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

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ABSTRACT Bifunctionalized silver nanoparticles (triazole-carboxyl Ag NPs) were synthesized through a click reaction and have a cooperative effect on recognition of Co^{2+}, resulting in appreciable changes in color and absorption properties over other metal ions tested, including Fe^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Li^{+}, Na^{+}, K^{+}, Cs^{+}. The functionalized silver nanoparticles became aggregated in solution in the present of Co^{2+} through cooperative metal−ligand interaction. The colorimetric sensor allows a rapidly quantitive assay of Co^{2+} down to the concentration of 7.0×10^{-6} M. Moreover, the triazole-carboxyl AgNPs can be capable of evaluating the exceeding standard of Co^{2+} in drinking water.

KEYWORDS: silver nanoparticles • click reaction • colorimetric detection • Co^{2+}

1. INTRODUCTION

The development of highly sensitive and selective analytical methodology of Co^{2+} is of great importance to avoid its toxic effects. Humans may be exposed to cobalt compounds from diet and occupational exposure in several industries such as hard metal industry, diamond polishing, and the porcelain, chemical, and pharmaceutical industries (1). Exposure to cobalt may cause toxicological effects, including vasodilatation, flushing, and cardiomyopathy in humans and animals (2, 3). Currently, some fluorescent probes have been employed to detect cobalt ion (4, 5). However, these methods are disadvantage of quenching problems and unsuitable for real-time detection. Therefore, it is challenging to develop an on-site method for real-time detection of Co^{2+}. Colorimetric methods can avoid these problems and the detection signal can be observed by naked eyes (6, 7).

Recently, a variety of highly selective and sensitive colorimetric sensors based on functional metal nanoparticles (NPs) have been designed, especially of gold and silver nanoparticles, due to their extremely high extinction coefficients and the strongly distance-dependent optical properties (8). For example, dispersed silver nanoparticles (Ag NPs) are slight yellow in color, whereas aggregated ones are red. More importantly, the introduction of ligands onto Ag NP surfaces provides not only stability to these nanoentities in different solvents, but also desirable surface functionalities (9−11, 13, 20). We recently reported *β*-cyclodextrin-4,4′-dipyridine inclusion complex modified Ag NPs as colorimetric Yb^{3+} probes (12) and *p*-Sulfonatocalix[4]arene-modified Ag NPs can be used as colorimetric probes for histidine (13). When the introduced ligand give a special response to analysis of substrate, the change in color and UV−vis spectroscopy can be detected because of the aggregation of these Ag NPs. However, if only the simple modification of metal NPs with single recognition site, they can not be well in sensitivity and selectivity. It has been reported that bifunctionalized sensors can further improve the sensing efficiency, because of the cooperative effect of ligands. Lin and co-worker have found that thioctic acid and crown bifunctionalized Au-NPs can recognize K^{+} more quickly (14). Huang and co-worker have further improved the selectivity of the probe by modifying the rhodamine B−Au NP surfaces with thiol ligands (15).

On the basis of the design of highly selective and sensitive Ag NPs probes for Co^{2+}, “click” reaction has been used as a simple and versatile coupling strategy for the functionalization of nanoparticles (16−19). This method for the surface of Ag NPs modification has been reported in our former study, utilizing the copper(I)-catalyzed formation between azides and terminal acetylenes (20). In this paper, we present a new strategy for the efficient recognition and determination of Co^{2+} in aqueous solution using bifunctionalized Ag NPs (triazole-carboxyl Ag NPs). In our proposed approach, the interaction between triazole Ag NPs and metal ions is weak; however, 2-mercaptoacetic acid can provide coordination site for metal ions (21). The metal ions are thus expected to bind with triazole (22−24), and carboxyl through cooperative metal−ligand interaction. In this context, we 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. Bifunctionalized Ag NPs can demonstrate the role of two ligands, making nanosubstrate response more sensitive. Because of

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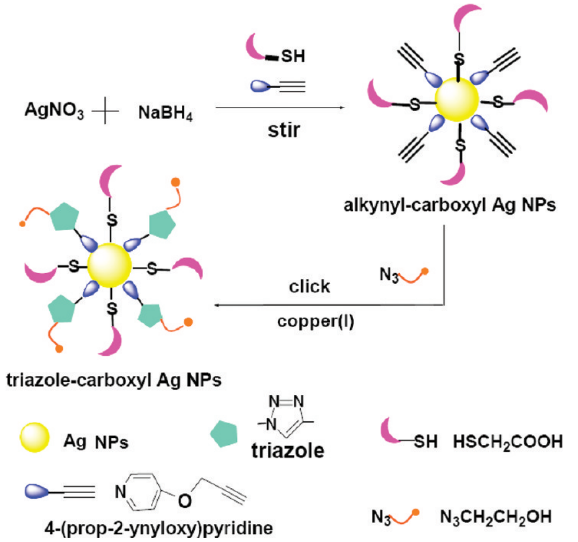
Scheme 1. Synthesis of Triazole-Carboxyl Ag NPs



the cooperative effect of ligands, the bifunctional Ag NPs show good sensitivity and selectivity. Up to date, the reports referred to bifunctionalized Ag NPs are rarely. The research of bifunctionalized Ag NPs is of great significance. Those bifunctionalized Ag NPs can be designed as smart probes, which have potential applications in pharmaceutical and biosensors.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. All chemicals used were of analytical grade or of the highest purity available. Silver nitrate($AgNO_3$, 99%), sodium borohydride ($NaBH_4$ 98%), and 2-mercaptoacetic acid were obtained from Tianjin Chemical Reagent Plant (Tianjin, China), the transition metal ions were obtained from Aldrich Chemicals(Milwaukee, WI) and used as received. 2-Chloroethanol was purchased from Yixing Weizhixin Chemical CO., Ltd. Sodium azide was purchased from Zhejiang Hailan Chemical CO., Ltd. The transition metal ions were dissolved in the deionized water and stored at room temperature. The synthesized procedure and characterization of 4-(prop-2-ynyloxy) pyridine and 2-azidoethanol are described in the Supporting Information.

2.2. Preparation of Bifunctional Ag NPs (triazole-carboxyl Ag NPs). 100 mL $AgNO_3$ aqueous solution (1.0 mL, 1×10^{-2} M) was reduced by sodium borohydride ($NaBH_4$, 12 mg) at room temperature to yield yellow colloidal silver particles. 4-(prop-2-ynyloxy) pyridine aqueous solution (1.0 mL, 1×10^{-3} M) and 2-mercaptoacetic acid aqueous solution (1.0 mL, 1×10^{-3} M) were added into Ag NPs solution (1×10^{-4} M), stirring for 2 h at room temperature. Alkynyl and carboxyl modified silver nanoparticles (alkynyl- carboxyl Ag NPs) were synthsized for the starting material of click reaction.

2-azidoethanol aqueous solution (1.0 mL, 1×10^{-3} mol/L) was added into alkynyl-carboxyl Ag NPs solution, stirring for 10 min. Finally, the mixtures of copper sulfate (1×10^{-6} M) and sodium ascorbic acid (1×10^{-7} M) were added into the above solution, stirring for 3 h at 60 °C. The mixtures have been placed into high intensity ultrasound bath for 10 min. The synthesized procedure was showed in Scheme 1. The synthesized triazole-carboxyl Ag NPs were purified by repeating centrifugation and redispersion in water. The finally dispersed Ag NPs can be used for metal ions detection.

Because of the hydrogen bonding between thioacetic acid and 4-(prop-2-ynyloxy) pyridine molecules, it is reasonable to believe that the surface of Ag NPs can be modified with thioacetic acid and 4-(prop-2-ynyloxy) pyridine molecule simultaneously. As shown in Figure S1 in the Supporting Information, the thioacetic acid and the traizole ligands can be arranged alternatively on the nanoparticle surface.

2.3. Preparation of Triazole-Ag NPs. 4-(Prop-2-ynyloxy) pyridine aqueous solution (1.0 mL, 1×10^{-3} M) was added into 100 mL of unmodified Ag-NPs solution (1×10^{-4} M), stirring for 2 h at room temperature. Alkynyl-Ag NPs were obtained in water. 2-Azidoethanol aqueous solution (1.0 mL, 1×10^{-3} M) was added into alkynyl-Ag NPs solution, stirring for 10 min. Finally, the mixture of copper sulfate (1×10^{-6} M) and sodium ascorbic acid (1×10^{-7} M) were added into alkynyl-Ag NPs solution, stirring for 3 h at 60 °C (the synthesized procedure and characterization are shown in Figure S2 in the Supporting Information).

2.4. Sample Preparation for Detecting Co^{2+} in Drinking Water. Drinking water sample were spiked with standard solutions containing Co^{2+} at concentrations over the range of 1−100 μM.

2.5. Equipment. The morphology of the new synthesized Ag NPs were characterized by transmission electron microscopy (TEM) by a Philips TecnaiG^2 TEM using an accelerating voltage of 200 kV. The UV−visible (UV−-vis) absorption spectra were taken at room temperature on a UV-2501 spectrophotometer (SHIMADZU CORPORATION) with a variable wavelength between 200 and 900 nm using a glass cuvette with 0.5 cm optical path. The infrared (IR) spectra were collected on a Thermo Nicolet NEXUS IR spectrometer in the wavenumber range 400−4000 cm^{-1} at a resolution of 4 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Characterization of the New Synthesized Ag-NPs. The TEM image shows triazole-carboxyl Ag NPs are highly dispersed and uniform in aqueous solution, with an average diameter 8 nm (Figure 1A). The click reaction between alkynyl-carboxyl Ag NPs and 2-azidoethanol gave rise to the cycloaddition products verified by infrared spectroscopy. Figure 2A clearly shows that alkynyl-carboxyl Ag NPs are obtained due to peaks at 2130 cm^{-1} (−C≡CH) and 1637 cm^{-1} (−COOH). Figure 2B shows characteristic skeleton peak of 2-azidoethanol is 2110 cm^{-1} ($-N_3$) and 2935 cm^{-1}($-CH_2-$). In Figure 2C, the IR spectrum of triazole-carboxyl Ag NPs shows the peaks of 2110 cm^{-1} ($-N_3$) and 2130 cm^{-1} (−C≡CH) have both disappeared, which indicates that the click reaction has happened on the surface of Ag NPs.

3.2. Stability of Triazole-Carboxyl Ag NPs. Triazole and carboxyl modified silver nanoparticles prepared by the described process displaced an absorption band at 405 nm. We examined the effect of pH on the UV−visible spectrum of the prepared triazole-carboxyl Ag NPs (see Figure S3 in the Supporting Information), the triazole-carboxyl Ag NPs are considerable stable in the interval 3.0−12.0. We examined the effect of pH on the Ag NPs in order to study the stability of prepared triazole-carboxyl Ag NPs. It is necessary to examine the effect of pH due to the optical properties of Ag NPs can be affected in different pH. In this Co(II) ion-sensing system, Ag NPs can be stable in the interval 3.0−12.0, and their optical properties can not be affected. The synthesized triazole-carboxyl Ag NPs solution can be stable for about 10 days.

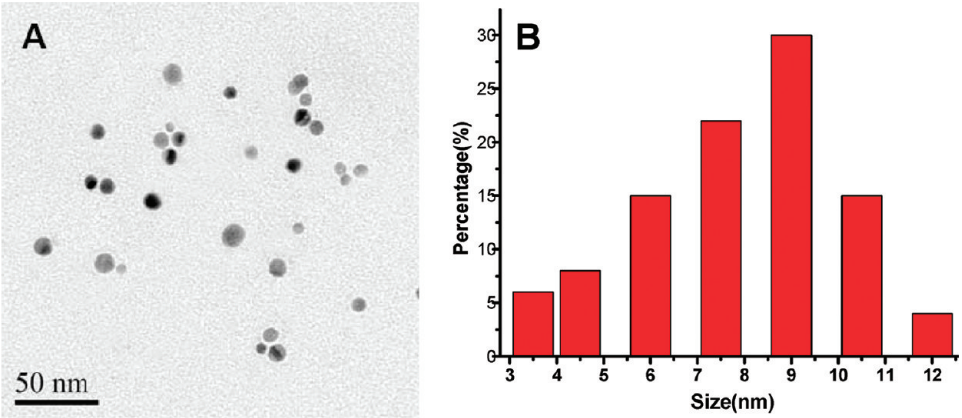


FIGURE 1. (A) TEM images of the triazole-carboxyl Ag NPs and (B) size distribution.

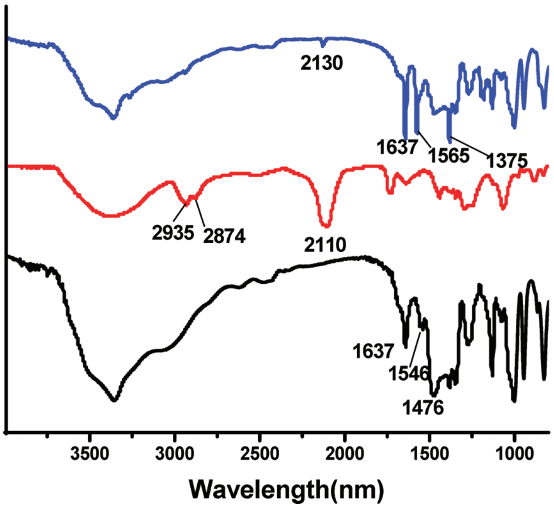


FIGURE 2. FT-IR spectra of (a) alkynyl-carboxyl Ag NPs, (b) 2-azidoethanol, (c) triazole-carboxyl Ag NPs.

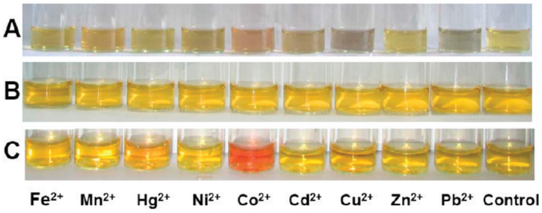


FIGURE 3. Photographic images of (A) carboxyl-Ag NPs, (B) triazole-Ag NPs, and (C) triazole-carboxyl Ag NPs solution in the presence of 10 μM different transition metal ions. Typically, 0.5 mL of 50 μM various transition metal ions were added into 2 mL Ag NPs solutions, and the combined solution was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

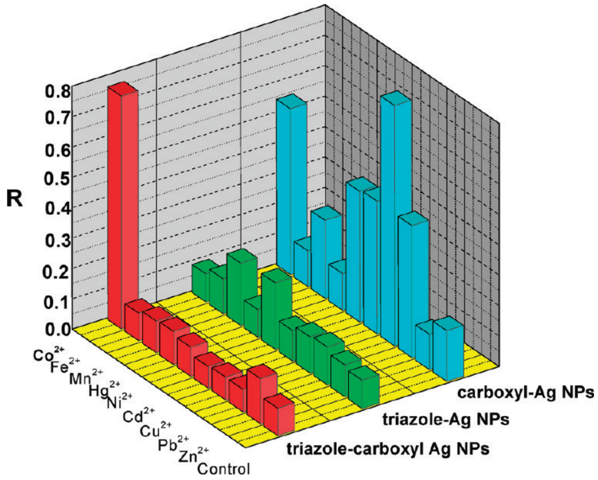


FIGURE 4. R (A_{550}/A_{405}) of triazole-carboxyl Ag NPs, triazole-Ag NPs, and carboxyl-Ag NPs solution in the present of different metal ions. Typically, 0.5 mL of 50 μM various transition metal ions were added into 2 mL Ag NPs solutions, and the combined solution was mixed well for 5 min and then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

3.3. Selective Recognition of Triazole-Carboxyl Ag NPs for Co^{2+}. Some research has shown that triazole (22−24) can bind with metal ions through metal−ligand interaction, as well as carboxyl (21). On the basis of this strategy, we have synthesized bifunctionalized triazole-carboxyl Ag NPs for metal ions sensing, and observed that they have a good recognition of Co^{2+}. Figure 3C displays the photographic images of triazole-carboxyl Ag NPs solution after adding various metal ions (0.01 mM) for 5 min; only the presence of Co^{2+} ion induces a distinct color change from yellow to red. Their UV−vis absorption spectra a shown in Figure S4 of the Supporting Information. The presence of Co^{2+} led to a decrease in absorption intensity at 405 nm, and a dramatic increase in the absorbance intensity at 550 nm.

To study combination site of Co^{2+}, we have employed carboxyl-Ag NPs and triazole-Ag NPs for further study. As shown in Figure 3A, many metal ions can respond to carboxyl-Ag NPs after various metal ions (0.01 mM) are added into Ag NPs solution for 5 min; its UV−vis absorption spectra are shown in Figure S5 in the Supporting Information. Figure 3B shows the photographic images of triazole-Ag NPs solution after adding various metal ions (0.01 mM) for 5 min; there are no obvious color changes in other solutions and the UV−vis absorption spectra are shown in Figure S6 in the Supporting Infomration. To quantify the spectral change at 405 and 550 nm, the absorbance ratio at two wavelengths ($R = A_{550}/A_{405}$) of triazole-carboxyl Ag NPs, triazole-Ag NPs, and carboxyl-Ag NPs in the presence of transition metal ions is determined. Figure 4 showed that the value R of triazole-carboxyl Ag NPs in the presence of Co^{2+} was ~7-fold larger than those achieved by other metal ions, which indicated that the value of A_{550}/A_{405} can be used to display the distinctive interaction between triazole-carboxyl Ag NPs and Co^{2+}. This experimental phenomenon

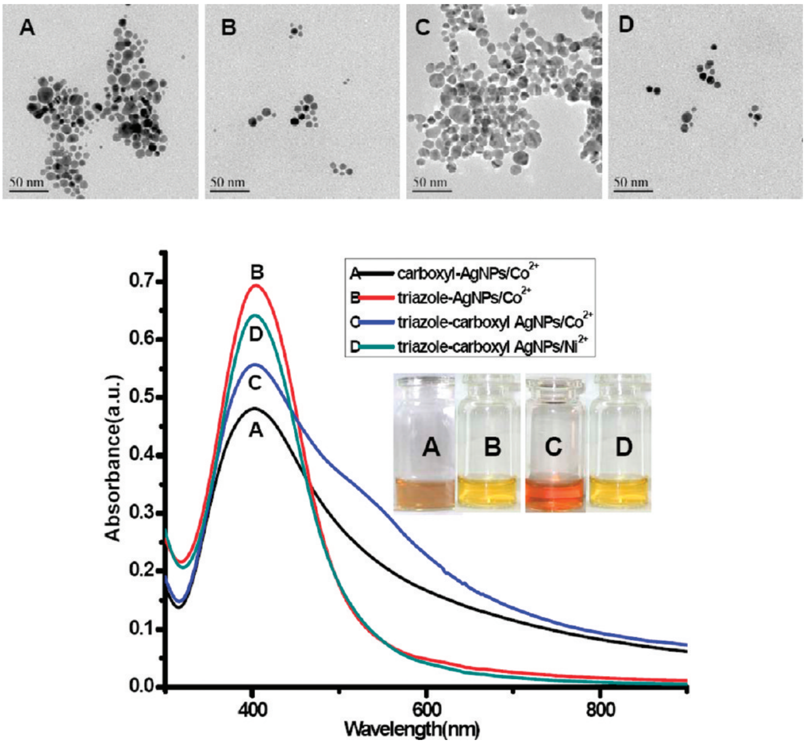
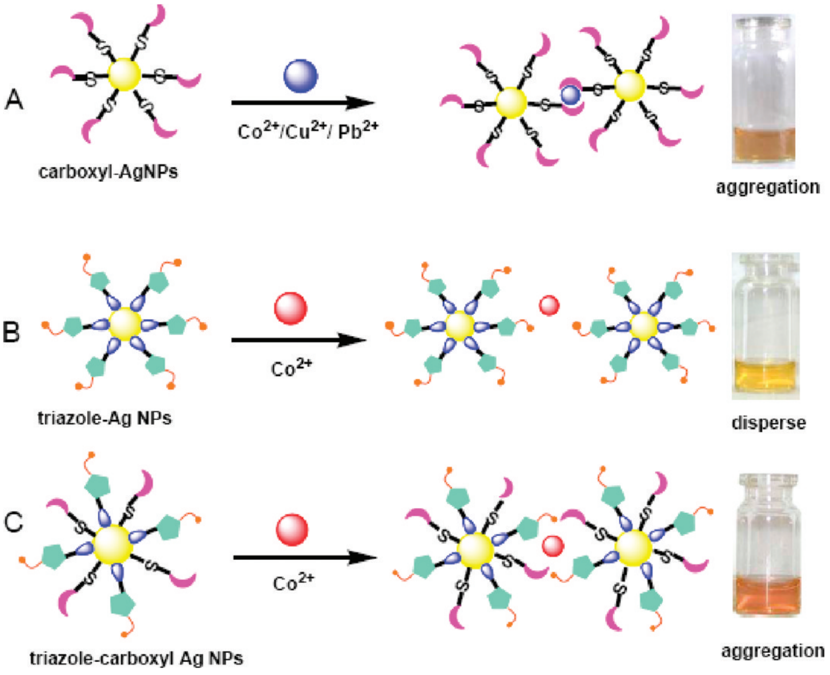


FIGURE 5. TEM micrograph, photo images, and UV−vis spectra of (A) carboxyl-Ag NPs in the presence of Co^{2+}, (B) triazole-Ag NPs addition in the presence of Co^{2+}, (C) triazole-carboxyl Ag NPs in the presence of Co^{2+}, (D) triazole-carboxyl Ag NPs in the presence of Ni^{2+}; all scales bars are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

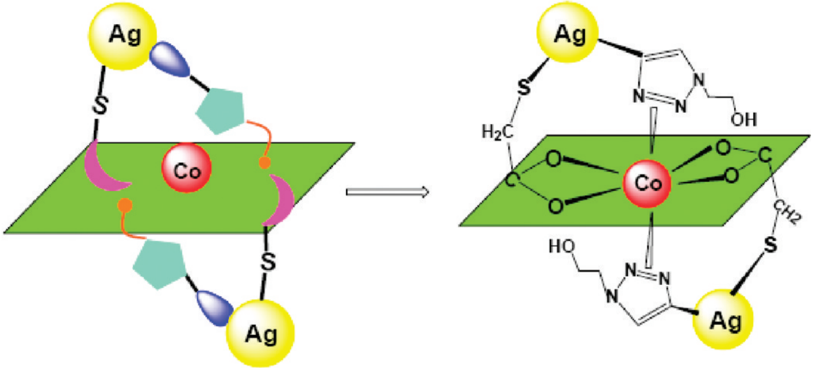
Scheme 2. Schematic of (A) $Co^{2+}/Cu^{2+}/Pb^{2+}$-Induced Carboxyl-Ag NPs Aggregation, (B) Triazole-Ag NP Solution in the Presence of Co^{2+}, (C) Co^{2+}-Induced Carboxyl-Ag NPs Aggregation



suggests that carboxyl and triazole can have a cooperative combination of Co^{2+}.

To study the recognition ability of triazole-carboxyl Ag NPs, we added a variety of transition and alkali metal ions (0.01 mM) into the triazole-carboxyl Ag NP solution. As shown in Figure S7 of the Supporting Information and Figure 3C, the alkali metal ions and other transition metal ions (0.01 mM) had no obvious effect on the color or UV−vis absorption, which indicates that the triazole-carboxyl Ag NPs have an efficient selective of Co^{2+}. As a control, transition metal ions (0.01 mM) were added into alkynyl-carboxyl Ag NPs; most of the tested transition metal ions can make those Ag NPs solution color change in 5 min, which suggests that Ag NPs do not have selective response to Co^{2+} before click

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



reaction. (Figure S8) This experimental phenomenon suggests that bifunctionalized Ag NPs have a good recognition of Co^{2+}.

The selective response of triazole-carboxyl Ag NPs to Co^{2+} was evaluated in the mixture of metal ions solution (M) that might interfere with Co^{2+} detection, including 0.05 mM each of Fe^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}. As Figure S9 in the Supporting Information shows, the triazole-carboxyl Ag NPs were stable in the mixtures of metal ions solution and no color change was observed. However, if 0.01 mM Co^{2+} was present in the mixtures, the color of the solution changed from yellow to red immediately. Thus, the triazole-carboxyl Ag NP probes showed a good recognition of Co^{2+} in the presence of competitive ions.

To investigate the color change of the triazole-carboxyl Ag NPs solution induced by Co^{2+}, we also performed a TEM study on these nanoparticles in the presense of Co^{2+} (0.01 mM) (Figure 5). We proposed that the color change of triazole-carboxyl Ag NPs may indicate strong aggregation of particles. From the TEM images and UV−vis absorption spectra, we observed that carboxyl-Ag NPs and triazole-carboxyl Ag NPs solution can response to Co^{2+}. Although carboxyl-AgNPs can respond to many metal ions, such as Co^{2+}, Cu^{2+}, and Pb^{2+}(Figure 2A), only triazole-carboxyl Ag NPs have a special response to Co^{2+} (Figure 2C). The possible mechanism of the phenomenon is shown in Scheme 2. If triazole and carboxyl bind with metal ions together, the selectivity is determined by their combination model on the surface of Ag NPs, as well as mental ion coordination mode. Some research has showed that cobalt ion is six-coordinated rule model (1). The carboxyl group in the mercaptoacetic acid and nitrogen in the triazole can form a six-coordinated

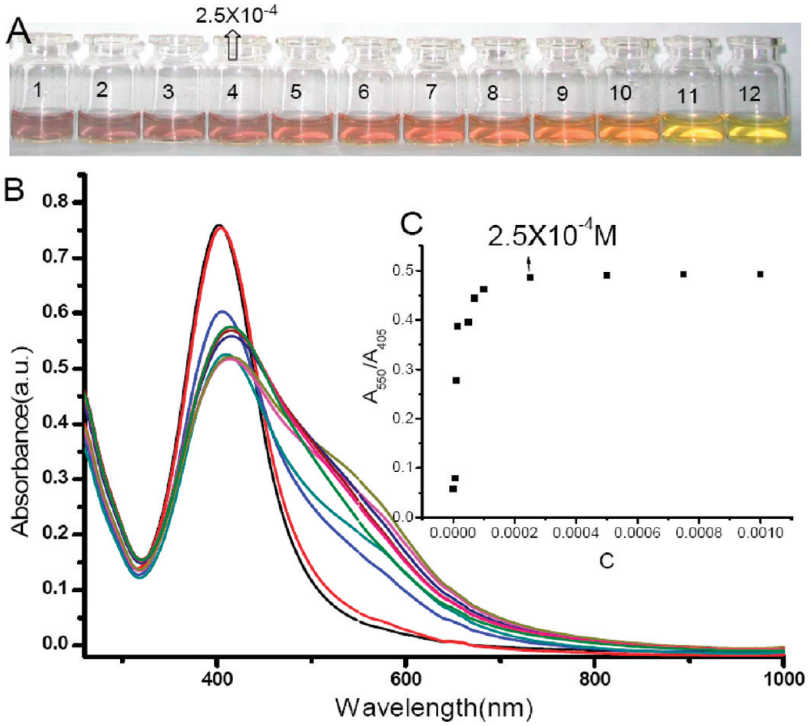


FIGURE 6. (A) Photo images of triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. The concentrations of Co^{2+} is (1) 1.0×10^{-3}, (2) 7.5×10^{-4}, (3) 5.0×10^{-4}, (4) 2.5×10^{-4}, (5) 1.0×10^{-4}, (6) 7.0×10^{-5}, (7) 5.0×10^{-5}, (8) 1.5×10^{-5}, (9) 1.0×10^{-5}, (10) 7.0×10^{-6}, (11) 5.0×10^{-6}, and (12) 0 M. (B) The UV−vis adsorption 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.

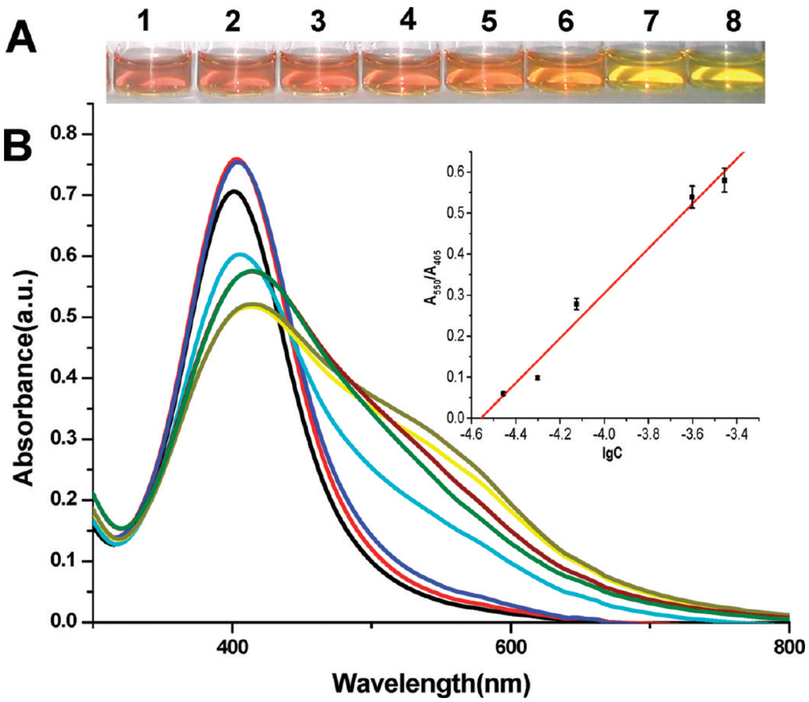


FIGURE 7. (A) Photo images of triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. The concentrations of Co^{2+} is (1) 1.0×10^{-4}, (2) 7.0×10^{-5}, (3) 5.0×10^{-5}, (4) 1.5×10^{-5}, (5) 1.0×10^{-5}, (6) 7.0×10^{-6}, (7) 5.0×10^{-6}, and (8) 0 M. (B) The UV−vis adsorption spectra of the triazole-carboxyl Ag NPs solution with various concentrations of Co^{2+}. The inset shows the dependence of the *R* values of triazole-carboxyl 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 triazole-carboxyl Ag NPs solutions, and the combined solution was mixed well for 5 min and then tested.

structure with cobalt. As shown in Scheme 2C and Scheme 3, it is reasonable to believe that Co^{2+} can fit better with the model of triazole-carboxyl Ag NPs than other transition ions tested. Therefore, the bifunctionalized Ag NPs show a good recognition of Co^{2+}.

Quantitative analysis was performed by titrating the Co^{2+} ions and monitoring the UV−vis absorption spectroscopic and the color of the system changes. Figure 6 shows the typical photo images and UV−vis spectroscopic response of triazole-carboxyl Ag NPs solution after adding different concentrations of Co^{2+} over 5 min; a clear color progression from yellow to orange to red with increasing Co^{2+} concentration was observed (Figure 6A). The absorption intensity of the Ag NPs at 405 nm decreased with increased Co^{2+}, whereas the band intensity at 550 nm increased (Figure 6B). There is an equilibration curve between *R* (A_{550}/A_{405}) and Co^{2+} concentration *C*. The curve can reach a platform when the concentration of Co^{2+} is above 2.5×10^{-4} M (Figure 6C). A linear correlation exists between *R* (A_{550}/A_{405}) and the logarithm of the Co^{2+} concentration *C* over the range of 5.0×10^{-6} to 1.0×10^{-4} M (Figure 7). The linear equation is $R = 2.357 + (0.5113 \times \log[C])$ with a linearity coefficient of 0.981. The colorimetric detection for Co^{2+} is 7.0×10^{-6} M, which is higher than the reported techniques such as inductively coupled plasma emission spectrometry (ICP, 8×10^{-8} M) (3), atomic absorption spectroscopy (AAS, 4×10^{-8} M) (25), etc. However, a colorimetric sensor can realize on-site and rapid detection with signal can be observed by the naked eye. In addition, quantitative analysis was performed in the presenvr of other competitive ions (see Figure S10 in the Supporting Information). The linearity changes in the presence of other competitive ions M (M is the mixture of metal ions in solution, including 0.05 mM each of Fe^{2+}, Mn^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}.) As Figure S10 in the Supporting Information shows, a linear correlation exists between *R* (A_{550}/A_{405}) and the logarithm of the Co^{2+} concentration *C* over the range of 5.0×10^{-6} to 5.0×10^{-4} M in the presence of other competitive ions M. The linearity of linear equation is $R = 1.32877 + (0.23638 \times \log[C])$ with a linearity coefficient of 0.99431. The colorimetric detection for Co^{2+} is 7.5×10^{-6} M in the presence of other competitive ions. What's more, the sensor is also capable of detecting drinking water samples that contain 1.0×10^{-5} M of Co^{2+}, as shown in Figure S11 in the Supporting Information.

4. CONCLUSIONS

In conclusion, we have synthesized bifunctionalized triazole-carboxyl Ag NPs that have a cooperative effect on recognition of Co^{2+} over 12 other metal ions in aqueous solution. 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.

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Supporting Information Available: General procedure for the synthesis of 4-(prop-2-ynyloxy)pyridine and 2-azidoethanol; photographic images and UV−vis absorption spectra of triazole-Ag NPs, carboxyl-Ag NPs, and triazole-carboxyl Ag NPs; selectivity of the sensor for Co^{2+} in the mixture of competitive ions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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