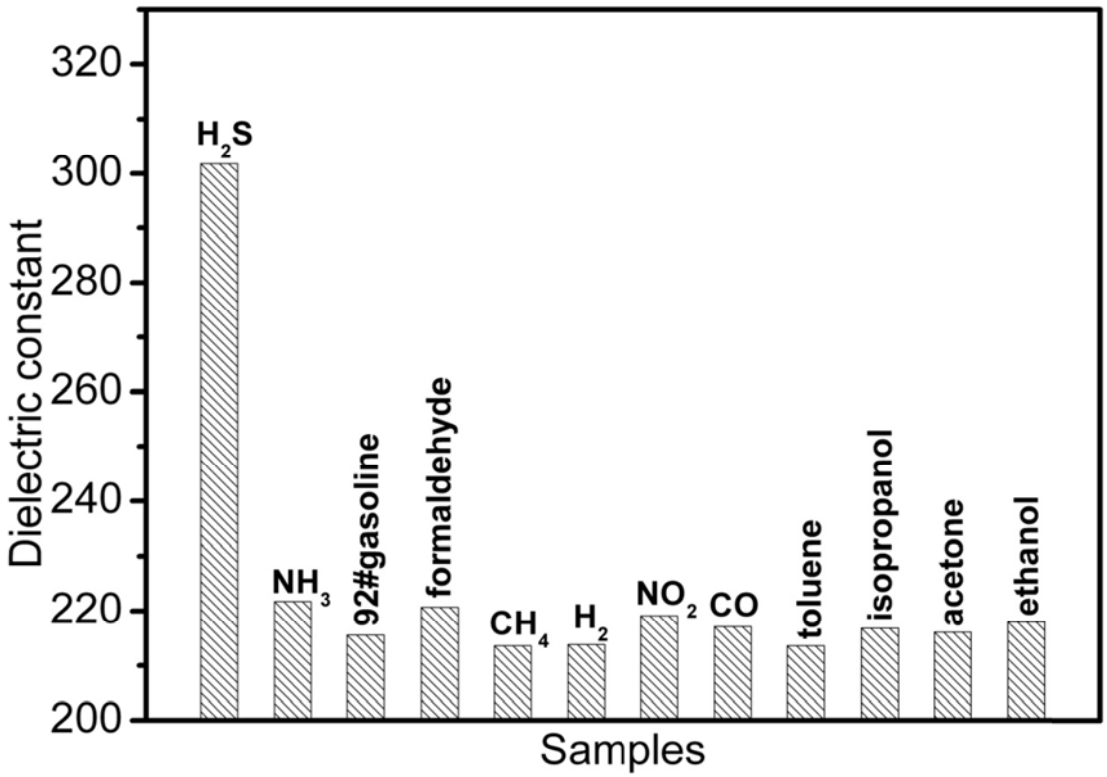

Fig.10 The measured dielectric constant (at 100 Hz) of the graphene-like amorphous CuB_{23} alloy nanosheets under 10 ppm different gases

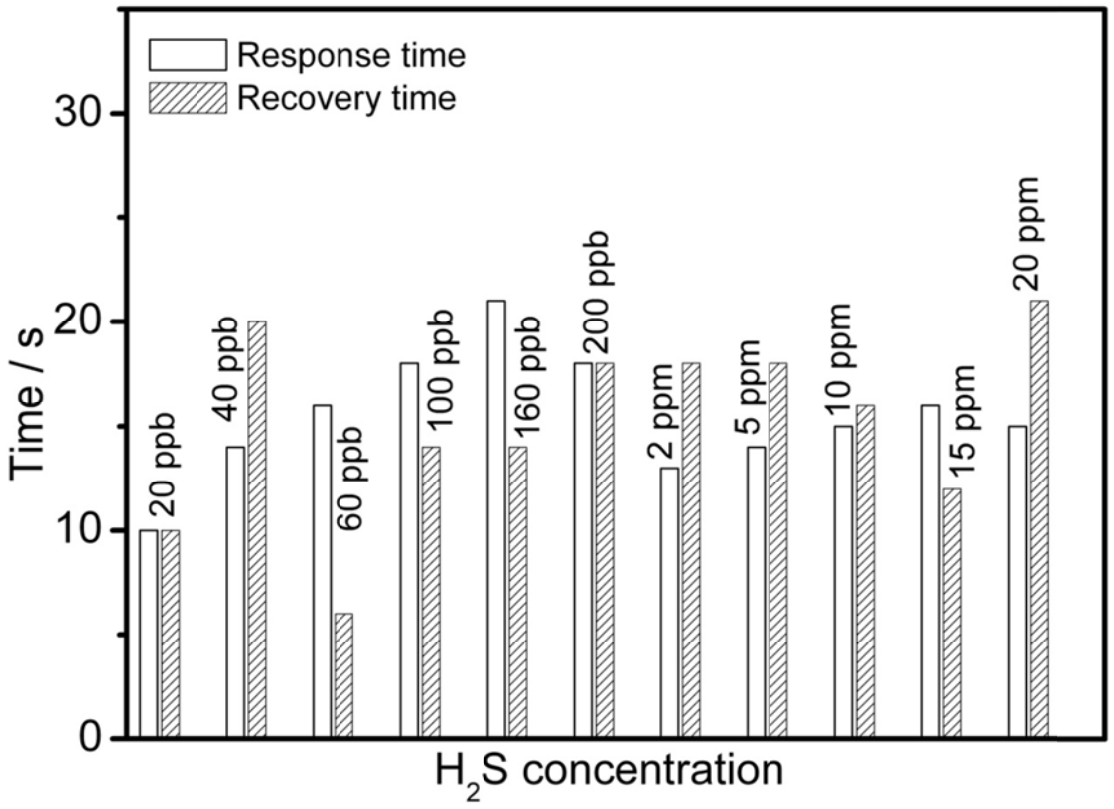

Fig.S11 Variation of response time and recovery time of the graphene-like amorphous CuB_{23} alloy nanosheets at different H_2S gas concentrations from 20 ppb to 20 ppm

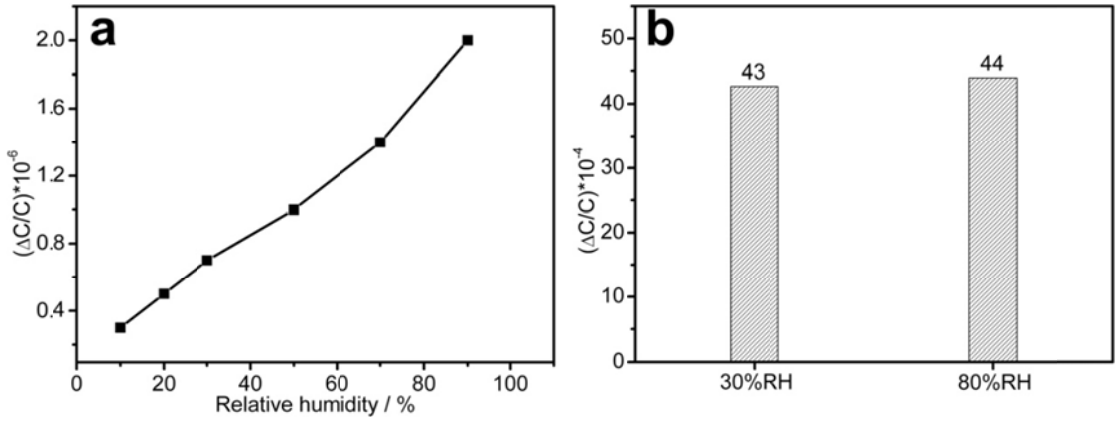

Fig.S12 Response of the graphene-like amorphous CuB_{23} alloy nanosheets (a) to different related humidity (RH) water vapor and (b) to H_2S at 30% RH and 80% RH, respectively