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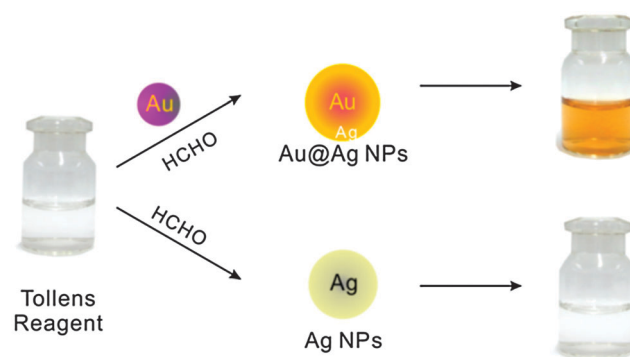
Gold nanoparticles (Au NPs) coupled with Tollens reagent were used for measuring formaldehyde. Au@Ag core-shell NPs were formed along with distinct color changes from pink to deep yellow. This colorimetric system was further immobilized into an agarose gel, which was used for monitoring of gaseous formaldehyde.

Formaldehyde (HCHO) is widely used in industry as a bonding agent, especially for building materials, such as wood furniture and paint. However, the use of these materials has caused the remaining HCHO concentration indoors to exceed certain threshold, which puts people's health at potential risk. For example, HCHO has been found to be highly associated with the sick building syndrome, such as eyes and nose irritation, fatigue, headache and coughing.¹ In addition, it has been classified as one of the human carcinogens by the world health organization (WHO).² The measurement of indoor HCHO is closely related to the safety of living, which emphasizes the need for a simple, sensitive and reliable method for measuring HCHO. Several approaches including chromatography,^{3a,b} electrophoresis,^{3c} fluorimetry,^{3d} enzyme-based biosensors^{3e,f} and gas sensors based on metal oxide^{3g-i} have been developed. These approaches are sensitive and reliable, but rely on the use of scientific instruments which are not easily accessible by the public. At the same time, special techniques are required for instrument operation and data assessment.

Colorimetric methods are alternative simple approaches for measuring HCHO, but extraneous organic chromophores with

delocalized conjugated functional groups (*e.g.*, acetylacetone, pararosaniline, chromotropic acid) are generally required as recognition units.⁴ Moreover, these approaches are not sensitive enough, are susceptible to interference, require strong acid or base, and/or are time-consuming.⁵ Recently, a colorimetric method for measuring HCHO has been proposed by using a Nafion film saturated with $[\text{Ag}(\text{NH}_3)_2]^+$ and ATP. However, the method required a long reaction time (1 h) and suffered from inadequate sensitivity.⁶ Suslick and co-workers fabricated a sensitive HCHO colorimetric sensor array based on the reaction between primary amine and HCHO. The sensor array was fully reversible, but relied on a series of pH indicators and statistical data-processing.⁷ Thus, a reliable, easy-to-operate, sensitive and low-cost HCHO detection method is still highly desired for daily use.

It is well documented in textbooks that HCHO can react with Tollens reagent (the key component is $[\text{Ag}(\text{NH}_3)_2]\text{OH}$) to produce a silver mirror. Similar to a previous report,⁸ we also have revealed that silver nanoparticles (Ag NPs) were produced when the concentration of HCHO was relatively low (Scheme 1, down row and Fig. S1a–c in the ESI†). There was an indistinguishable color change from colorless to slightly yellow along with the appearance of a surface plasmon resonance (SPR) band at 416 nm



Scheme 1 Schematic diagrams of the Tollens reaction with (upper row) and without (down row) Au NPs.

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† Electronic supplementary information (ESI) available: Experimental procedures and Fig. S1–S13. See DOI: 10.1039/c4cc00914b

(Fig. S1d, ESI†). As shown in the upper row of Scheme 1, when Au NPs were introduced in this classic reaction, the generated silver nanoshells were coated onto Au NPs, leading to the formation of Au@Ag core-shell nanostructures. The shell thickness of the produced NPs was strongly dependent on the concentration of HCHO. The change of shell thickness was accomplished with a distinct color change from pink to deep yellow, which can serve as a colorimetric approach for measuring HCHO.

The Au NPs were synthesized by reducing the HAuCl₄ with trisodium citrate, and the as-synthesized Au NPs exhibited spherical shapes and uniform sizes (13.0 ± 1.5 nm diameter, Fig. S2 in the ESI†). The sole addition of Tollens reagent or HCHO into the suspension of Au NPs did not lead to obvious spectral or color changes (Fig. S3 in ESI†). In contrast, the addition of incremental amounts of HCHO into the mixture of Au NPs and Tollens reagent led to apparent color changes from pink, to orange, and finally to deep yellow (Fig. 1a). These distinct color changes were obtained in several minutes (Fig. S4, ESI†) at room temperature (25 °C), which provides a rapid and simple way to measure HCHO without using instrumentation and chromophores. The lowest eye-distinguishable concentration can be as low as 100 nM (3 ng mL^{-1}).

A UV-Vis spectrometer was used to monitor the spectra during the addition of HCHO into the mixture of Au NPs and Tollens reagent. Fig. 1b shows that the SPR band of Au NPs peaked at 520 nm blue-shifted, along with the emergence of a second SPR band at around 410 nm, which implied the formation of core-shell NPs.⁹ The absorbance at 410 nm increased with the incremental concentration of HCHO (Fig. 1b). There was a good linear relationship between the A_{410}/A_{520} ratio and HCHO concentrations in the range of 0.1–40 μM (Fig. 1b, inset), which also enables a quantitative readout using UV-Vis spectroscopy. The lowest detectable concentration was found to be 50 nM (1.5 ppb). To the best of our knowledge, this is the smallest LOQ for HCHO based on colorimetric methods.^{1b,4h,5,6,10}

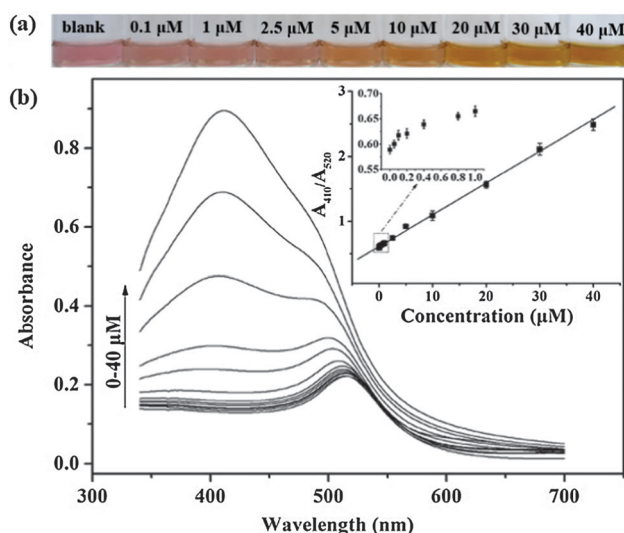


Fig. 1 (a) Photographs and (b) UV-vis spectra of the colorimetric assay for measuring HCHO at various concentrations. Inset in figure (b) shows the linear relationship between the A_{410}/A_{520} ratio and HCHO concentration.

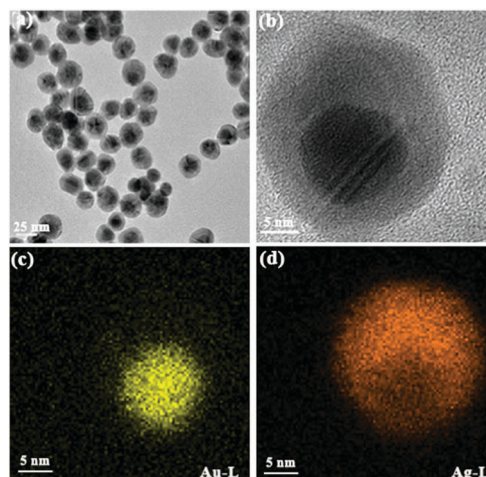


Fig. 2 Representative (a) TEM, (b) HR-TEM and elemental maps for the core (c) and the shell (d) of the obtained nanoparticles.

The relative standard deviation of the assay is less than 1.6% (Fig. S5, ESI†).

The structure and chemical composition of the produced NPs were characterized using transmission electron microscopy (TEM). Fig. 2a shows that most of the NPs were spherical and exhibited inhomogeneous electronic density with a darker central part and a lighter outer part. A high-resolution TEM (HR-TEM) image (Fig. 2b) clearly displays a spherical NP with apparent different optical contrast in the core and in the shell, respectively. Energy-dispersive X-ray elemental analysis was used to map the element distribution in a typical nanoparticle. As depicted in Fig. 2c and d, the elemental composition of the core was gold, and that of the shell which surrounded the gold core was silver, verifying the formation of Au@Ag core-shell structures. The possibility of forming alloys was excluded by the fact that nitric acid dissolved the Ag shell alone but barely affected the Au cores (Fig. S6 in ESI†).

To get more insight into the mechanism of the approach, TEM was used to measure the dimension of Au@Ag core-shell NPs produced by the reaction with different concentrations of HCHO. Fig. 3 indicates that the dimensional size of the Au@Ag

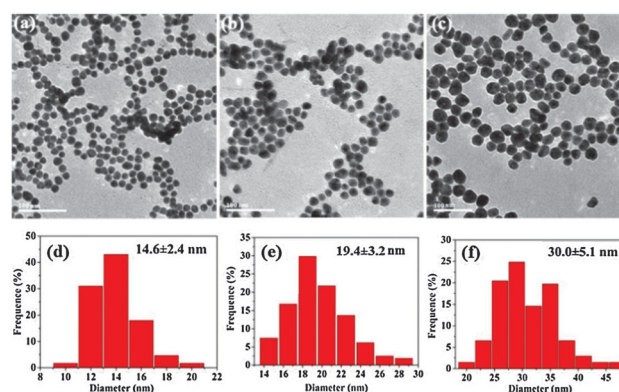


Fig. 3 TEM images and size distribution histograms of the Au@Ag core-shell NPs generated by the Tollens reaction in the presence of Au NPs with HCHO concentration of (a, d) 5 μM ; (b, e) 25 μM ; and (c, f) 100 μM . More than 130 NPs were measured for each histogram.

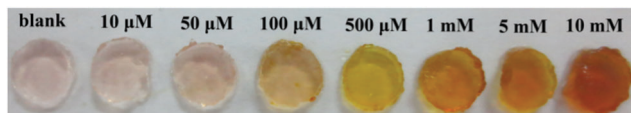


Fig. 4 Photographs of the agarose gel test strips for the detection of HCHO with various concentrations.

core-shell NPs increased as the concentration of HCHO increased, which corresponded well with the energy dispersive X-ray and X-ray diffraction analysis results (Fig. S7 and S8 in ESI†). In addition, as presented in Fig. S9 (ESI†), the plasma resonance of Au@Ag core-shell NPs was highly dependent on the thickness ratio of the silver shell to the gold core, and its slight difference can lead to an observable change in absorption spectra and apparent color. This leads to the development of a highly sensitive approach for HCHO measurement.

The selectivity of this assay was studied against common indoor or outdoor gases, especially those with chemical reducibility, such as alcohol, ketone, aniline and phenol. The concentrations of interferences were set at least 100 times that of HCHO. As shown in Fig. S10 (ESI†), there is no obvious interference observed. Acetaldehyde, benzaldehyde and glucose were tested to further evaluate the selectivity of our method. Fig. S11 (ESI†) shows that these aldehydes only produced little interference. A similar approach has been developed for colorimetric detection of glucose,¹¹ but our results indicate that glucose exhibited limited response at room temperature even after the reaction for 40 min. Such a good selectivity is attributed to the fact that HCHO is the simplest molecule with virtually two aldehyde groups,¹² and so it can react with the Tollens reagent quickly and leads to deposition of a thicker silver shell onto the gold core. It should be noted that if all the tested aldehydes are collected from gas phase using a diffusion based collector, the discrimination would be even greater.¹³

The Au NPs along with Tollens reagent can be further immobilized into the solid matrix for practical use. An agarose gel was employed to embed the Au NPs and Tollens reagent, since it is transparent, porous, and contains a large amount of water to allow the occurrence of the Tollens reaction. The obtained agarose gels were used for colorimetric detection of aqueous HCHO. As shown in Fig. 4, the color of the agarose gels changed from pink to yellow as the HCHO concentration increased. The results (Fig. S12 in ESI†) also showed that the agarose gels were able to measure the concentration of gaseous HCHO as low as 80 ppb, which is the safety limit regulated by WHO.⁷ The measurement range can reach up to 20 ppm which is regulated by the Occupational Safety and Health Administration as an immediately dangerous limit to life or health. The time required for the visual measurement of HCHO at 20 ppm was less than 1 min (Fig. S13, ESI†), which is beneficial for immediate assessment of potential risk and danger.

In summary, we have developed a rapid, low-cost and highly sensitive colorimetric assay for HCHO measurement. By introducing

Au NPs into the classic Tollens reaction, Au@Ag core-shell NPs were produced when exposed to HCHO. The thickness of the silver shell was strongly dependent on the concentration of HCHO, which further generated significant color changes for visual readout. The approach was further transformed into a solid matrix by using agarose gels to immobilize the Au NPs and Tollens reagent. The produced agarose gels can measure HCHO quickly, which is beneficial for immediate assessment of potential risk and danger.

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