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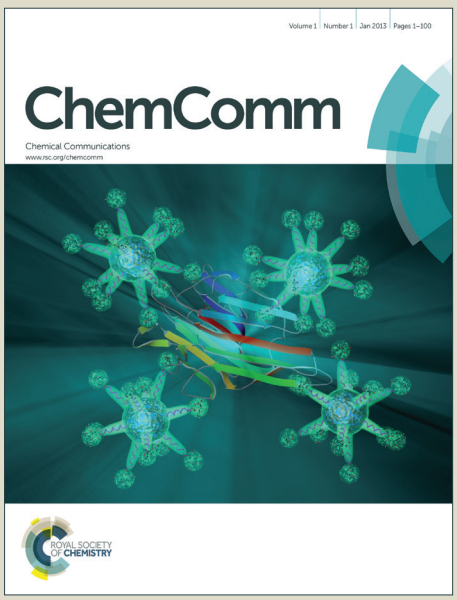

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A colorimetric agarose gel for formaldehyde based on nanotechnology involved Tollens reaction

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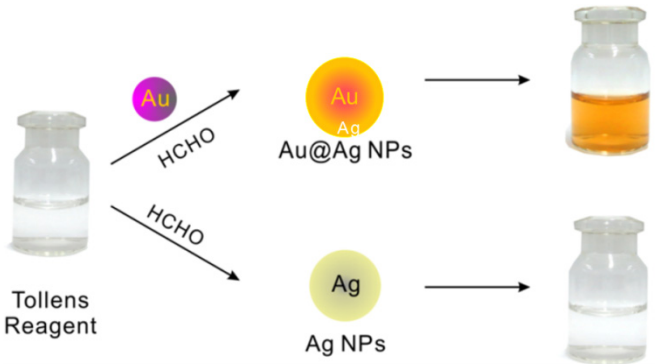
Gold nanoparticles (Au NPs) coupled with Tollens reagent were used for measuring formaldehyde. Au@Ag core-shell NPs were formed along with distinct color changes from pink to deep yellow. This colorimetric system was further immobilized into agarose gel, which was used for monitoring of gaseous formaldehyde.

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 remaining HCHO concentration indoor exceeding certain threshold, which puts potential risk to people's health. 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 to be 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] fluorometry,[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 $[Ag(NH_3)_2]^+$ 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 the textbook that HCHO can react with Tollens reagent (the key component is $[Ag(NH_3)_2]OH$) to produce 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 Figure S1a-c in the supporting information (SI)). There was an indistinguishable color change from colorless to slightly yellow along with an appearance of a surface plasmon resonance (SPR) band at 416 nm (Figure S1d). As shown in the upper row of Scheme 1, when Au NPs were introduced into 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 depending on the concentration of HCHO. The change of shell thickness accomplished with a distinct color change from pink to deep yellow, which can serve as a colorimetric approach for measuring HCHO.



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

The Au NPs were synthesized by reducing the $HAuCl_4$ with trisodium citrate, and the as-synthesized Au NPs exhibited spherical shapes and uniform sizes (13.0±1.5 nm diameter, Figure S2 in the SI). The sole addition of Tollens reagent or HCHO into the suspension of Au NPs did not lead to obvious spectral or color changes (Figure S3 in SI). 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 (Figure 1a).These distinct color changes were finished in several minutes (Figure S4) at room temperature (25 ^{o}C), which provides a rapid and simple way to measure HCHO without using instrumentation and chromophore. The lowest eye-distinguishable concentration can be as low as 100 nM (3 ng mL^{-1}).

UV-Vis spectrometer was used to monitor the spectra during the addition of HCHO into the mixture of Au NPs and Tollens reagent. Figure 1b shows the SPR band of Au NPs peaked at 520 nm blue-shifted, along with an emergence of a second SPR band at around 410 nm, which implied the formation of core/shell NPs.[10] The absorbance at 410 nm increased with the incremental concentration of HCHO (Figure 1b). There was a good linear relationship between the ratio of A_{410}/A_{520} and HCHO concentrations in the range of 0.1-40 μM (Figure 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, 6a, 9] The relative standard deviation of the assay is less than 1.6% (Figure S5).

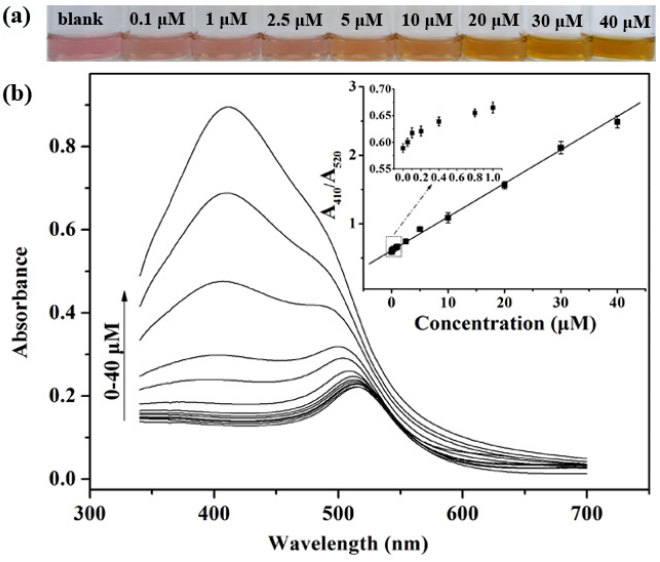


Figure 1. (a) Photographs and (b) UV-vis spectra of the colorimetricassay for measuring HCHO with various concentration. Inset in Figure (b) is the linear relationship between the absorbance at 410 nm and HCHO concentration.

The structure and chemical composition of the produced NPs was characterized using transmission electron microscopy (TEM). Figure 2a shows that most of the NPs were spherical and exhibited inhomogenous electronic density with a darker central part and a lighter outer part. A high-resolution TEM (HR-TEM) image (Figure 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 Figure 2c and d, the elemental composition of the core was gold, and that of the shell which surrounding 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 (Figure S6 in SI).

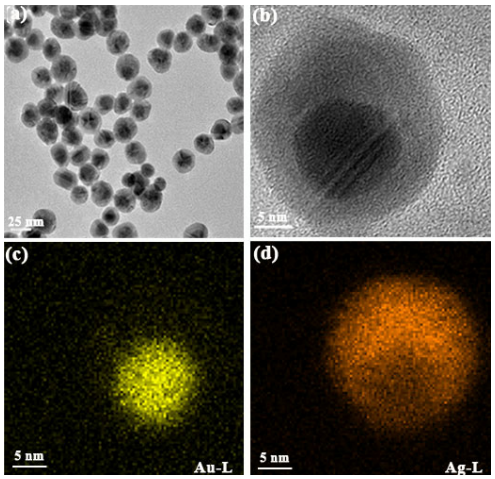


Figure 2. Representative (a) TEM, (b) HR-TEM and elemental maps for the core (c) and the shell (d) of the obtained nanoparticles.

To get more insight on 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. Figure 3 indicates the dimensional size of the Au@Ag 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 (Figure S7 and S8 in SI). In addition, as presented in Figure S9 (SI), the plasma resonance of Au@Ag core/shell NPs was highly dependent on the thickness ratio of silver shell to 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.

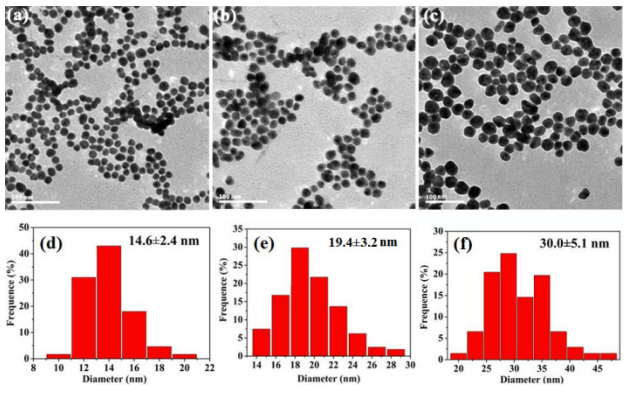


Figure 3. TEM images and size distribution histograms of the Au@Ag core/shell NPs generated by the Tollens reaction in the presence of Au NPs with HCHO concentration at (a, d) 5 μM; (b, e) 25 μM; and (c, f) 100 μM. More than 130 NPs were measured for each histogram.

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 Figure S10 (SI), there is no obvious interference observed. Acetaldehyde, benzaldehyde and glucose were tested to further evaluate the selectivity of our method. Figure S11 shows these aldehydes only produced little interference. A similar approach has been developed for colorimetric detection of glucose, but to our surprise, the authors revealed that the method exhibited excellent selectivity for glucose over HCHO. [11] Our results indicate that glucose exhibited limited response at room temperature even after the reaction of 40 min. Such a good selectivity is attributed 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 thicker silver shell onto 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 approach can be further immobilized into solid matrix for a practical use. 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 Tollens reaction. The obtained agarose gels were used for colorimetric detection of aqueous HCHO. As shown in Figure 4, the color of the agarose gels changed from pink to yellow as the HCHO concentration increased. Results (Figure S12 in SI) 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 immediately dangerous limit to life or health. The time required for the visual measurement of HCHO at 20 ppm was less than 1 min (Figure S13), which is beneficial for immediate assessment of potential risk and danger.

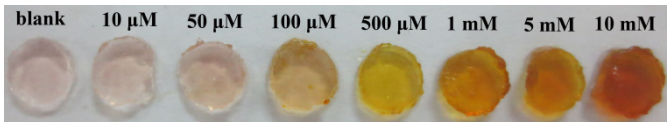


Figure 4. Photographs of the agarose gel test strips for the detection of HCHO with various concentration.

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 solid matrix by using agarose gel to immobilize the Au NPs and Tollens reagents. The produced agarose gels can measure HCHO quickly, which is beneficial for immediate assessment of potential risk and danger.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures and Figure S1-S14 See DOI: 10.1039/c000000x/

1 (a) T. Salthammer, *Angew. Chem. Int. Ed.* 2013, **52**, 3320; (b) N. Shinohara, T. Kajiwara, M. Ohnishi, K. Odama, Y. Yanagisawa, *Environ. Sci. Technol.* 2008, **42**, 4472.
2 http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf.
3 (a) Z. Y. Gu, G. Wang and X . P. Yan, *Anal. Chem.* 2010, **82**, 1365; (b) R. W. Gillett, H. Kreibich and G. P. Ayers, *Environ. Sci. Technol.* 2000, **34**, 2051; (c) N. Dossi, S. Susmel, R. Toniolo, A. Pizzariello and G. Bontempelli, *Electrophoresis* 2009, **30**, 3465; (d) Q. Ma, H. L. Cui and X. G. Su, *Biosens. Bioelectron.* 2009, **25**, 839; (e) X. D. Wang and O.S. Wolfbeis. *Anal. Chem.* 2013, **85**, 487; (f) H. Kudo, X. Wang, Y. Suzuki, M. Ye, T. Yamashita, T. Gessei, K. Miyajima, T. Arakawa and K. Mitsubayashi, *Sensor Actuator B-Chem* 2012**, 161**, 486; (g) J. Flueckiger, F. K. Ko and K. C. Cheung, *Sensors* 2009, **9**, 9196; (h) F. C. Chung, R. J. Wu and F. C. Cheng, *Sensor Actuator B-Chem* 2014**, 190**, 1; (i) Y. M. Zhang, Y. T. Lin, J. L. Chen, J. Zhang, Z. Q. Zhu and Q. J. Liu, *Sensor Actuator B-Chem* 2014**, 190**, 171.
4 (a) T. Salthammer, S. Mentese and R. Marutzky, *Chem. Rev.* 2010**, 110**, 2536; (b) R. R. Miksch, D. W. Anthon, L. Z. Fanning, C. D. Hollowell, K. Revzan and J. Glanville, *Anal. Chem.* 1981, **53**, 2118; (c) S. Dong and P. K. Dasgupt, *Environ. Sci. Technol.* 1987, **21**, 581; (d) Q. Li, P. Sritharathikhum, M. Oshima and S. Motomizu, *Anal. Chim. Acta* 2008**, 612**, 165;(e) M. E. J. Baker, R. Narayanaswamy, *Analyst,* 1994, **119**, 959; (f) O. Bunkoed, F. Davis, P. Kanatharana, P. Thavarungkul and Sémas P. J. Higson, *Anal. Chim. Acta* 2010**, 659**, 251; (g) A. P. Altshuller, D. L. Miller and S. F. Sleva, *Anal. Chem.* 1961, **33**, 621; (h) C. S. Woo and S. E. Barry, *Environ. Sci. Technol.* 1998, **32**, 169.
5 A. Vairavamurthy, J. M. Roberts and L. Newman, *Atmos. Environ.* 1992, **26**, 1965.
6 Q. Zhang, C. Z. Huang, J. Ling and Y. F. Li, *J. Phys. Chem. B* 2008, **112**, 16990.
7 L. Feng, C. J. Musto and K. S. Suslick, *J. Am. Chem. Soc.* 2010, **132**, 4046.

8 Y. D. Yin, Z. Y. Li, Z. Y. Zhong, B. Gates, Y. N. Xia and S. Venkateswaran, *J. Mater. Chem.* 2002, **12**, 522.

9 X. Wang, Y. Si, J. Wang, B. Ding, J. Yu and S. S. Al-Deyabd, *Sensors Actuators B-Chem* 2012,**163**, 186.

10 (a) C. M. Gonzalez, Y. Liu and J. C. Scaiano *J. Phys. Chem. C* 2009**, 113**, 11861; (b) X. Zhang, H. Wang and Z. H. Su, *Langmuir* 2012, **28**, 15705; (c) R. J. Freeman, M. B. Hommer, K. C. Grabar, M. A. Jackson and M. J. Natan, *J. Phys. Chem.* 1996, **100**, 718; (d) L. Chuntonov, M. Bar-Sadan, L. Houben and G. Haran, *Nano Lett.* 2012, **12**, 145; (e) C. B. Norris, P. R. Joseph, M. R. Mackiewicz and S. M. Reed, *Chem. Mater.* 2010, **22**, 3637.

11 T. S. Li, K. Zhu, S. He, X. Xia, S. Q. Liu, Z. Wang and X. Y. Jiang, *Analyst*, 2011, **136**, 2893.

12 (a) $CH_3CHO+2[Ag(NH_3)_2]OH \rightarrow CH_3COONH_4+2Ag+3NH_3+H_2O$;
(b)$HCHO+2[Ag(NH_3)_2]OH \rightarrow HCOONH_4+2Ag+3NH_3+H_2O$;
$HCOONH_4+2[Ag(NH_3)_2]OH \rightarrow (NH_4)_2CO_3+2Ag+3NH_3+H_2O$.

13 J. Li and P. K. Dasgupta, *Anal. Chem.* 1994, **66**, 551.

