Supplementary Information

Colorimetric Detection of Al (III) in Vermicelli Samples Based on Ionic Liquid Groups Coated Gold Nanoparticles

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EXPERIMENTAL SECTION

Materials and Instrumentation $HAuCl_4 \cdot 3H_2O$, $NaBH_4$ were purchased from Sinopharm Chemical Reagent Co., Ltd and ionic liquid (1-ethyl-3-methylimidazolium thiocyanate) was purchased from Shanghai Cheng Jie Chemical Co.LTD. The UV-Vis spectra were recorded with a UV2450 spectrophotometer (Shimadzu). Dynamic light scattering (DLS) and zeta potential (ζ) were performed on a Zeta Sizer Nano ZS (Malvern Zetasizer 3000HS and He/Ne laser at 632.8 nm at scattering angles of 90 at 25 °C). Transmission electron microscope (TEM) images were obtained by using Tecnai G2 20 S-TWIN at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) characterization was carried out on ESCALAB250Xi, Thermo Fisher. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) results were received by Perkin Elmer Optima 6300DV.

Preparation of IL-capped Au NPs 100 μg/mL $HAuCl_4 \cdot 3H_2O$ and 1 μL ionic liquid (1-ethyl-3-methylimidazolium thiocyanate) were dissolved in 20 mL deionized water (DI water) in a round-bottom flask. Then we put it in the ice-bath. 2 mg $NaBH_4$ was dissolved in 10 mL DI water in another tube and precooled in ice-bath for 10 minutes. Then we added $NaBH_4$ solution into the round-bottom flask dropwise with violent stirring, yielding a red solution. After continued stirring for 1 hour, we stopped and placed the synthesized IL-Au NPs in 4 ^{o}C refrigerator.

Experimental Procedure for the Selectivity and Sensitivity of this Assay We added different metal ions to IL-Au NPs (1 mL), containing Na^+, K^+, Fe^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, each with a final concentration of 10 μM. The addition of Al^{3+} caused color change of DMSA-Au NPs. The mixtures were kept for 10 min, the pictures were taken and meanwhile UV-Vis absorption spectra were obtained. To verify the selectivity of IL-Au NPs further, we did the same procedures and the concentration of Na^+, K^+ is 100 μM, the concentration of Ca^{2+}, Fe^{3+} is 20 μM, the concentration of Cr^{3+}, Ce^{3+}, Cu^{2+}, Hg^{2+}, Ag^+ is 10 μM.

To evaluate the sensitivity of the IL-Au NPs assay for Al^{3+}, we used DI water to dissolve $AlCl_3$ to prepare a stock solution, added different concentrations of $AlCl_3$ solutions (10 μL) to IL-Au NPs (1 mL), and the final concentrations of $AlCl_3$ were set to be 0, 1 μM, 2 μM, 5 μM, 10 μM, 20 μM, 50 μM and 100 μM. The resulting mixtures were continuously shaken for 10 min, the pictures were taken and meanwhile the corresponding UV-Vis absorption spectra were recorded.

All the measurements were repeated 5 times for each concentration. We also obtained the DLS data and TEM image to confirm our results.

Analysis of Al^{3+} in real samples The real samples we used were vermicelli sold in the market. For the analysis of this sample, we carried out the pretreatment according to the literature[1]. Briefly, we sealed vermicelli (dried, kibbling, 0.5 g), HNO3 (7 mL) and 30% H_2O_2 (2 mL) into a Teflon equipped stainless steel autoclave, which was then placed in a drying oven (DHG-9123A, Shanghai Yiheng Scientific Instrument Limited Company), After hydrothermal treatment at 130 ^{o}C for 4 h, the autoclave was cooled to room temperature. The obtained solution is heated to get rid of acid on an electric heating plate. We transferred the solution into a volumetric flask, and then added H_2O to increase the volume of solution up to the standard mark of volumetric flask. Then we applied ICP-OES to characterize the concentration of 10 metal elements in the solution,

including Al, Na, K, Ba, Ca, Fe, Mn, Ni, Zn, Pb. We picked one vermicelli sample almost without Al (0.37 μM) to spike $KAl(SO_4)_2 \cdot 12H_2O$ and the other containing Al (386.67 μM) to detect using our assay. The procedure of $KAl(SO_4)_2 \cdot 12H_2O$ detection in vermicelli samples was similar to that of the colorimetric detection of Al^{3+}. We can use the value of A_{650}/A_{520} and linear relationship received in detection of $KAl(SO_4)_2 \cdot 12H_2O$ to obtain the concentration of Al.

Supporting figures and tables:

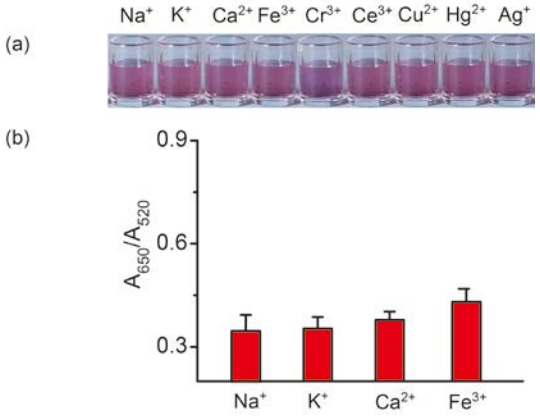


Figure S1. The response of IL-Au NPs with the addition of supplementary metal ions. The concentration of Na^+, K^+ is 100 μM, the concentration of Ca^{2+}, Fe^{3+} is 20 μM, the concentration of Cr^{3+}, Ce^{3+}, Cu^{2+}, Hg^{2+}, Ag^+ is 10 μM.

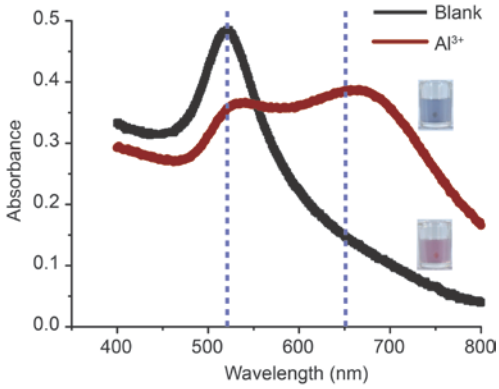


Figure S2. Characterization of Al^{3+} induced aggregation of ionic liquid coated Au NPs, UV-Vis absorption and pictures of IL-Au NPs without and with the addition of Al^{3+}.

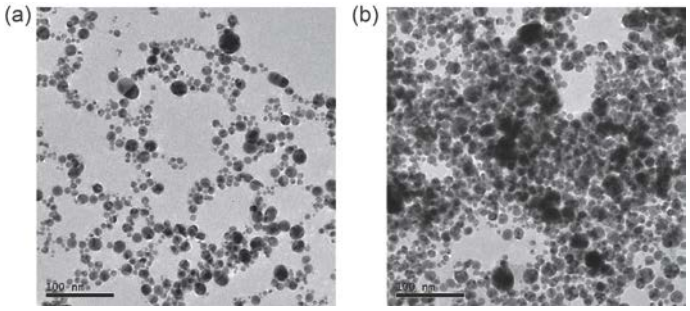
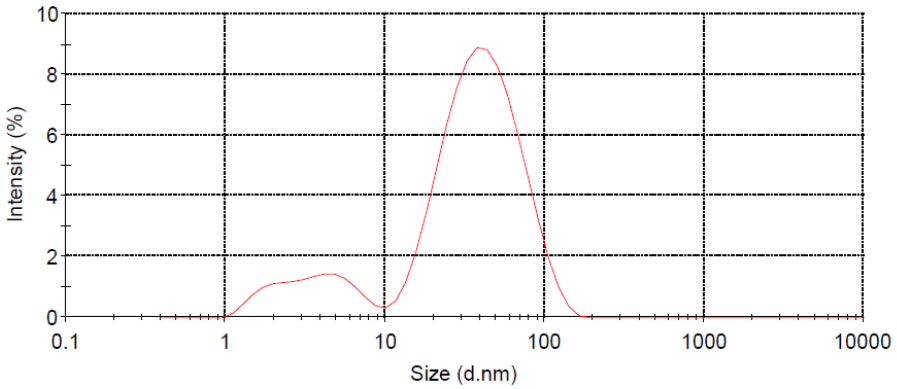


Figure S3. TEM images of dispersed IL-Au NPs without Al^{3+} (a) and aggregated IL-Au NPs with the addition of Al^{3+} (b).

(a)



(b)

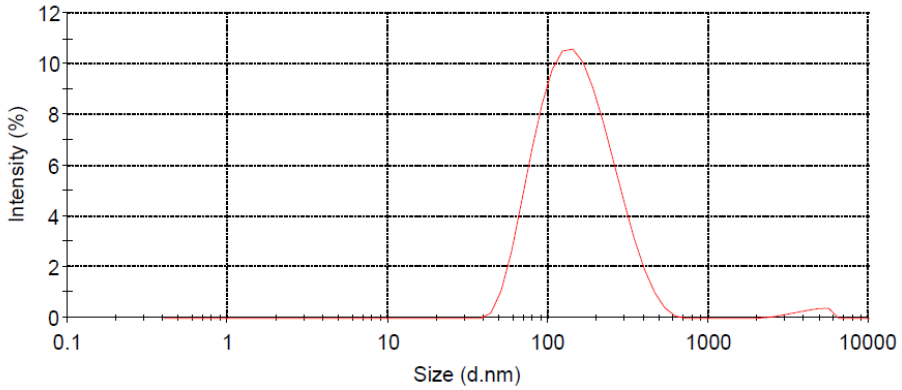


Figure S4. DLS measurements for IL-Au NPs before (a) and after adding Al^{3+} (b).

Table S1. The concentration of different metal ions in vermicelli sample (with very little Al) detected by ICP-OES.

Metal	Concentration (μM)
Al	0.37
Na	412.90
K	215.12
Ba	2.22
Ca	299.26
Fe	240.7
Mn	8.44
Ni	0.06
Zn	6.30
Pb	undetected

Reference:

(1) Y. M. Guo, Y. Zhang, H. W. Shao, Z. Wang, X. F. Wang, X. Y. Jiang, *Anal. Chem.* **2014**, *86*, 8530-8534.