Paper presentation

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Cooperative Binding of Bifunctionalized and Click Synthesized Silver Nanoparticles for Colorimetric Co^{2+} Sensing

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ACS APPLIED MATERIALS & INTERFACES

Introduction

1. The sources for cobalt are hard metal industry, diamond polishing, and the porcelain, chemical, and pharmaceutical industries.
2. Exposure to cobalt may cause toxicological effects, including vasodilatation, flushing, and cardiomyopathy in humans and animals .
3. Due to the quenching of fluorescent probes the real time detection is not possible and it can be over come in colorimetric method.
4. Why gold and silver nanoparticles is because of high extinction coefficients and large particle distance dependent optical properties.
5. The introduction of ligand not only provides stability but also desirable surface functionalities.
6. This group recently reported -cyclodextrin-4,4'-dipyridine inclusion complex modified Ag NPs as colorimetric Yb^{3+} probes and p-Sulfonatocalix[4]arene-modified Ag NPs can be used as colorimetric probes for histidine.

7. It has been reported that bifunctionalized sensors can further improve the sensing efficiency, because of the cooperative effect of ligands. Lin etal reported that thiocticacid and crown bifunctionalized Au-NPs can recognize K^+ more quickly. Huang etal improved the selectivity of probe by modifying the rhodamine B-Au NP surfaces with thiol ligands.

In this paper,

- They synthesized Ag NPs by Click reaction between terminal alkyne and azide in the presence of Cu(I). They have showed that bifunctionalized and click synthesized silver nanoparticles can have a cooperative effect on recognition of Co^{2+}, resulting in appreciable changes in color and absorption properties over other metal ions tested.
- Up to date, the reports referred to bifunctionalized Ag NPs are rarely.
- These can be developed as potential probes in pharmaceutical and biosensors.

Scheme 1. Synthesis of Triazole-Carboxyl Ag NPs

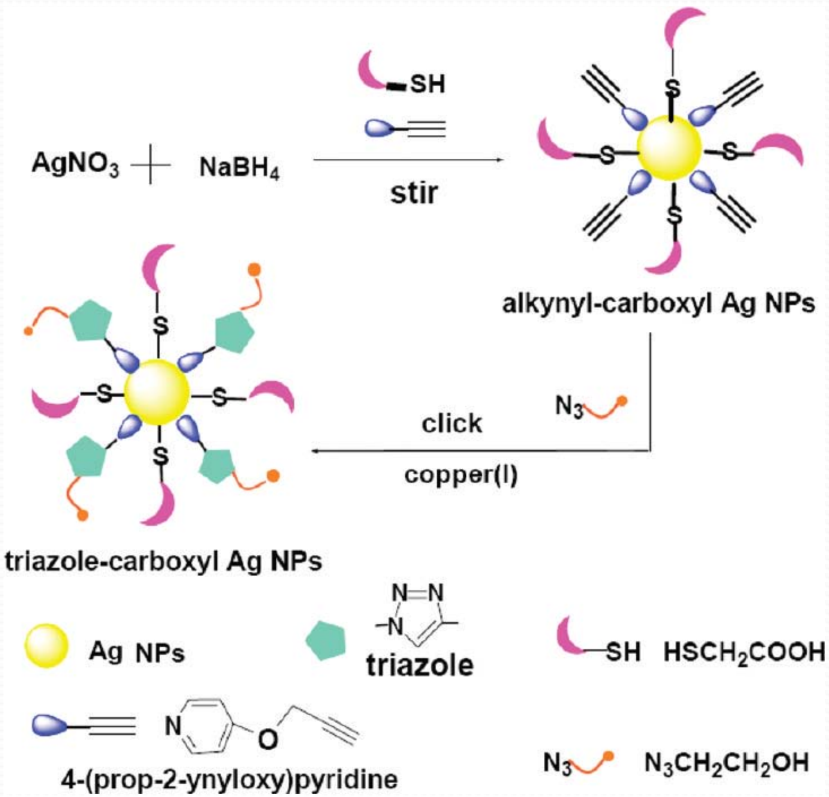
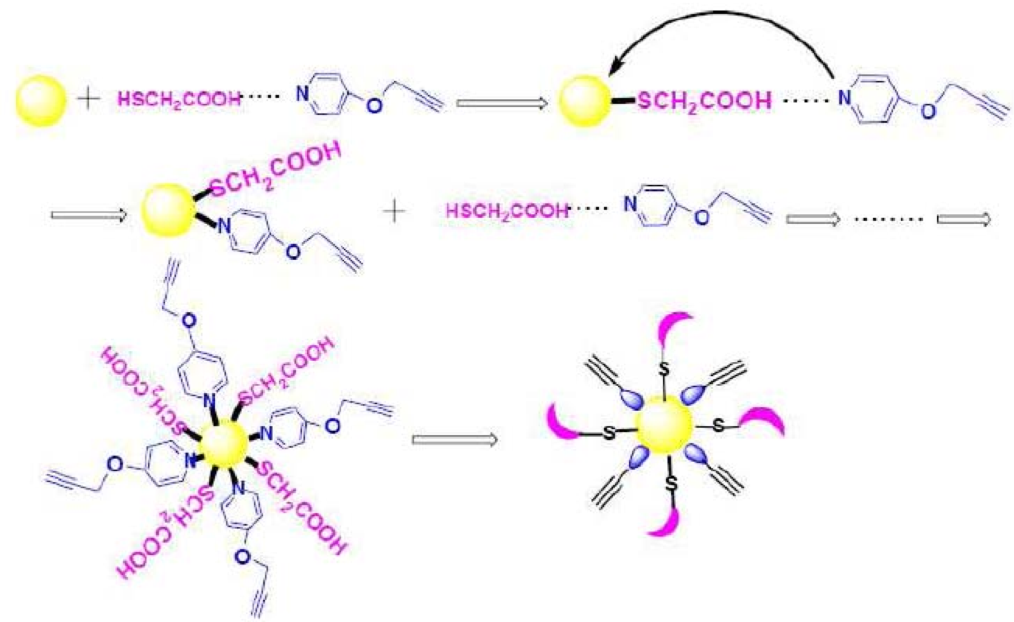


Figure.S1 Scheme of the arrangement between thioacetic acid and 4-(prop-2-ynyloxy)pyridine molecules



Results and Discussion

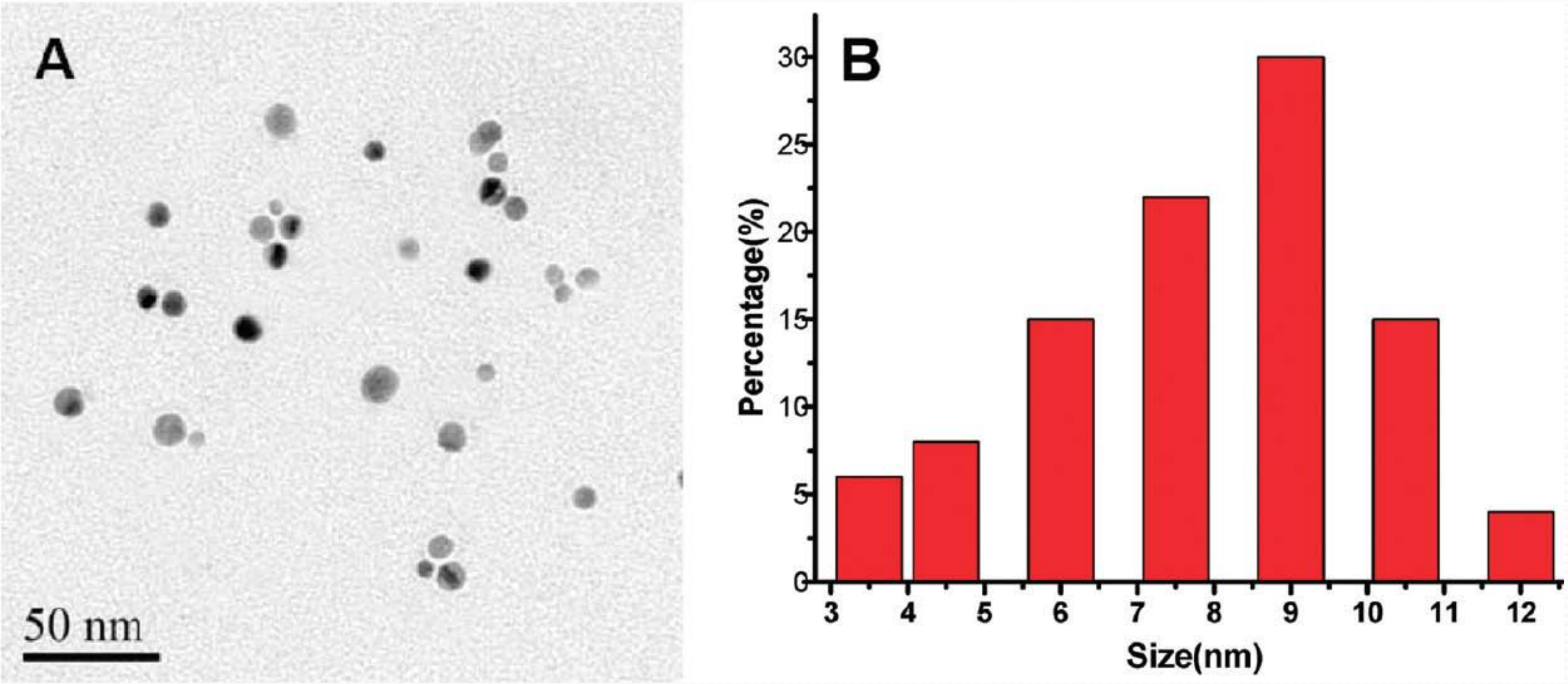


FIGURE 1. (A) TEM images of the triazole-carboxyl Ag NPs and (B) size distribution.

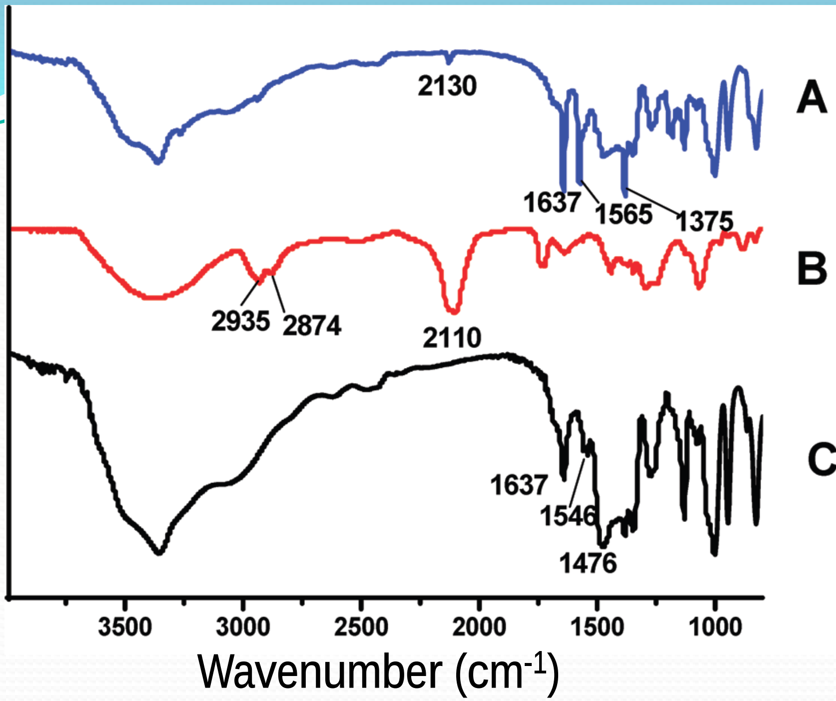


FIGURE 2. FT-IR spectra of (a) alkynyl-carboxyl Ag NPs, (b) 2-azidoethanol, (c) triazole-carboxyl Ag NPs.

These Ag NPs are stable in pH=3.0-12.0

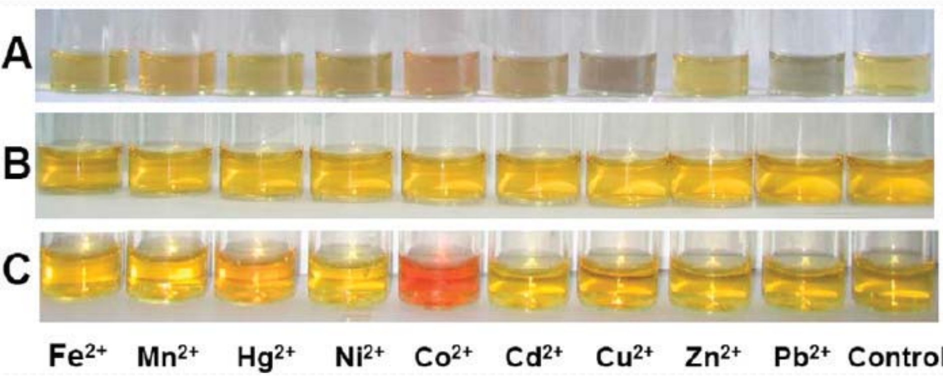


FIGURE 3. Photographic images of (A) carboxyl-Ag NPs, (B) triazole- Ag NPs, and (C) triazole-carboxyl Ag **NPs solution in the presence of 10 μM different transition metal ions. Typically, 0.5 mL of 50 μM various** transition metal ions were added into 2mL Ag NPs solutions, and the combined solution was mixed well for 5 min and then tested.

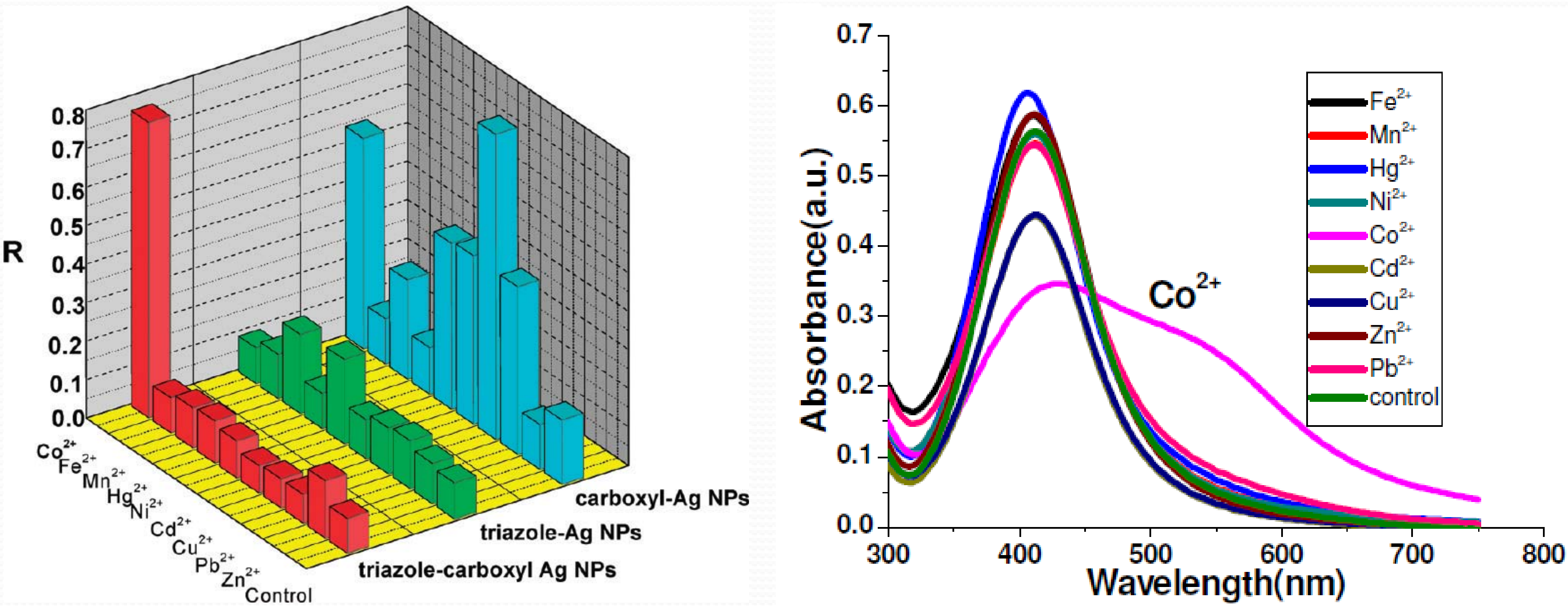


FIGURE 4. R (A_{550}/A_{405}) of triazole-carboxyl Ag NPs, triazole-Ag NPs, and carboxyl-Ag NPs **solution in the present of different metal ions. Typically, 0.5 mL of 50 μM various transition metal** ions were added into 2 mL Ag NPs solutions, and the combined solution was mixed well for 5 min and then tested.

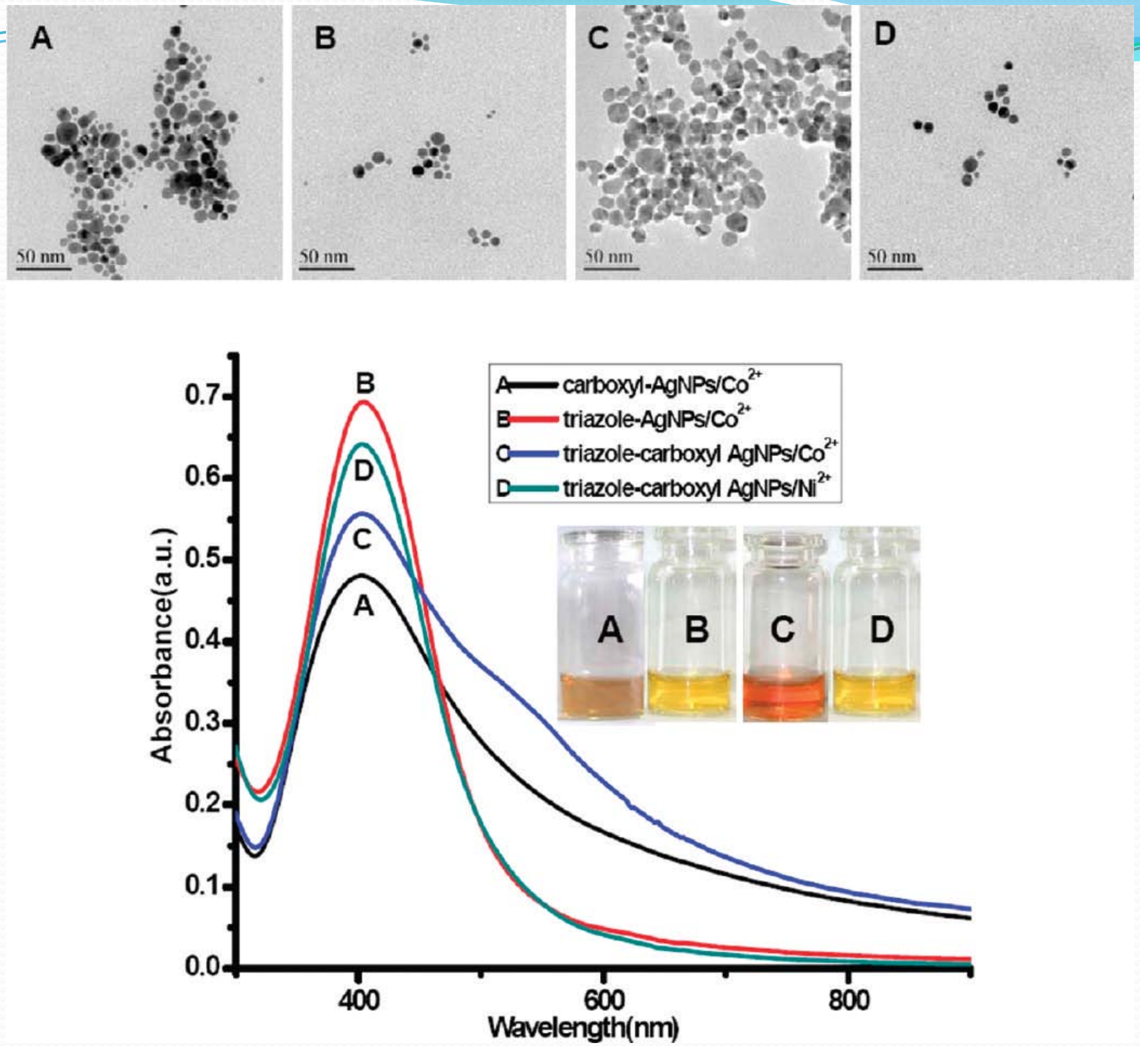
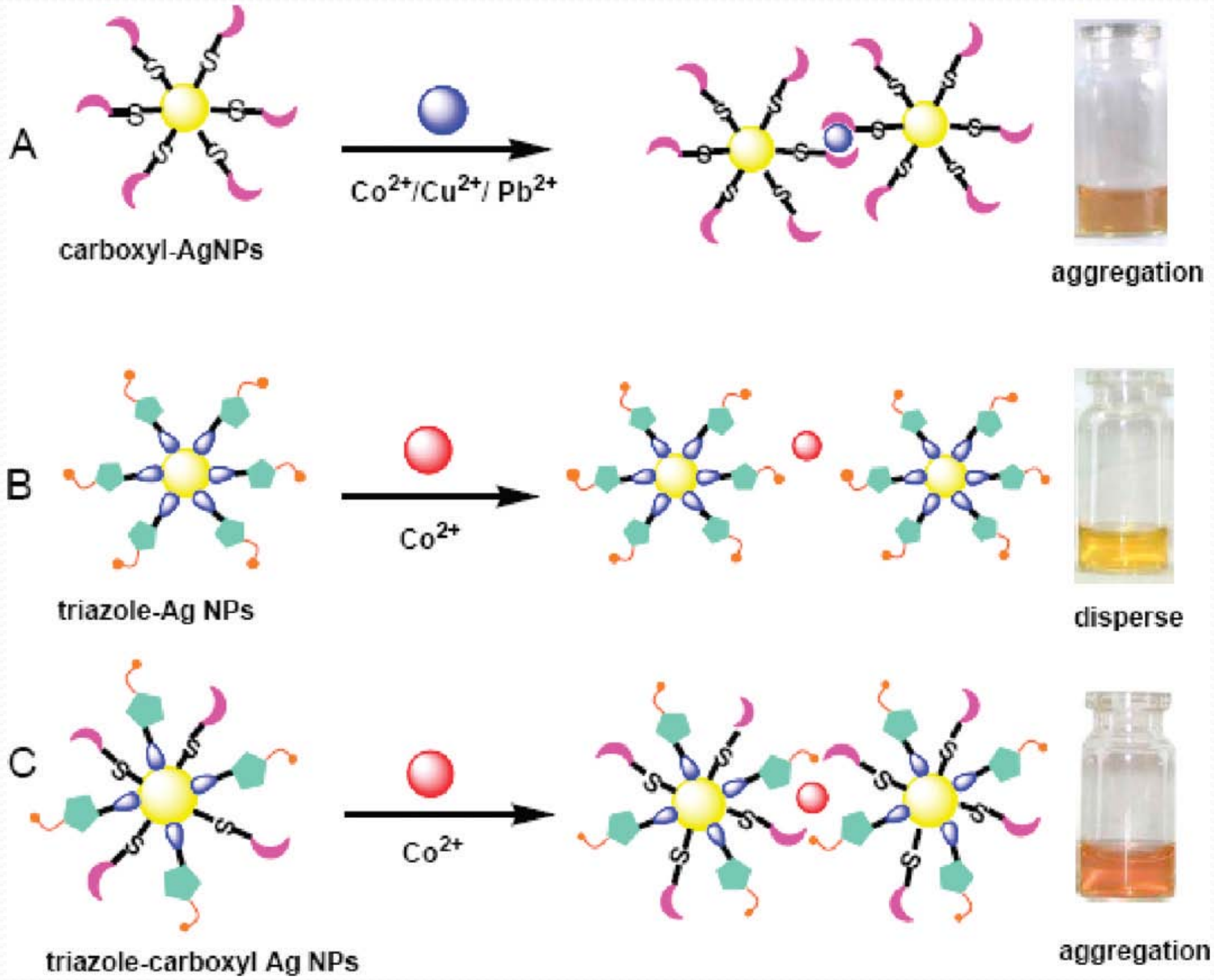
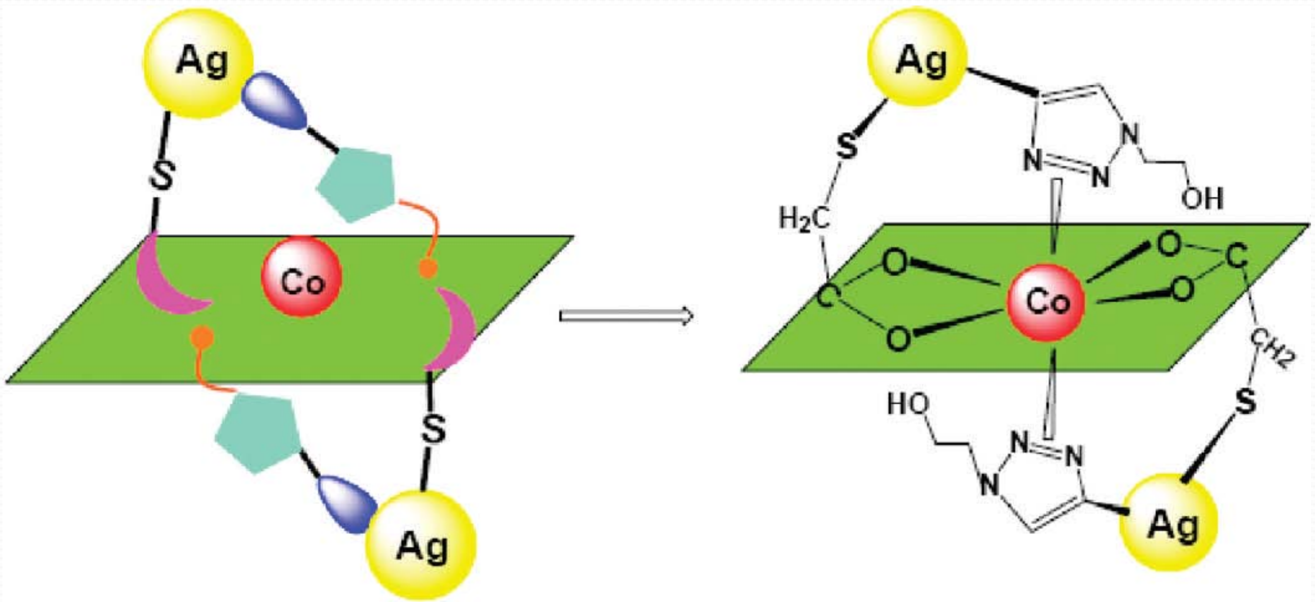


FIGURE 5. TEM micrograph, photo images, and UV-vis spectra of (A) carboxyl-Ag NPs in the presence of Co^{2+}, (B) triazole-Ag NPs addition in the presence of Co^{2+}, (C) triazole-carboxyl Ag NPs in the presence of Co^{2+}, (D) triazole-carboxyl Ag NPs in the presence of Ni^{2+}; all scales bars are 50 nm; $[Co^{2+}]$) $[Ni^{2+}]$) 1.0 × 10^{-5} M.

Scheme 2. Schematic of (A) Co^{2+}/Cu^{2+}/ Pb^{2+}-Induced Carboxyl-Ag NPs Aggregation, (B) Triazole-Ag NP Solution in the Presence of Co^{2+}, (C) Co^{2+}-Induced Carboxyl-Ag NPs Aggregation



Scheme 3. Schematic of Co^{2+}-Induced Triazole-Carboxyl Ag NP Aggregation



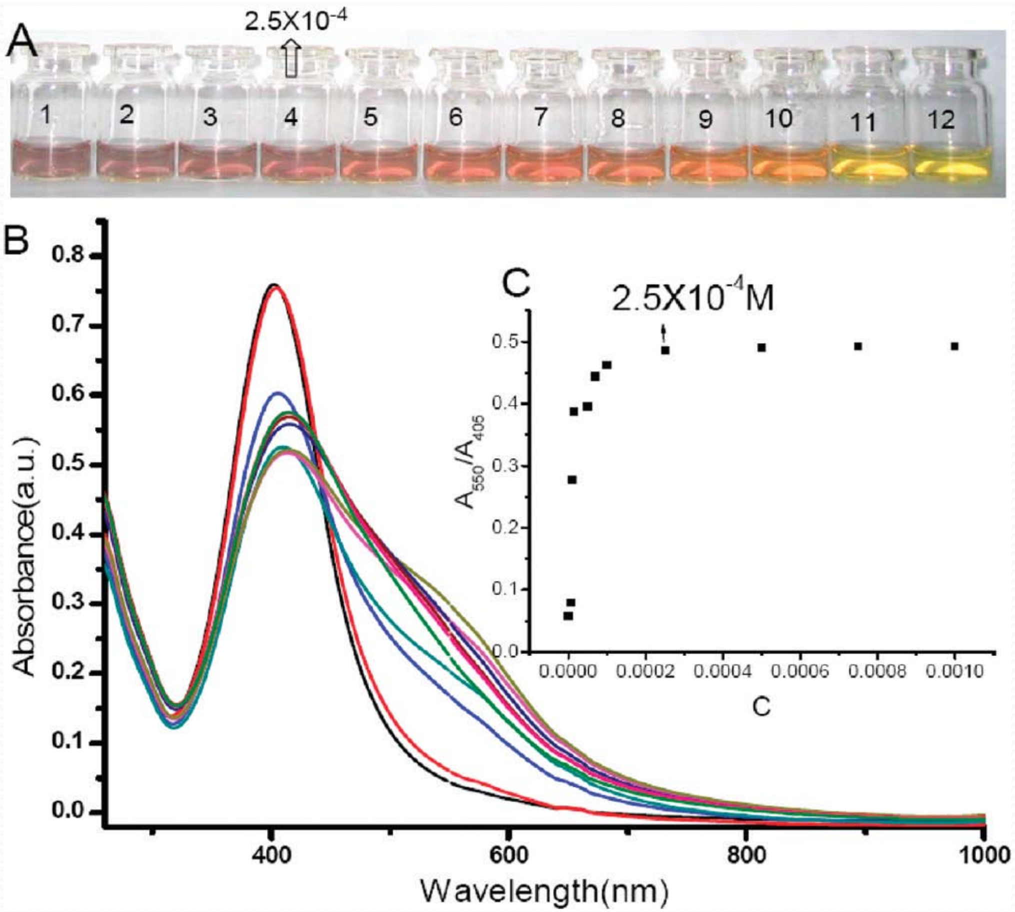


FIGURE 6. (A) Photo images of triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. The concentrations of Co^{2+} is (1) 1.0×10^{-3}, (2) 7.5×10^{-4}, (3) 5.0×10^{-4}, (4) 2.5×10^{-4}, (5) 1.0×10^{-4}, (6) 7.0×10^{-5}, (7) 5.0×10^{-5}, (8) 1.5×10^{-5}, (9) 1.0×10^{-5}, (10) 7.0×10^{-6}, (11) 5.0×10^{-6}, and (12) 0 M. (B) The UV-vis absorption spectra of the triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. (C) The equilibrium curves between R (A_{550}/A_{405}) and the Co^{2+} concentration C. Typically, 0.5 mL of various concentrations of Co^{2+} were added into 2.0 mL triazole-carboxyl Ag NPs solutions, and the combined solution was mixed well for 5 min and then tested.

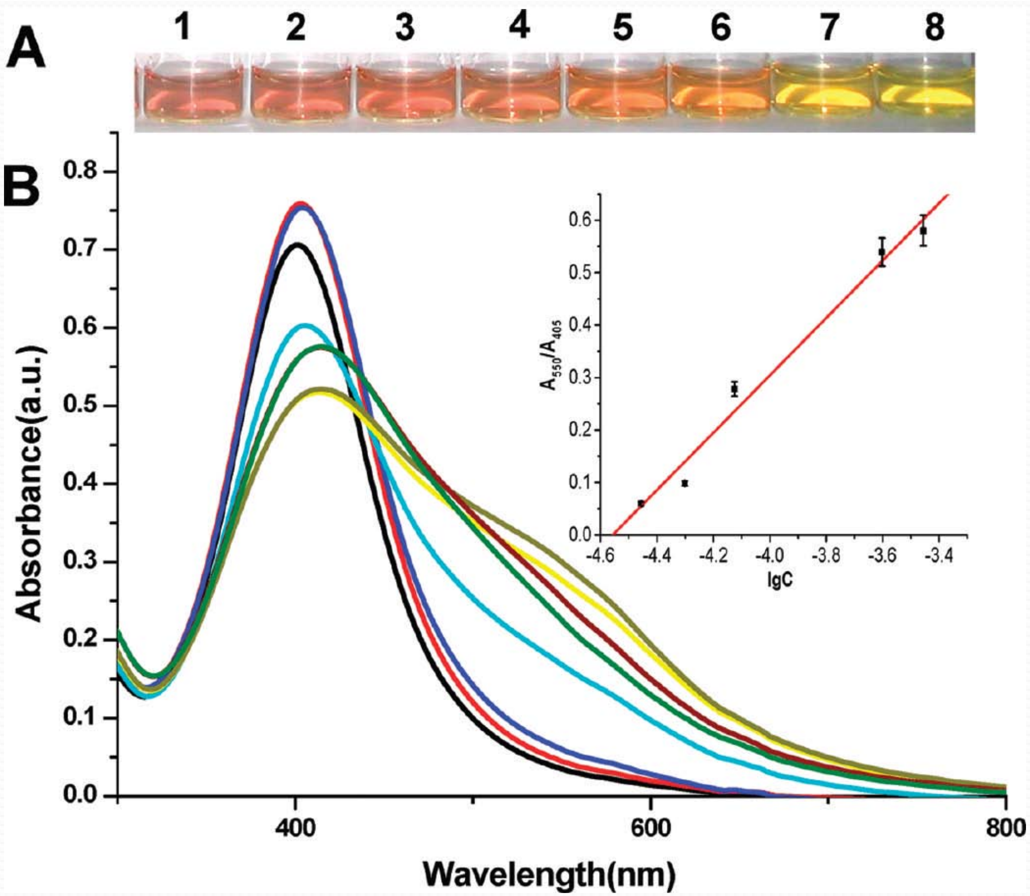


FIGURE 7. (A) Photo images of triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. The concentrations of Co^{2+} is (1) 1.0×10^{-4}, (2) 7.0×10^{-5}, (3) 5.0×10^{-5}, (4) 1.5×10^{-5}, (5) 1.0×10^{-5}, (6) 7.0×10^{-6}, (7) 5.0×10^{-6}, and (8) 0 M. (B) The UV-vis absorption spectra of the triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. The inset shows the dependence of the R values of Triazolecarboxyl Ag NPs on the increasing concentration of Co^{2+}. Typically, 0.5 mL of various concentrations of Co^{2+} were added into 2.0 mL triazolecarboxyl Ag NPs solutions, and the combined solution was mixed well for 5 min and then tested

Conclusions

- The bifunctionalized triazole-carboxyl Ag-NPs were synthesized which have cooperative effect on the recognition of Co^{2+} over other metal ions.
- The Co^{2+}-induced Ag NPs aggregation results in a marked red shift in the UV-vis absorption spectra and a visible color change from yellow to red, which proves a sensitive detection of Co^{2+} with a detection limit of 7.0×10^{-6} M.
- The triazole-carboxyl Ag NPs can be capable of evaluating the exceeding standard of Co^{2+} in drinking water with a colorimetric detection limit 1.0×10^{-5} M

Thank you

Next …

1. Preparation of organic soluble Ag NPs for removal of organic contaminants.
2. Capping of Ag NPs by optical and geometrical isomers and study of interaction by metal ions with spectroscopy.
3. To make Ag@MSA, Ag@citrate systems for colorimetric sensing of metal ions.