

Sub-ppm electrical detection of hydrogen sulfide gas at room temperature based on printed copper acetate-gold nanoparticle composite films

J. Sarfraz,^{*a} A. Määttänen,^a B. Törngren,^a M. Pesonen,^b J. Peltonen,^a P. Ihalainen^a

^a Laboratory of Physical Chemistry, Åbo Akademi University, Porthaninkatu 3-5, FI-20500 Turku, Finland

E-mail: jsarfraz@abo.fi

^b Center for Functional Materials, Physics, Åbo Akademi University, Porthaninkatu 3-5, FI-20500 Turku, Finland.

Supporting Information Material and methods

A multilayer curtain coated ^[1] or laboratory coated paper substrate developed for printed functionality ^[2] was used for the fabrication of printed H₂S sensors. The gold electrodes were fabricated using dodecanethiol-protected AuNP synthesised following the procedure reported by Hostetler et al. ^[3] The AuNP (15 wt. %) were dispersed in xylenes and inkjet-printed on the paper substrate. The Au interdigitated electrodes containing AuNP were devised so that finger structures of the electrodes were made conducting by IR sintering and the gaps between the fingers contained non-contacting AuNP (Fig. S3). The silver electrodes were inkjet-printed using a silver nanoparticle (40 wt% of Ag) based ink (SunTronic U5603, Sun Chemicals). A solution of copper (II) acetate (CuAc) in water/ethylene glycol/Isopropyl alcohol (8:1:1 volume ratio) was inkjet-printed on the interdigitated electrodes. A gas cylinder with 200 ppm H₂S gas mixture in nitrogen (AGA) was used as a H₂S source. The resistance was followed as a function of time by a two-point measurement method using a digital multimeter (Keithley 2100). The upper limit for the resistance measurement was 100 MΩ. The H₂S concentration in the measurement box was controlled by a calibrated sensor provided by alphasense.

XPS spectra were obtained with a Physical Electronics Quantum 2000 scanning spectrometer, using a monochromatic Al K α x-ray source (1486.6 eV). The measurements were carried out on three different spots for each sample. The elemental composition and atomic concentration (at %) of the different elements was derived by calculating the area of the peaks and correcting for the sensitivity factors (using the software MultiPak v6.1A from Physical Electronics). It should be noted that analysis points independent of gold electrodes were selected for comparison, and the variation of gold amount detected at the surface was from 1 to 7 at%.

The sensors were plasma treated with an air plasma cleaner model PDC-32G manufactured by Harrick. The unit applies a maximum of 18W to the RF coil. The sensors were plasma treated for two minutes. Semiconducting type of film was measured with the help of two thermoelectric electric magnetic field (thermo-e.m.f.) probes. A heating coil was attached to the hot probe and the other probe was kept at room temperature. A temperature gradient causes a thermo-e.m.f. in the films. The sign of voltage indicates the semiconducting type (p- or n-type) of the films.

A NTEGRA Prima (NT-MDT, Russia) atomic force microscope (AFM) was used for analyzing the topography of the samples. The microscope was placed on an active vibration isolation table (TS-150, Table Stable Ltd., Switzerland) eliminate external vibrational noise. Topographical imaging was carried out by an intermittent-contact mode under ambient conditions (RH = 26 ± 4%, RT = 26 ± 2 °C) using gold-coated silicon probes (model NSG10, NT-MDT). The images (1024 × 1024 pixels) were captured at ambient conditions using a damping ratio of 0.6-0.7 and a scan speed of 0.3-0.7 Hz. AFM Images were processed and analyzed with the Scanning Probe Image Processor software (SPIP, Image Metrology, Denmark).

X-ray diffraction (XRD) was performed with a Bruker D8 Discovery (Bruker-AXS, Karlsruhe, Germany) using CuK α radiation ($\lambda=1.54184$ nm). For phase identification a PDF-2 database (2010) was used. The crystal sizes were calculated with the Topas 4.2 software (Bruker-AXS). Grazing incidence diffraction (GID) mode is used to study thin films with thickness range of 50 - 2000nm. The incident angle theta in GID is 0.2 to few degrees.

Results

Fig. S1 shows GID spectra for the drop casted copper acetate film on glass substrate exposed to different concentrations of H₂S for one hour at 45% relative humidity. The particle size increases with the increasing concentration of H₂S. The grain size of copper sulphide thin films is calculated by using the Scherer's relation:

$$D = 0.9\lambda / \beta \cos \theta,$$

using peak position $2\theta = 28.76 - 29.86$.

The particle size for reference sample (unexposed CuAc film) was determined by AFM topographical measurements of the film on ultraflat mica substrate.

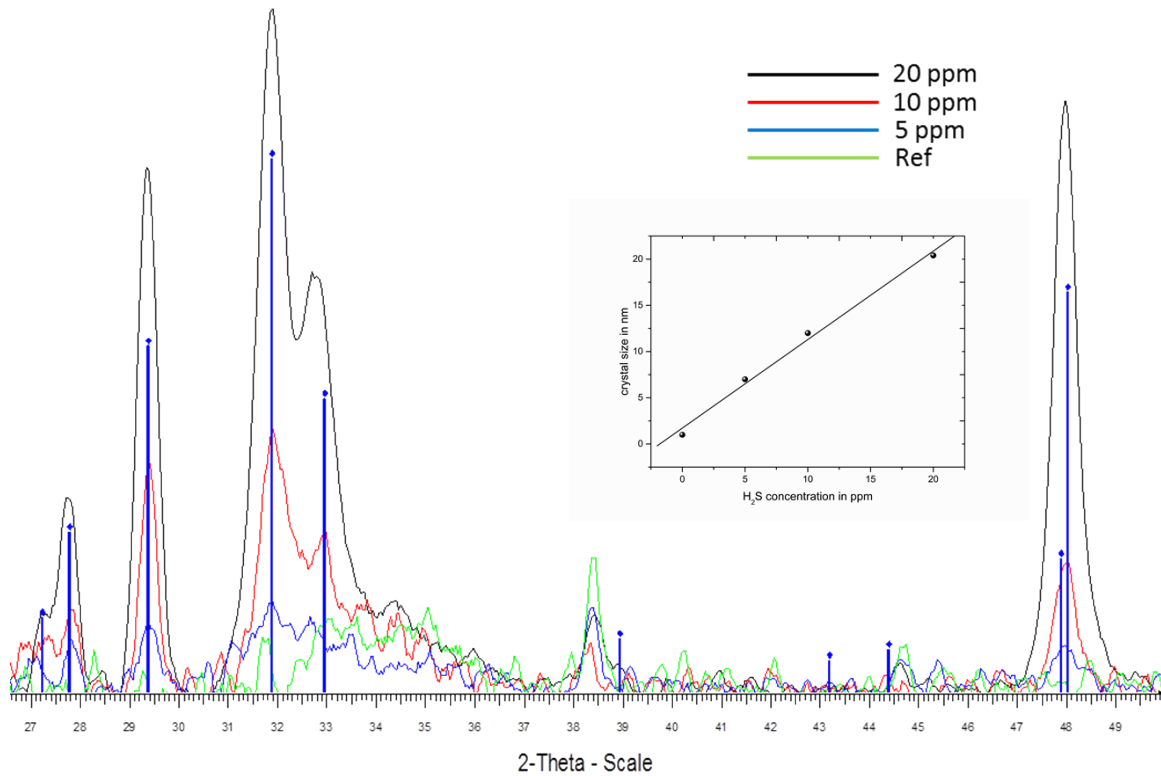


Fig. S1. GID spectra of the drop casted copper acetate film on glass substrate exposed to different concentrations of H₂S for one hour at 45% relative humidity. The obtained GID spectra matches with the copper sulfide (CuS) covellite phase pattern. The inset shows the increase in the crystal size as a function H₂S concentration.

Fig. S2 shows the increase in the average particle height from 1-2 nm to 10-15 nm after 2 min plasma treatment of the printed CuAc film on paper substrate.

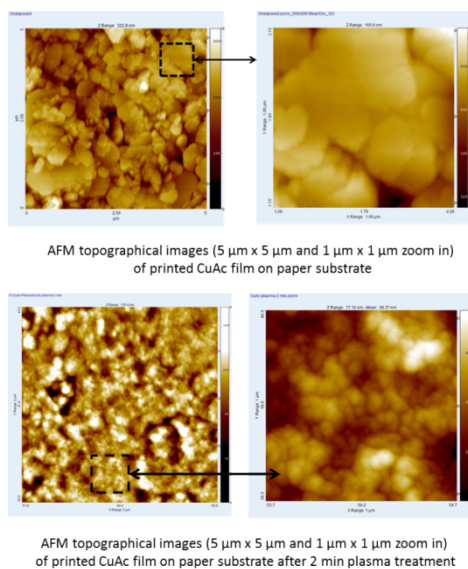


Fig. S2. AFM topographical images of printed CuAc films before and after 2 min plasma treatment.

Fig. S3 shows inkjet-printed interdigitated gold/AuNP electrode structure. The finger sections in gold/AuNP electrode in Fig. S3 were much thicker and denser than the gap sections which enabled the proper sintering of AuNP in the fingers. This turned the nonconducting reddish-black gold film to golden color and conductive. On the other hand, the thin and less dense gap section remained blackish in color and nonconductive even after IR sintering. AFM images of the gold electrode and the AuNP between the electrode fingers can be seen in the Fig. S3. The height of AuNP in the gap sections was between 3 - 14 nm.

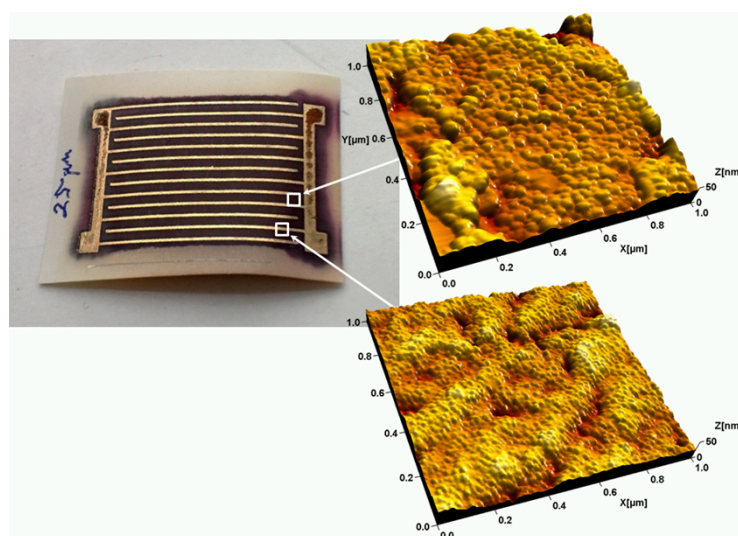


Fig. S3. A digital photograph and AFM topographical images of interdigitated Au electrodes with non-conducting AuNP layers (reddish-black) between the conductive fingers (golden).

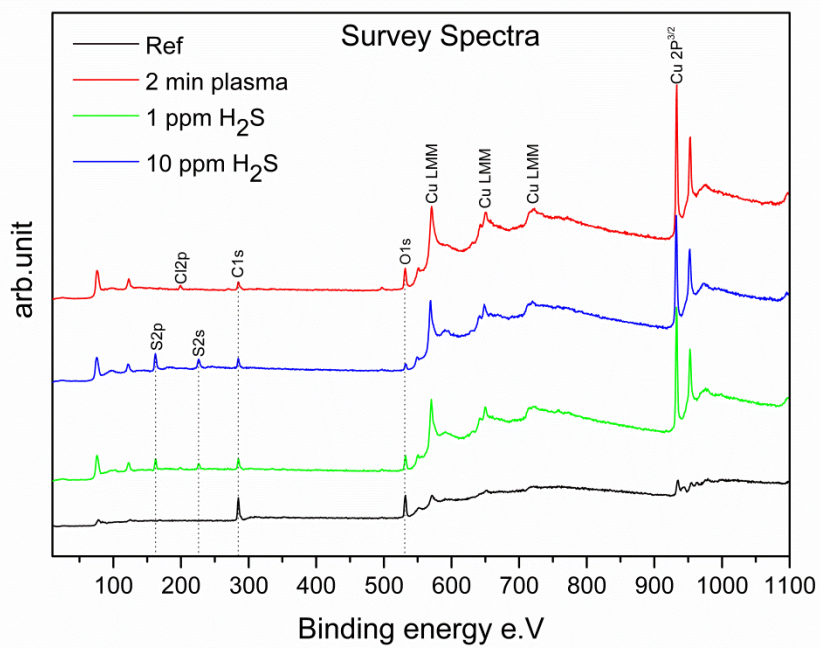


Fig. S4. XPS survey spectra for different samples

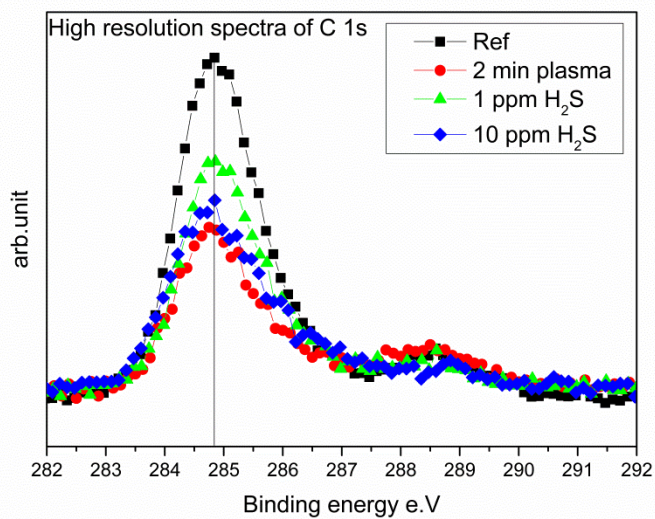


Fig. S5. XPS high resolution spectra for Carbon 1s peak

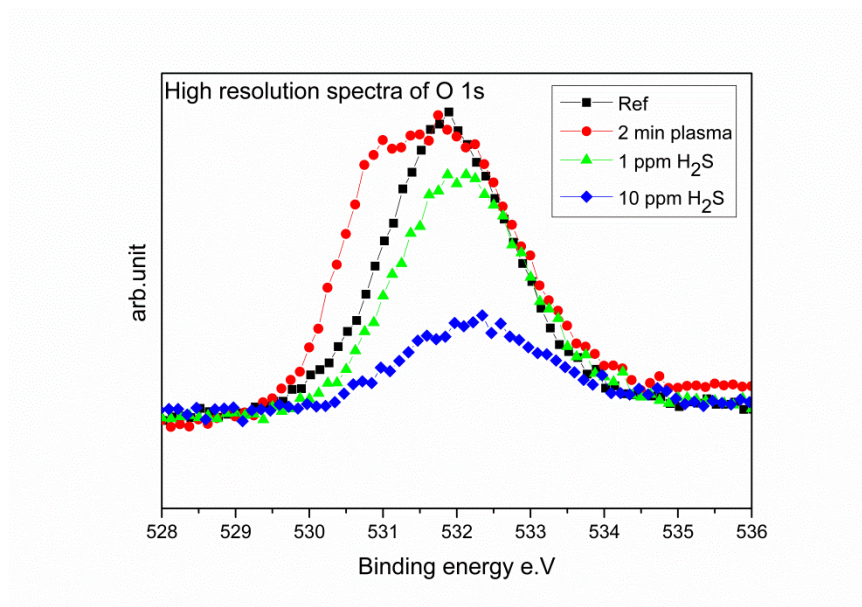


Fig. S6. XPS high resolution spectra for Oxygen 1s peak

[1] Bollström,R., Pettersson,F., Dolietis,P., Preston,J., Österbacka,R., & Toivakka,M., *Nanotechnology*, 25, 094003.

[2] Bollström,R., Määttäen,A., Tobjörk,D., Ihalainen,P., Kaihovirta,N., Österbacka,R., Peltonen,J., Toivakka,M.,2009,10,5,1020-1023.

[3]Hostetler,J., Wingate,E., Zhong, C.-J., Harris,E., Vachet,W., Clark,R., Londono,D., Green,J., Stokes,J., Wignall,D., Glish,L., Porter,D., Evans,D. & Murray,W., *Langmuir*,1998,14,17-30.