# **Electronic Supplementary Information**

# A colorimetric agarose gel for formaldehyde measurement based on nanotechnology involving Tollens reaction

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# Experimental

### Chemicals

Agar powder, chloroauric acid (HAuCl<sub>4</sub> ·3H<sub>2</sub>O) and acetaldehyde (40 %) were purchased from

Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Formaldehyde (37 %, drug test only)

was bought from Wokai Bio-tech Co., Ltd (Shanghai, China).All other reagents were of analytical

grade and used as received.

# Instrumentation

Ultrapure water (18.2 M $\Omega$  cm) was obtained from a Millipore Autopure WR600A system and

used throughout. UV-Vis spectra were recorded using a UV-2450 Spectrophotometer (Shimadzu) with 1-cm path length quartz cuvettes. A Canon IXUS-125HS digital camera was used to take optical photographs. Transmission electron microscopy (TEM) images were captured using a JEM 1400 microscope (JEOL). High-resolution TEM (HR-TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive X-ray elemental mapping measurements were performed on a Tecnai F30 microscope (Philips, FEI, TECNAI). Powder X-ray diffraction was carried out on an X'Pert PRO MPD diffractometer (PANalytical). A Nano-ZS ZEN3600 Particle Size Analyzer (Malvern) was used to characterize the size distribution of the Au NPs.

#### Synthesis of citrate stabilized Au NPs

The Au NPs were prepared using a standard citrate method. <sup>1</sup> Briefly, 10 mL of trisodium citrate (38.8 mM) was quickly injected into 100 mL HAuCl<sub>4</sub> (1 mM), which was heated and stirred under reflux. This reaction mixture was further heated and stirred under reflux for another 15 min. In this period, the solution color changed from pale yellow to wine red. Finally, the solution was cooled to room temperature under stirring and stored in a refrigerator at 4 °C for further use. The concentration of the Au NPs as determined by UV-Vis spectrometry was estimated to be 12 nM.

#### **Preparation of Tollens stock solution**

The preparation of Tollens stock solution was modified from the reference<sup>2</sup> and described as follows: to 1-mL AgNO<sub>3</sub> solution (0.5 M) was added 1040  $\mu$ L aqueous ammonia (25%-28%), followed by the addition of NaOH (3 M, 650  $\mu$ L). Water was used to reach the final volume of 20 mL. This Tollens stock solution contains about 25 mM of [Ag(NH<sub>3</sub>)<sub>2</sub>]OH and 1 mM free NH<sub>3</sub>·H<sub>2</sub>O.

#### **Colorimetric detection of aqueous HCHO**

An aliquot of 500  $\mu$ L Au NPs (6 nM), 3750  $\mu$ L water, 250  $\mu$ L Tollens reagent were sequentially added into a sample vial. 500- $\mu$ L of aqueous HCHO with various concentrations was added into this reaction mixture. This colorimetric assay was performed at room temperature (20±2 °C) for 15 min unless otherwise specified. After reaction, the absorption spectra were recorded using a spectrometer and the corresponding photographs were taken using a digital camera.

#### Preparation of the agarose gels

To boiled water (5 mL) was added agar powder (0.1 g). The solution was heated and stirred until the agar powder dissolved completely. Then, agar solution (1.5 mL) was pipetted to a Petri dish (I.D. 3.5 cm). When the agar solution was cooled to about 50 °C, Au NPs colloidal (6 nM, 0.4 mL) and Tollens reagent (0.5 mL) were added into the agar solution. Finally, the agar solution was molded into gel by placing the Petri dish into a refrigerator at 0 °C for 2 min. The as-prepared agarose gel was cut into smaller ones with spherical shape (I.D. 0.8 cm) for further use.

#### Colorimetric detection of aqueous HCHO using the agarose gels

The agarose gels were immersed into 5-mL of HCHO aqueous solution with various concentrations. Thirty minutes later, they were taken out and photographed. This experiment was carried out at ambient temperature (28±2 °C).

#### **Preparation of gaseous HCHO**

Various amounts of aqueous HCHO standards were injected into gas sampling bags with constant volume (30 L), which were then filled with air in order to generate standard gaseous HCHO. Prior to analysis, the air sampling bags were heated at 50 °C to ensure the homogeneous diffusion of gaseous HCHO.

# Colorimetric detection of gaseous HCHO using the agarose gels

Various concentrations of gaseous HCHO (0, 80 and 750 ppb, and 20 ppm ) were inhaled into 100-mL medical syringes, in which agarose gels were introduced beforehand. The syringes were then carefully sealed using silicon plug. The incubation was carried out at ambient temperature  $(30\pm 2 \text{ °C})$  for a certain period of time.



Figure S1. TEM images (a-c) and (d) UV-Vis spectra of the Ag NPs generated by the Tollens

reaction. The concentration of HCHO was 100  $\mu M.$ 



*Figure S2.* (a) TEM images and (b) DLS analysis results of the as-synthesized Au NPs.



*Figure S3* The UV-Vis spectra of (a) the mixture of Tollens reagent and HCHO; (b) the Au NPs; and (c) the mixture of Au NPs and HCHO. The corresponding photographs are displayed in Figure inset. The concentration of HCHO was 100  $\mu$ M for (a) and (c).



*Figure S4* (a) Photographs of the colorimetric assay for HCHO (20  $\mu$ M) with time (b) Time profiles of the colorimetric assay for HCHO at different concentrations. This experiment was

carried out at 25 °C.



Figure S5. UV-Vis spectra of the colorimetric assay for six replicates of HCHO (25 µM). Figure

inset represents the corresponding photographs.



*Figure S6* (a) Photographs and (b) UV-Vis spectra of the Au@Ag core-shell NPs processed with different volumes of 0.1 M HNO<sub>3</sub>. Volumes presented in the figure were added into the Au@Ag core-shell NPs solution to make the final volume of 1 mL, and the spectra were recorded after acid addition. Different amounts of HNO<sub>3</sub> (0, 100, 200, 210, 220 and 230  $\mu$ L) were added to the freshly prepared bimetallic NPs. Figure S4a shows that, as the amount of HNO<sub>3</sub> added increased, the color of solution progressively changed from yellow, then to orange, and finally to reddish, implying the dissolution of Ag shell. The addition of more aliquots (210-230  $\mu$ L) of HNO<sub>3</sub> did not dissolve the Au core, and so the solution retained its reddish color. Figure S5b shows that there are two SPR bands located at around 414 and 489 nm prior to HNO<sub>3</sub> addition. As HNO<sub>3</sub> was added, the intensity of the former band decreased and tended to disappear, whereas the latter band redshifted to 520 nm, which is the characteristic SPR peak of Au NPs. Unlike core-shell particles, nitric acid can dissolve alloys and leads to a solution with a gray appearance.<sup>3</sup>



*Figure S7.* Representative EDX spectra of the (a) Ag NPs generated by the Tollens reaction in the absence of Au NPs with HCHO at 100  $\mu$ M; Au@Ag core-shell NPs generated by the Tollens reaction in the presence of Au NPs with HCHO at (b) 5  $\mu$ M (c) 25  $\mu$ M (d)100  $\mu$ M. The measurements were performed on the surface of a single nanoparticle with the square area of about 30 nm in side length. The atomic ratio of Ag:Au is (a) 15:0, (b) 2.50:16.98, (c) 5.48:4.84 and (d) 14.77:4.44.



*Figure S8.* Powder XRD profiles of the Au@Ag core-shell nanoparticles generated by the Tollens reaction in the presence of Au NPs with HCHO at (a) 25  $\mu$ M (b) 75  $\mu$ M (c) 100  $\mu$ M. Au and Ag possess very similar lattice constants of 0.408 and 0.409 nm, and so it is difficult to differentiate them with XRD pattern. However, the existence of Au/Ag was confirmed with the diffraction peaks at 2 $\Theta$ =38.2 °C, 44.3 °C, 64.5 °C and 77.4 °C, due to the reflections of Au/Ag (111), (200), (220) and (311). With increasing the concentration of HCHO, all the Au/Ag reflections were intensified. In view of the fact that the content of Au is constant in this colorimetric system, these enhanced reflections are probably due to the increase of Ag shell to Au core. The diffraction peak at 2 $\Theta$ =32.3 °C indicates the presence of AgCl crystallites, which is probably formed by the reaction between [AuCl<sub>4</sub>]<sup>-</sup> and [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.



*Figure S9.* UV-Vis spectra and photographs (Figure inset, rightmost row) of the (a) Au NPs; and the Au@Ag core-shell NPs generated by the Tollens reaction in the presence of Au NPs with HCHO at (b) 5  $\mu$ M (c) 25  $\mu$ M and (d) 100  $\mu$ M. The spherical particles (Figure inset, middle row) means the Au NPs, and Au@Ag core-shell NPs with different shell-to-core ratios. The t value represents the thickness of Ag shell, and all the t values in this Figure were calculated based on the average values from at least 100 nanoparticles from Figure 3. The monometallic Au NPs (t=0) shows one characteristic SPR peak at 520 nm. At a relatively small t (0.8 nm), the Au@Ag core-shell NPs show two characteristic SPR band located at around 410 and 507 nm, representative of

Ag shell and Au core, respectively. The wrapping effect of Ag shells on Au cores was verified by the blue-shift of the low energy SPR band and the emergence of a high energy SPR band around at 410 nm. As the t value increased (3.2 nm), the peak position of Au core continuously shifted to blue, and the peak intensity originated from Ag shell was also intensified. As the thickness of Ag shell increased to 8.5 nm, the peak of Au core was completely shielded and the intensity of Ag shell reached its maximum. Correspondingly, the color of the solution change from reddish, then to orange, and eventually to deep yellow, depending on the ratio of Ag shell thickness to the diameter of Au core. This HCHO-induced color changes could be readily observed by the naked eyes. These results also reveal us that the proposed colorimetric assay could be utilized for the synthesis of Au@Ag core-shell NPs, in which the dimension (i.e., thickness of the shells to size of the cores) of the bimetallic core-shell NPs can be readily controlled by independently varying the HCHO concentration.



*Figure S10.* The responses of the colorimetric assay for 10 indoor or outdoor gases in aquous solution. 1.Blank; 2. HCHO; 3. Mixture of bezene (B), toluene (T), ethylbenzen (E)and xylene (X); 4. Dichloromethane; 5. Chloroform; 6. Aniline; 7. Acetone; 8. Trichlorophenol; 9. Petroleum naphtha; 10. Methanol; 11. 1-methylphenol. The concentration was 50 μM for HCHO; 5 mM for dichloromethane, chloroform, aniline, acetone, trichlorophenol and1-methylpheonol, 1.2 M for methanol; 60 mM for Naphtha; and 60 mg/mL for the BTEX.



*Figure S11.* (a) photographs of the colorimetric assay for the selected aldehydes after 1 min (upper row) and 15 min (lower row); (b) the kinetic curves of the colorimetric assay for the selected aldehydes. The concentration of each aldehyde was at 75  $\mu$ M.



Figure S12. Photographs of agarose gels for the detection of gaseous HCHO at different

concentrations. The incubation time was 4 h.



*Figure S13.* Photographs of (a) two pieces of agarose gels, and (b) both of them are subsequently exposed to air (free of HCHO, agarose gel 1) and 20 ppm HCHO (agarose gel 2) for 1 min. Specifically, agarose gel 1 and 2 was cut from a freshly prepared agar gel on a Petri dish. These two pieces of agarose gels were immediately taken photographs, which were displayed in Figure a. Then, agarose gel 1 and 2 was separately placed in two 100-mL medical syringes filled with air (free of HCHO) and 20 ppm HCHO. One minute later, these two pieces of agarose gels were taken out and photographed.

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