Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information for

Au@Ag core/shell nanoparticles as colorimetric probes for cyanide sensing

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EXPERIMENTAL SECTION

Chemicals and solutions. Agar powder, chloroauric acid ($HAuCl_4 \cdot 3H_2O$), KSCN, NaBr, $NaBrO_3$, $NaClO_4$, $NaClO_4$, $NaClO_3$, Na_2CO_3, $NaHCO_3$, $NaNO_3$, $NaNO_2$, Na_3PO_3, Na_2SO_4, Na_2SO_3, $NaBO_3$, CH_3COONa, KI, KIO_3, KCl, $MgCl_2$,

$BaCl_2$, $CoCl_2$, $NiCl_2$, $CaCl_2$, $ZnCl_2$, $AlCl_3$, $Pb(NO_3)_2$ and $CuCl_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Stock solution of KCN (50 mg L^{-1}) was provided from National Institute of Metrology (Beijing, China). Formaldehyde (37 %) was purchased from Wokai Bio-tech Co., Ltd (Shanghai, China). Tollens reagent was prepared by mixing aqueous ammonia (1240 μL, 25%-28%) and NaOH (650 μL, 3 M) into $AgNO_3$ (6 mL, 0.1 M). Water was used to fix the final volume to 20 mL. The Tollens reagent was diluted 6 times using water for further use. All other reagents were of analytical grade and used without further purification.

Instrumentation. Ultrapure water (18.2 MΩ cm) was obtained from a Millipore Autopure WR600A system and used throughout. The UV-vis spectra were recorded using a UV-2450 spectrophotometer (Shimadzu). A Canon IXUS-125HS digital camera was used for photographing. Transmission electron microscopy (TEM) images were obtained with a JEM 1400 microscope (JEOL). High-resolution TEM (HR-TEM) and energy dispersive X-ray elemental mapping measurements were carried out using a Tecnai F30 microscope (Philips, FEI, TECNAI). The elemental analysis was performed on an ICP-MS 7500a system (Agilent). Electrospray ionization-time-of-flight (ESI-TOF) mass spectra were recorded on a Micromass LCT spectrometer (Waters) with a negative mode. Zeta potentials were measured using a Zeta Sizer Nano ZS (Malvern Nano-ZS ZEN3600).

Synthesis of Au@Ag core/shell NPs. Citrate stabilized Au NPs (13-nm diameter) were synthesized using a standard citrate method. The concentration of the as-synthesized Au NPs was 12 nM as determined by UV-vis spectrometry. Au@Ag core/shell NPs were synthesized as follows. An aliquot of 2000 μL Au NPs (6 nM), 6440 μL water, 600 μL Tollens reagent and 960 μL of aqueous HCHO (10 mM) were sequentially added into a sample vial. The mixed solution was incubated for 20 min and its color was changed from pink to deep yellow, indicating the formation of Au@Ag core/shell NPs.

Colorimetric cyanide detection. Cyanide standard solutions (2.5 mL) with various concentrations were added to Au@Ag core/shell NPs solutions (2.5 mL). The mixtures were incubated at ambient temperature (25 ^{o}C) for 10 min unless stated otherwise. After incubation, the UV-vis spectra of the solutions were recorded using a spectrophotometer and the corresponding apparent color of the solution were captured using the digital camera.

Preparation of agarose gel test strips. Agar powder (0.1 g) was added into boiled water (5 mL). The solution was heated and stirred to ensure the complete dissolution of agar powder. Subsequently, the solution (1.5 mL) was transferred to a Petri dish (I.D. 3.5 cm). To the agar solution was added 2 mL of Au@Ag core/shell NPs solutions. Finally, the agar solution was molded into gel by placing the Petri dish into a refrigerator at -18 ^{o}C for 2 min. The as-prepared agarose gel was punched out into spherical shape (I.D. 0.8 cm) for cyanide measurement.

Real sample analysis using the test strips. The environmental water samples (sea, lake and tap water, and industrial effluent) were spiked with a series of cyanide standard solutions from 0 to 120 μM. An aliquot of 2.5-mL environmental water samples were placed in the sample vial. Then, the as-prepared test strips were immersed into the sample solution and kept for 20 min. Finally, the test strips were moved out and taken photographs.

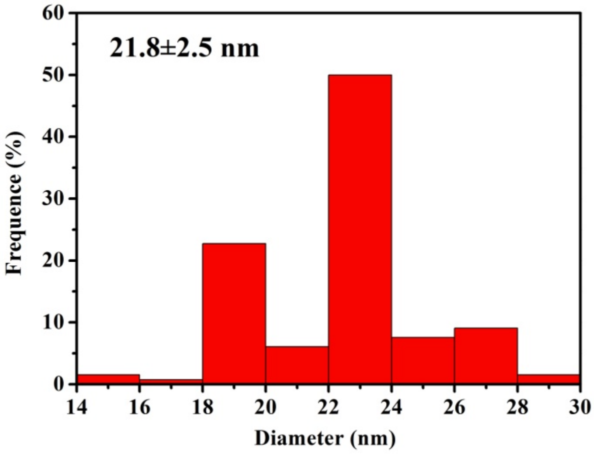

Fig. S1 The size distribution histogram of the Au@Ag core/shell NPs generated by the Tollens reaction in the presence of Au NPs. The concentration of Au NPs, $[Ag(NH_3)_2]OH$ and HCHO was 1.2 nM, 0.24 and 0.96 mM, respectively. More than 100 NPs in Fig. 1a was used to obtain this histogram.

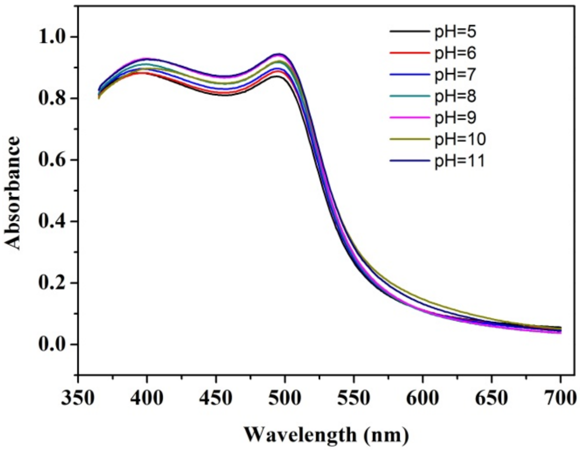

Fig. S2 The UV-vis spectra of the Au@Ag core/shell NPs solution at different pH.

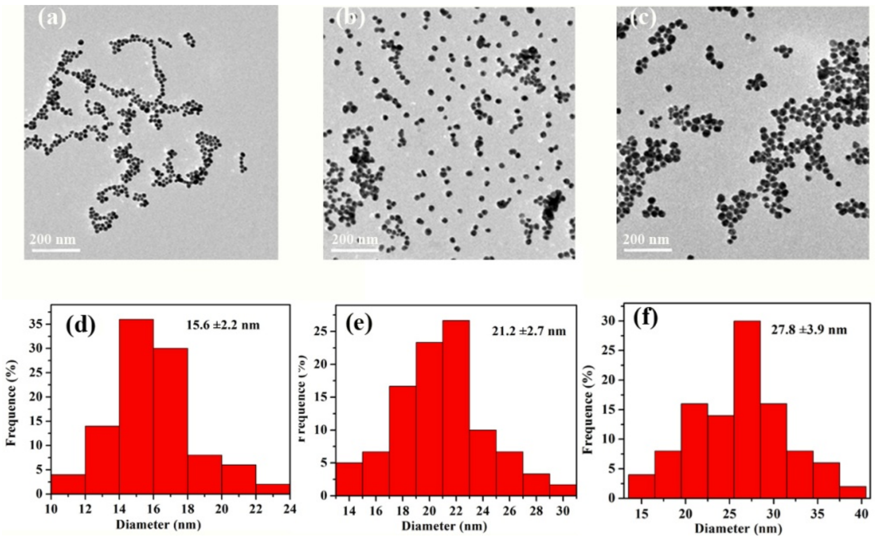

Fig. S3 TEM images and size distribution histograms of the Au@Ag core/shell NPs generated by the Tollens reaction in the presence of Au NPs with HCHO concentration at (a, d) 10 μM; (b, e) 50 μM; and (c, f) 80 μM. The concentration of Au NPs and $[Ag(NH_3)_2]OH$ was 0.6 nM and 1.2 mM, respectively. More than 100 NPs in Fig.S3a-c were used to obtain the histograms.

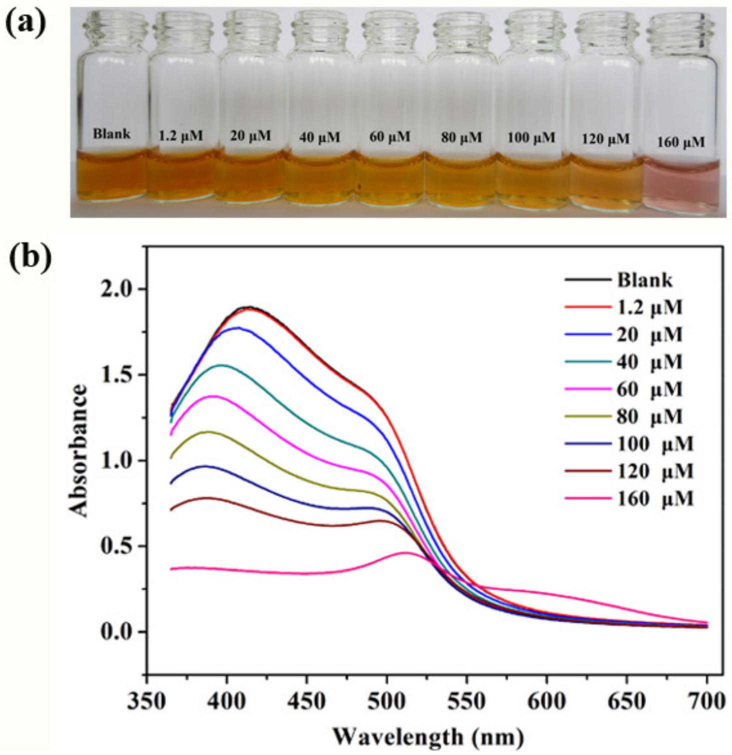

Fig. S4 (a) Photographs and (b) UV-vis spectra of the Au@Ag core/shell NPs with the addition of increasing cyanide. The core/shell NPs were prepared using the concentration of Au NPs, $[Ag(NH_3)_2]OH$ and HCHO at 1.2 nM, 0.48 and 1.92 mM, respectively.

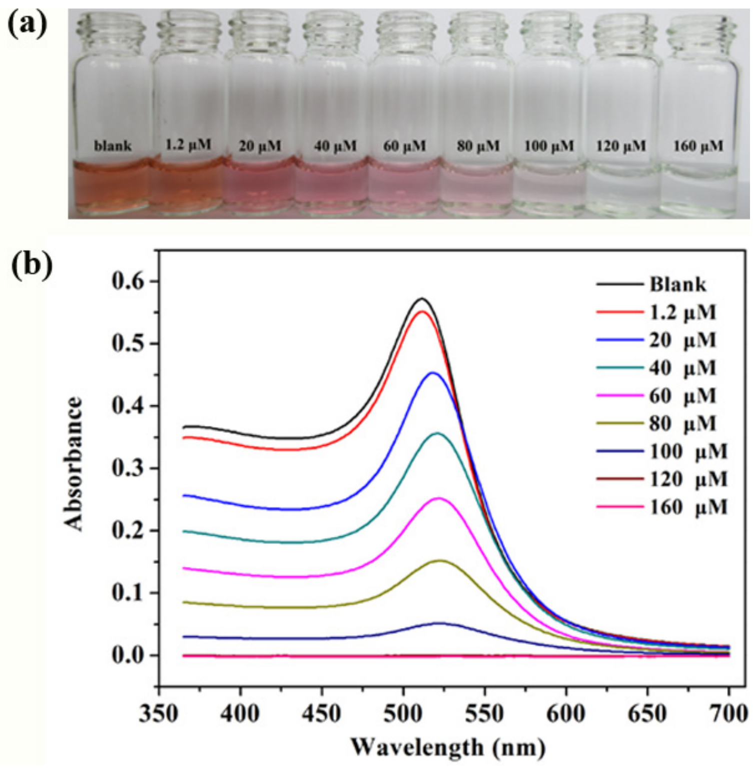

Fig. S5 (a) Photographs and (b) UV-vis spectra of the Au@Ag core/shell NPs with the addition of increasing cyanide. The core/shell NPs were prepared using the concentration of Au NPs, $[Ag(NH_3)_2]OH$ and HCHO at 1.2 nM, 0.06 and 0.24 mM, respectively.

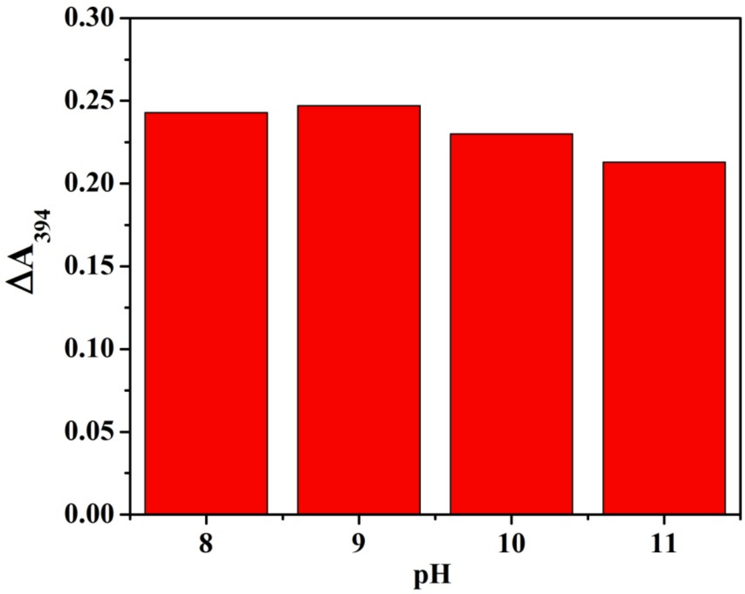

Fig. S6 The ΔA_{394} of the Au@Ag core/shell NPs in the presence of cyanide (20 µM) with different pH values.

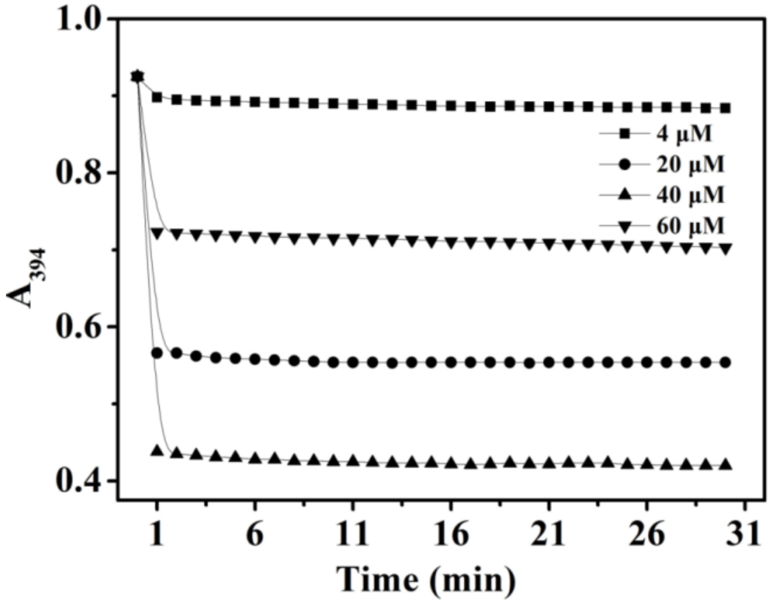

Fig. S7. The plot of A_{394} versus reaction time at different cyanide concentrations.

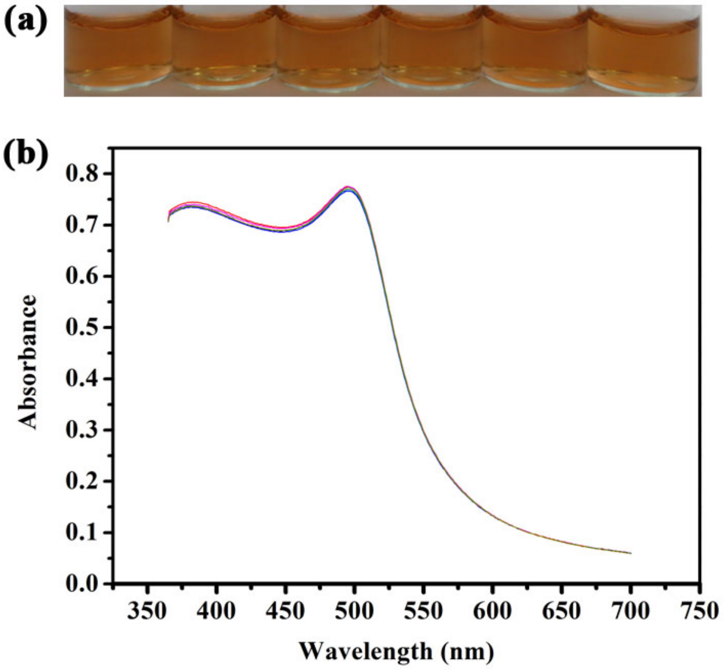

Fig. S8. (a) Photographs and (b) UV-vis spectra of the colorimetric assay for six replicates of cyanide (20 μM).

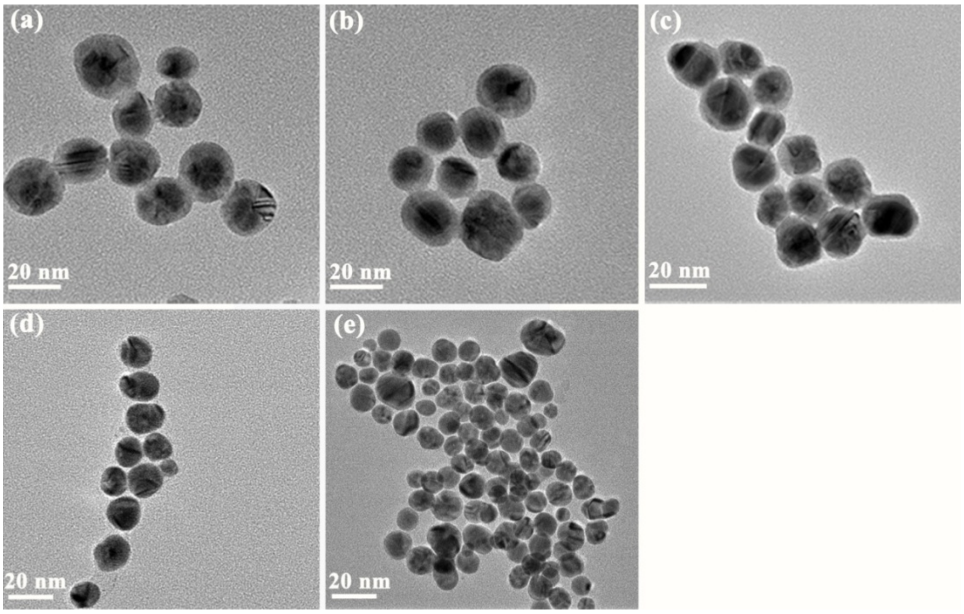

Fig. S9. TEM images of Au@Ag core/shell NPs with the addition of cyanide at (a) 0 (b) 12 (c) 40 (d) 92 and (e) 108 μM.

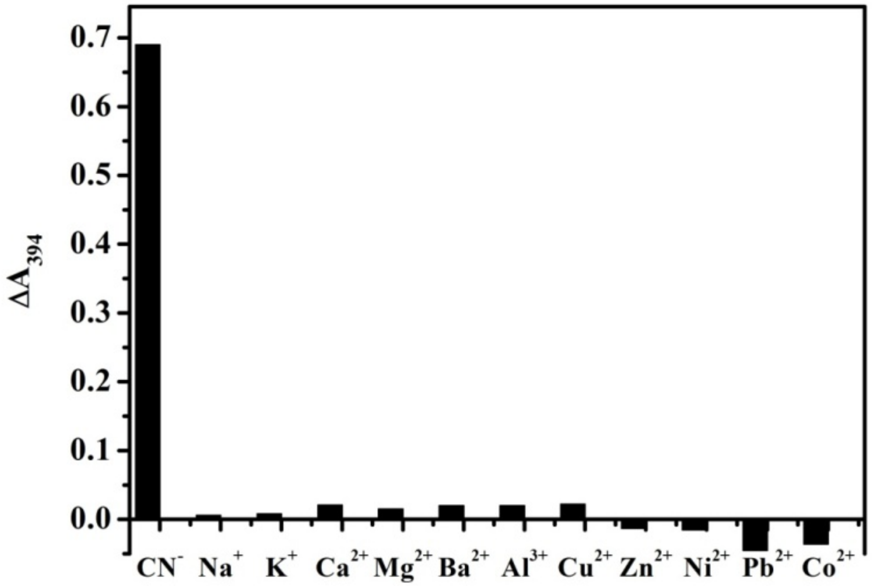

Fig. S10. The selectivity of the proposed assay for the cyanide over the cations. The concentration for each analyte: cyanide, 80 μM; Na^+ and K^+, 4 mM; other cations, 400 μM.

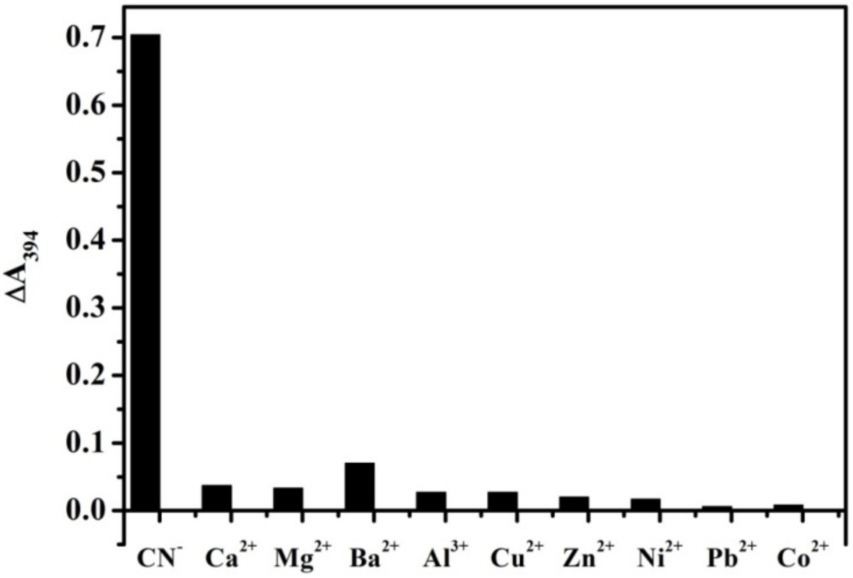

Fig. S11. The selectivity of the proposed assay for cyanide over the cations using EDTA as a masking agent. The concentration for each analyte: cyanide, 80 μM; other cations, 1.6 mM.

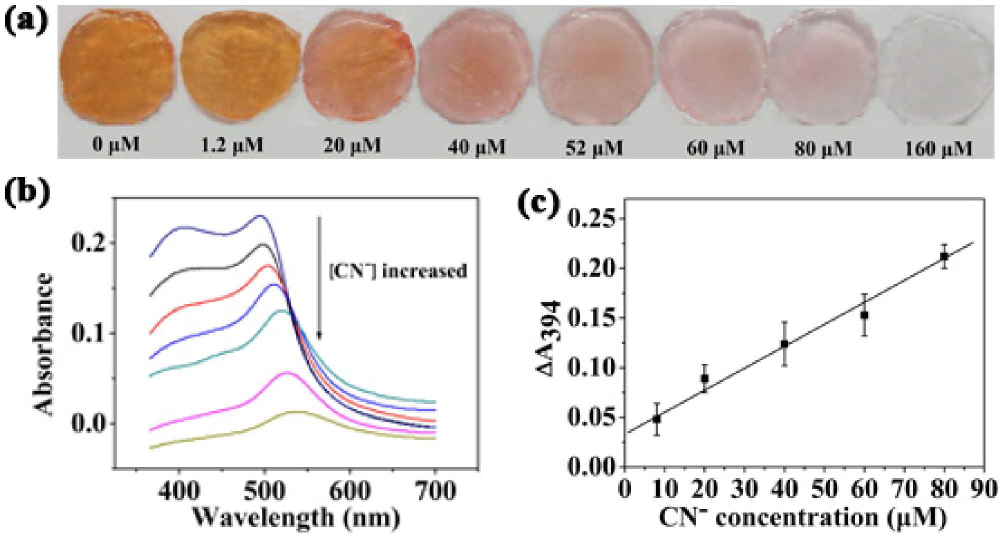

Fig. S12. (a) Photographs and (b) UV-vis spectra of the agarose gels for the measurement of cyanide with various concentrations; (c) the plot of ΔA_{394} of the agarose gels versus cyanide concentration.

Fig. S13. (a) photographs of the test strips exposed in the gaseous hydrogen cyanide (from left to right: the hydrogen cyanide concentration was 0, 5, 10, 20 and 30 μg L^{-1}, respectively)

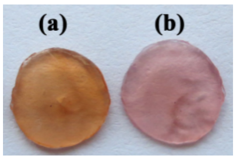

Fig. S14. Photographs of the test strips exposed in (a) the air and (b) the cigarette smoke

Table S1. Comparison of our approach with other colorimetric assays

Probes	Method	Medium	LOD (μM)	Test strips	Etching time (min)	Reference
Au@Ag core/shell NPs	Colorimetry/ Absorption	Pure water	0.4	Yes	1	This study
ATP-AuNPs	Colorimetry/ Absorption	Pure water	14	No	2	1
SDS-Ag NPs	Colorimetry/ Absorption	Pure water	1.8	No	2	2
chitosan-Au NPs	Colorimetry/ Absorption	Pure water	0.96	Yes	30	3
PS-Au NPs	Colorimetry/ Absorption	Pure water	0.5	No	30	4
Rhodamine B-Au-Fe_3O4 NP	Fluorescence	Pure water	0.4	No	>30	5
polyacetylene-AuNPs	Fluorescence	Mixture of ethanol/THF and water	3	No	5	6
FITC-BSA-Au NPs	Fluorescence	Pure water	1	No	60	7
Au NCs	Fluorescence	Pure water	0.2	No	20	8
RB-Au NPs	Fluorescence	Pure water	0.08	No	20	9
MDMO-PPV-Au NPs	Fluorescence	Pure water	0.6	No	20	10
PFS-Ag NPs	Fluorescence	Pure water	0.25	No	20	11
Polyfluorene-AuNPs	Fluorescence	Pure water	0.3	No	Not	12

mentioned

Table S2. The silver and gold content in the suspension of Au@Ag core/shell colloidal with the addition of cyanide at different concentration.

Cyanide added (μM)	Ag content (mg L^{-1})	Au content (mg L^{-1})
0	0.29	0.49
8	1.04	0.59
72	6.92	2.62
120	7.01	12.5

Reference

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