Electronic Supplementary Material (ESI) for Chemical Communications

Colorimetric detection of copper ion in tap water during the synthesis of silver/dopamine nanoparticles

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Electronic Supplementary Information (ESI) available:

Experimental Section

Chemicals and Materials. The 3-hydroxytyramine hydrochloride (dopamine) was purchased from J&K Chemical Ltd. (China). Silver nitrate ($AgNO_3$) and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Copper sulfate and other metal salts were at least analytical grade and used as received. Ultrapure water was prepared by using Milli-Q water purification system (Millipore, Bedford, MA, USA). The stock solutions for copper ions, other metal ions, dopamine (4 mM), $AgNO_3$ (8 mM), and sodium hydroxide (NaOH, 100 mM) were all prepared with ultrapure water. All experiments were operated at room temperature.

Instrument. UV-Vis spectra were recorded by nucleic acid/protein analyzer DU 800 (Beckman Instruments, Inc.). The optical photographs were taken by an aigo T-1028 digital camera. Transmission electron microscope (TEM) studies were carried out with the H-7500 (Hitachi, Japan) operating at 80 kV accelerated voltage. The FTIR spectrum was measured by the GX FTIR system (PerkinElmer).

Colorimetric Detection of copper ions. First, 10 μL of dopamine (4 mM) and corresponding concentrations of copper ions were mixed in a 1.5 mL centrifugal tube. Then, 1 mL of ultrapure water, 15 μL of NaOH (0.1 M) and 30 μL of $AgNO_3$ (8 mM) were added to the tube in sequences. The mixture was incubated at room temperature for 9 minutes before UV-Vis measurements and photograph-taken. The final concentrations of copper ions in the tube were 0, 0.05, 0.1, 0.5, 1, 2, 3, 4, 6, 7 and 8 μM correspondingly.

The spiked-recovery detection of copper ions in tap water was manipulated in the same procedure. The tap water was collected from our laboratory and filtered through 0.22 μm nylon filter before analysis.

In the control experiment, 10 μL dopamine (4 mM), 10 μL copper ions (1 mM), 1 mL ultrapure water, 15 μL NaOH (0.1 M), 10 μL EDTA (10 mM) and 30 μL $AgNO_3$ (8 mM) were added to the tube in sequences. The mixture was incubated at room temperature for 9 minutes before UV-Vis measurements and photograph-taken.

Preparation for XPS analysis. The reaction solution was centrifuged at 12000 rpm for 5 minutes and the deposit was redispersed in water. The above procedure was manipulated two times for removing the free Cu^{2+} and the obtained deposit was utilized for XPS analysis.

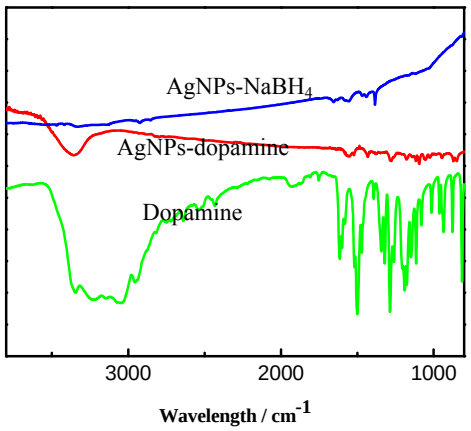

Fig. S1 FTIR spectra of dopamine, AgNPs (synthesized by dopamine or $NaBH_4$)

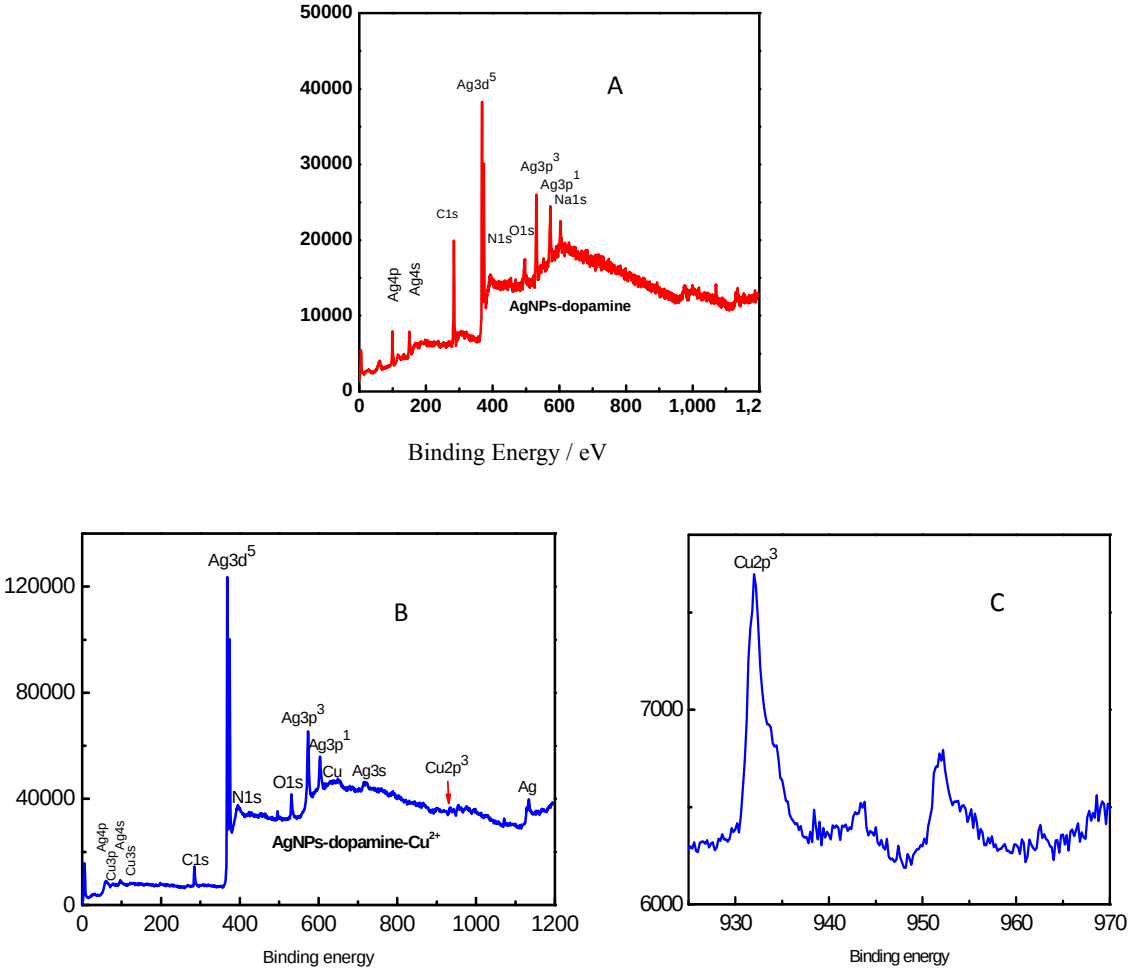

Fig. S2 XPS spectrum of dopamine-stabilized AgNPs in the (A) absence and (B) presence of 10 μM Cu^{2+}; (C) narrow peak of $Cu2p^3$ in the presence of 10 μM Cu^{2+} (from Fig. B).

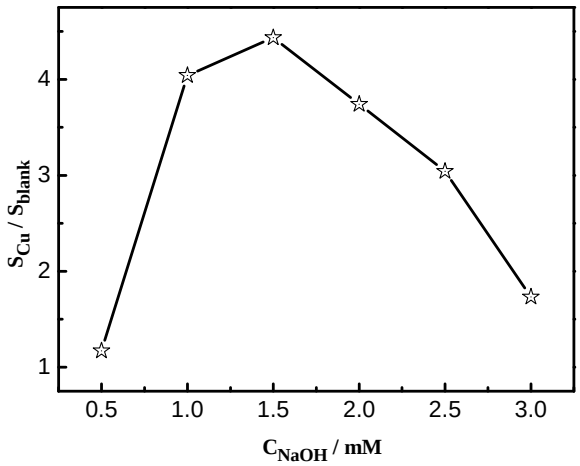

Fig. S3 Response of dopamine-functionalized AgNPs to 1.5 μM Cu^{2+} sample (S_{Cu}) and the blank solution (S_{blank}) against NaOH concentration. Experimental conditions: 40 μM dopamine, 160 μM $AgNO_3$, 1.5 μM Cu^{2+}, different concentrations of NaOH. Incubation time: 30 minutes.

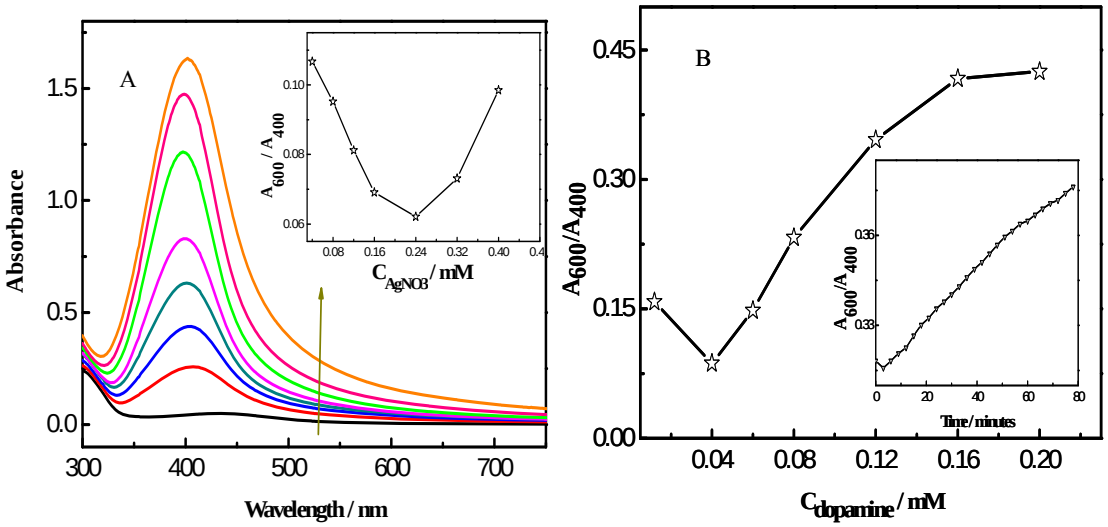

Fig. S4 A) UV-Vis spectrum of the reaction system after mixing 40 μM dopamine, 1.5 mM NaOH and different amounts of $AgNO_3$, $AgNO_3$ concentration from lower to upper: 1) 0 μM; 2) 40 μM; 3) 80 μM; 4) 120 μM; 5) 160 μM; 6) 240 μM; 7) 320 μM, 8) 400 μM. Inset gives A_{600}/A_{400} against the $AgNO_3$ concentration. Incubation time: 30 minutes. B) The plot of A_{600}/A_{400} against dopamine concentration. Experimental conditions: 240 μM $AgNO_3$, 1.5 mM NaOH and corresponding amounts of dopamine. Incubation time: 30 minutes. Inset describes the kinetics/time curve every 3 minutes interval in 78 minutes (A_{600}/A_{400} against time). Experimental conditions: 40 μM dopamine, 1.5 mM NaOH, 240 μM $AgNO_3$ and 2 μM Cu^{2+}.