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Cu_2O/Co_3O_4 Nanoarrays for Rapid Quantitative Analysis of Hydrogen Sulfide in Blood

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1. Experimental Section

Sensing Measurement

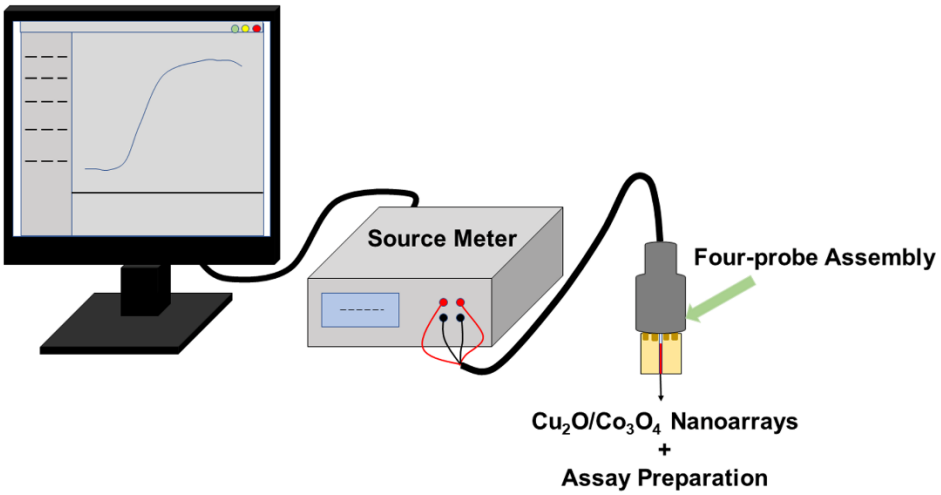

Fig. S1. Schematic sensing measuring system

Fig.S1 shows the sensing measuring system, which uses the four-probe assembly to test the response of the sensor. The diameter of each probe is 2 mm, and the distance between the center of the two probes is 2 mm. The Vaseline coating is 1mm wide and 15 mm long, with a test area (1 mm × 15 mm) between the two vaseline coatings. Press the probe onto the uncoated end (3 mm). After adding the liquid to be measured (1 μL), a source meter is used to record the response of the sensor.

2. The process of increasing H_2S concentration in human blood samples

First take 200 μL blood, and then add 2 μL Na_2S solution of different concentrations. For example, if the H_2S concentration increases by 10 μM, 1.01 mM Na_2S solution shall be added.

3. The purpose of adding nitric acid

In the deposition process, hydroxide was first formed on the front of the deposit due to its lowest deposition potential[1]. The reaction can be written as equation (1). Hydroxide was involved in the whole deposition process of Cu_2O and Co_3O_4 as the source of oxygen. Copper and cobalt ions were driven by the electric field to the cathode, where they were reduced and deposited on the surface at lower and upper parts of the half-sine wave, as described in equation (2) and (3).

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$2Cu^{2+} + 2OH^- + 2e^- \rightarrow Cu_2O + H_2O \quad (2)$$

$$3Co^{2+} + 8OH^- \rightarrow Co_3O_4 + 4H_2O + 2e^- \quad (3)$$

Here, the nitric acid dropped into the solution is not only involved in the chemical reaction, but also plays a role in the process of increasing the conductivity of the solution and promoting the deposition of ions.

4. Computational details

The first-principles calculations based on density-functional theory (DFT) were performed by the Vienna ab initio simulation package (VASP)[2], using the projector-augmented-wave potential[3]. The Perdew-Burke-Ernzerhof (PBE)[4] generalized gradient approximation (GGA) was used to describe the exchange-correlation potential. The kinetic energy cutoff is set to 400 eV and the convergence threshold for energy is 10^{-5} eV. All atom positions are fully optimized until the forces on each atom is less than 0.02 eV/Å. A grid of 17×17×17 Monkhorst-Pack k-point is used to optimize bulk unit cell. The Brillouin zone integration is performed with a 7×7×1 k-mesh for geometry optimization and self-consistent calculations. To simulate isolated thin films, a sufficiently large vacuum space of 15 Å is used to rule out any interactions between the neighboring films. The adsorption energies of H_2S adsorbed on Cu_2O and Co_3O_4 are calculated as follows:

$$E_{ads} = E_{H_2S/X} - E_X - E_{H_2S}$$

where $E_{H_2S/X}$ and E_{H_2S} are the total energies of H_2S adsorbed on Cu_2O (Co_3O_4) and the free H_2S gas molecules and E_X is the energy of Cu_2O (Co_3O_4).

5. References

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3. G. Kresse, D. Joubert, *Phys. Rev*, 1999, **59**, 1758.
4. J. P. Perdew, K. Burke, *Phys. Rev*, **77**, 3865.