Supporting Information

High sensitive and colorimetric detection of hydrogen sulphide by in situ formation of Ag_2S@Ag nanoparticles in polyelectrolyte multilayer film

Hongxia Fu and Xinrui Duan*

Key laboratory of analytical chemistry for life science of Shaanxi Province, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi, 710119, P. R. China. E-mail: duanxr@snnu.edu.cn

Experimental Section

Materials and instrument: All reagents were obtained commercially and used without further purification. Analytical grade Silver nitrate ($AgNO_3$), sodium chloride (NaCl), sodium sulfite (Na_2SO_3), and sodium sulfide (Na_2S) were purchased from Beijing Chemical Reagents Company. Propargylglycine, Poly(styrene sulfonate) (PSS, MW～70 000), and poly(diallyldimethylammoniumchloride)(PDDA, 20 wt% in water, MW～200 000-350 000) were purchased from Sigma-Aldrich and were used as received. Millipore Simplicity 185 purification unit purified water (18.2 MΩ cm) used for rinsing and preparing all solutions.

Preparation of PDDA/PSS films: Glass slide were immersed in a piranha solution (7:3 mixture of 98% H_2SO_4 and 30% H_2O_2) at 80°C for 2 hours and then rinsed with excess amount of water. PDDA/PSS multilayers were assembled on treated glass slide according to reported procedure[1]. PEM films were assembled by sequential dipping of glass slide in PDDA (1.0 mg/mL, with 3 M NaCl) and PSS (1.0 mg/mL, with 3 M NaCl) aqueous solutions for 30 min each with rinsing with extensive amount of water in between each deposition step until the desired number of layers was obtained. The cycle was repeated 5 times to yield a $(PDDA/PSS)_5$ film. Silver ions were exchanged with sodium ion in the PDDA/PSS multilayer films by immersing the films in an $AgNO_3$ solution (0.010 M) for 20 min, and the films were then rinsed with water thoroughly and dried in a N_2 gas. These films are denoted $(PDDA/PSS)_5$/Ag(I).

Characterization of Ag_2S@Ag nanoparticles: Scanning electron microscopy (SEM) images was obtained on FEI Quanta 200 SEM at 20-30 KV. All PEMs were dried with nitrogen gas and sputter coated with gold for 80 s before imaging. For FE-TEM imaging and EDX analysis, Ag_2S@Ag NPs PEM films was scratched off the glass surface in water. The film was floating on the water surface and later was caught by a TEM copper grid. Imaging and EDX analysis was conducted by a FEI Tecnai G2 F20 FE-TEM under STEM or STEM-EDX mode.

UV-Vis spectra and Microplate Measurements: $(PDDA/PSS)_5$/Ag(I) coated glass slides were placed on top of the 96 well plate for hydrogen sulfide measurements. All wells adjacent to the sample well was left empty. All UV-Vis spectra were recorded on TU-1901 spectrometer. Absorbance Measurements were done using a Biotek Epoch plate reader at 330 nm. Standard curve were obtained by diluted Na_2S standard solutions in 10 mM phosphate buffer (pH 7.0). 300 μL of each solution was transferred into the 96-well plate, and the plate was covered immediately with $(PDDA/PSS)_5$/Ag(I) coated glass slides at 37^{o}C. After 2 hours, the absorbance of the microplate with glass slides was measured to create a standard curve.

Silver amplification: $(PDDA/PSS)_5/Ag_2S$ coated glass slides were immersed in the solutions containing silver nitrate (0.5mM) and sodium sulfite (10 mM) under UV irradiation at a wavelength of 365nm at Room temperature for 2 hours, visible changes indicating on the formation of Ag nanoparticles can be observed after two hours. Then the glass slides were rinsed with water for 3 min and dried in a stream of N_2. UV-Vis spectra were recorded on TU-1901 spectrometer and the absorbance of the microplate with glass slides was measured at 430 nm to create a standard curve.

Cell measurements: Cancer cell line HepG2 was obtained from Type Culture Collection of the Chinese Academy of Sciences, Shanghai, China. Cells were maintained in Dulbecco's modified Eagle's medium (DMEM) and supplemented with 10% fetal bovine serum (FBS), 100 U/mL penicillin, 100 μg/mL streptomycin and 2 mM L-glutamine in a 5% CO2 humidified incubator at 37°C. FBS was obtained from Hyclone laboratories Inc. Other media

components were obtained from Sigma. In a typical experiment, 10k cells were seeded in 96 wells plate 12 hours before measurement. All wells adjacent to the sample well were left empty. Right before measurement, cell culture medium was changed to 150 µL measuring medium (DMEM with 5% FBS, 10 mM of pH=7.0 HEPES buffer, 100 U/mL penicillin, 100 µg/mL streptomycin and 2 mM L-glutamine). Then 0.25 mM of cysteine (CYS) and 0.5 µM of Pyridoxal phosphate (PLP) were added to every wells. 1 mM of DL-propargylglycine (PAG) was used as CSE inhibitor to reduce H_2S production. Wells without cells was used as blank contains 150 µL medium plus same amount of CYS and PLP. The plate was covered immediately with $(PDDA/PSS)_5/Ag(I)$ coated glass slides and then incubate at 37°C for 2 hours. Resulting $(PDDA/PSS)_5/Ag_2S$ coated glass slides were proceed to silver amplification process. All the absorbance were measured at wavelength of 430 nm.

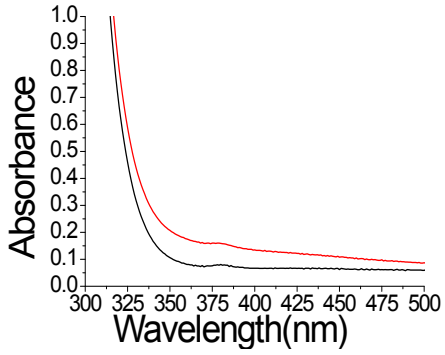

Figure S1 Spectra of UV-Vis absorbance of $(PDDA/PSS)_5/Ag(I)$ (Black line) and $(PDDA/PSS)_5/Ag_2S$ (red line). 1 mL of 10 mM Na_2S in pH 7.0 phosphate buffer were used to react with $(PDDA/PSS)_5/Ag(I)$ for 1 hour to generate $(PDDA/PSS)_5/Ag_2S$.

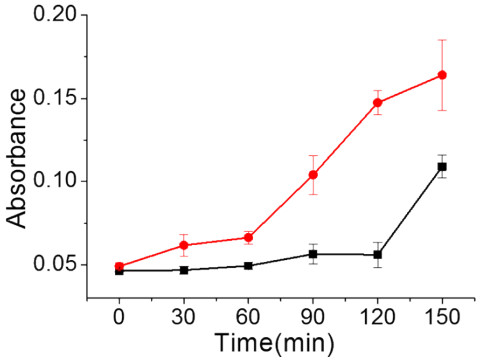

Figure S2 Effect of amplification time on the detection of hydrogen sulphide. Error bars represent standard deviation (n=3). H_2S gas from10 µM Na_2S solution was used to react with $(PDDA/PSS)_5/Ag^+$ to generate $(PDDA/PSS)_5/Ag_2S$, which further treated with mixture of AgNO3 and Na2SO3 solution with different time to generate (PDDA/PSS)5/Ag2S@Ag.

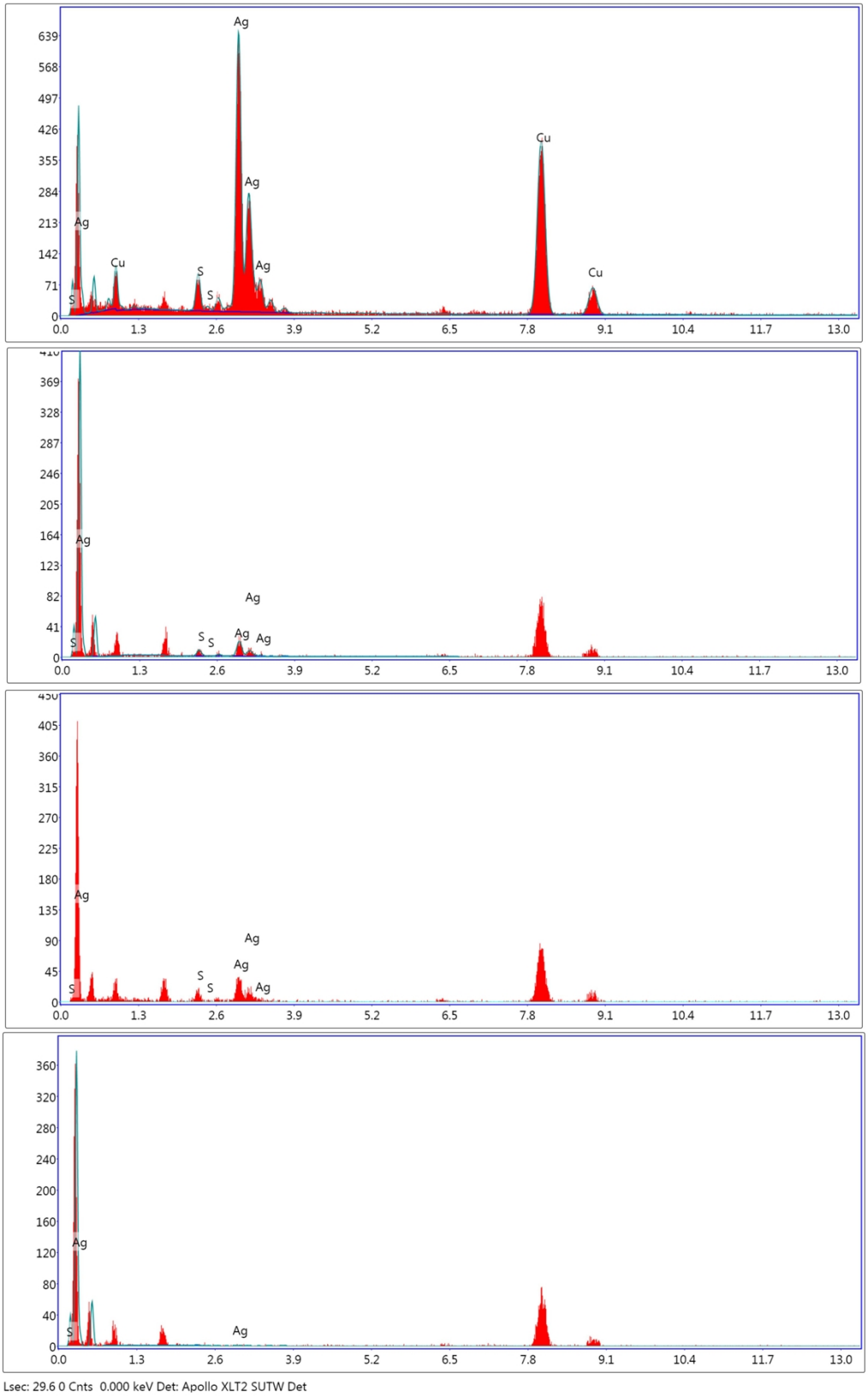

Figure S3 from top to bottom: EDX spectra of spot 1, area 1, areal 2, and area 3.

Reference：

1. Zan, X.; Su, Z. Incorporation of Nanoparticles into Polyelectrolyte Multilayers via Counterion Exchange and in Situ Reduction. *Langmuir* **2009**, *25*, 12355–60.