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A gold nanoparticle-based colorimetric sensing ensemble for the colorimetric detection of cyanide ions in aqueous solution

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ABSTRACT

A colorimetric sensing ensemble was prepared by mixing readily prepared adenosine triphosphate (ATP)-stabilized AuNPs with Cu^{2+}–phenanthroline complexes. The sensing mechanism of the ensemble was examined by UV–vis spectrometry and transmission electron microscopy. The studies showed that the Cu^{2+}–phenanthroline complex was converted to free phenanthroline when exposed to cyanide anions and the free phenanthroline caused the ATP-stabilized AuNPs to aggregate, which in turn, resulted in a visible color change in the AuNP solution. The ensemble could detect cyanide ions in aqueous solution at physiological pH, either spectrophotometrically or visually, with high selectivity toward cyanide anions over a range of mono- and di-anions commonly found in biological and environmental systems. This sensing ensemble also allows a quantitative assay of the analyte in a neutral aqueous solution, down to a concentration of 10^{-5} M.

Cyanide is extremely toxic with even a small amount of this species being lethal to humans. The toxicity results from its binding to cytochrome-c in the mitochondria, which prevents respiration.[1,2] Nevertheless, cyanide is produced in large quantities and used in various industrial processes, which has led to environmental contamination.[3] Therefore, the routine detection of cyanide is an important aspect of the environmental monitoring of rivers and large bodies of water as well as for evaluating food safety. As a result, the detection of cyanide has attracted considerable attention in recent years, and many cyanide sensors have been developed.[4–37] Several strategies for detecting cyanide have been developed based on fluorogenic and chromogenic organic dyes,[4–26] semiconductor nanoparticles,[27,28] chromatography,[29,30] electrochemical sensors,[31,32] and polymers.[33,34] Colorimetric chemosensors are particularly attractive because they can be read by the naked eye, and in some cases at the point of use. While many carefully designed colorimetric chemosensors for cyanide have been reported, there are limited examples that are satisfactory with respect to their sensitivity, selectivity, and compatibility within a purely aqueous environment[35–37]

Gold nanoparticles (AuNPs) are ideal chromophores because they have 3–5 orders of magnitude higher extinction coefficients than organic dye molecules.[38–40] Moreover, the unique distance-dependent optical properties of AuNPs can be programed chemically by using specific host compounds, such as DNA, to induce a dramatic color change from red to blue.[38–40] Many AuNP-based colorimetric sensors have been developed to detect metal ions, proteins, DNA, and small molecules owing to their high extinction coefficients and distance-dependent optical properties.[41,42] However, very few colorimetric systems using gold nanoparticles have been developed for the detection of anions.[43–46]

This Letter reports an operationally simple, selective, and sensitive colorimetric sensing ensemble, which employs a combination of adenosine triphosphate-stabilized AuNPs (sAuNPs) as the reporter unit and a Cu^{2+}–phenanthroline complex as the receptor unit for the detection of cyanide anions in aqueous solution. The competitive assay approach is used widely in the development of organic dye-based chemosensors for anions.[47–51] The sAuNPs, as the colorimetric reporter in the colorimetric sensing ensemble, were prepared by mixing 13 nm AuNPs and ATP, and were stable over a wide pH range, even in a high salt concentration.[52,53] Typically, sAuNPs quickly aggregate when exposed to metal ligands, such as thiol and pyridine compounds.[54–56] The Cu^{2+}–phenanthroline complex, which is the cyanide receptor component of the sensing ensemble, was prepared by mixing phenanthroline and copper ions. Cyanide anions form stable complexes with many transition metals and abstract Cu^{2+} ions from Cu^{2+} complexes to form new, even more stable complexes. Accordingly, Cu^{2+}–phenanthroline, when exposed to cyanide anions, can be decomplexed to give free phenanthroline. This property has been used recently to develop selective chemosensors for cyanide.[27,28,33,35,37] Combining this information on the properties of sAuNPs, cyanide anion and Cu^{2+}–phenanthroline complexes led to the design of a sensing ensemble, in which (a) the Cu^{2+}–phenanthroline complex would be converted to free phenanthroline when exposed to cyanide

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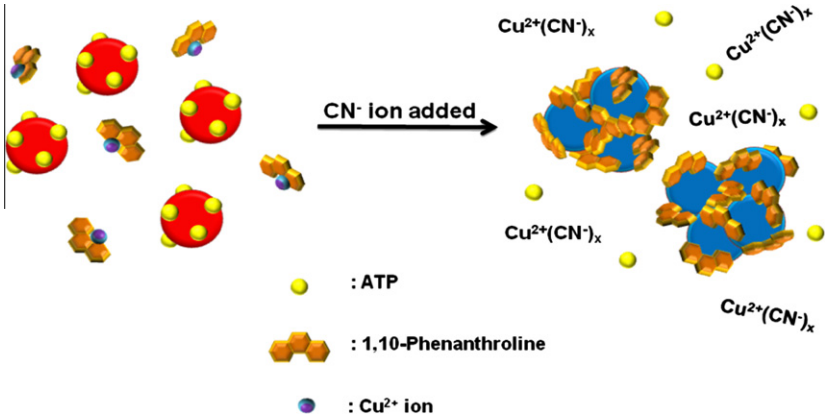

Scheme 1. A schematic diagram of the cyanide anion sensing ensemble.

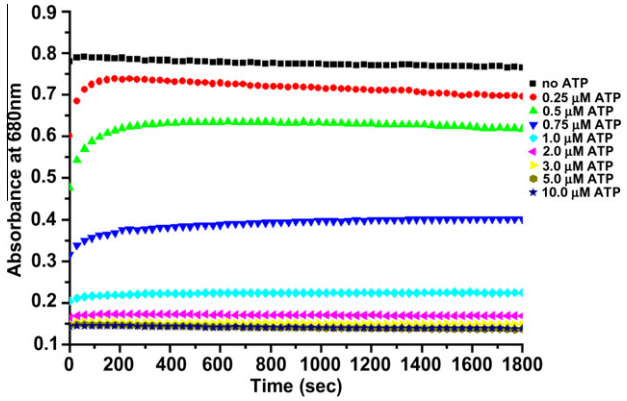

Figure 1. Stabilities of the sAuNPs to Cu^{2+}–phenanthroline in the presence of various concentrations of ATP.

anions and (b) the free phenanthroline would bind to sAuNPs, causing them to aggregate, which would cause a visible color change in the AuNP solution (Scheme 1).

A ligand-exchange reaction is a general phenomenon in which a chemical change occurs when one ligand is replaced with a second ligand. Therefore, the sAuNPs in the presence of Cu^{2+}–phenanthroline can bind to phenanthroline after a ligand-exchange reaction, which can induce the aggregation of sAuNPs. When AuNPs stabilized with <1 μM ATP were exposed to Cu^{2+}–phenanthroline, the color of the sAuNP solution changed within 30 min. However, when the AuNPs stabilized with >2 μM ATP were exposed to Cu^{2+}–phenanthroline, the color of the sAuNP solution did not change, even after 30 min (Fig. 1). Therefore, the sensing ensemble for cyanide was prepared by sAuNPs stabilized with 3 μM ATP and

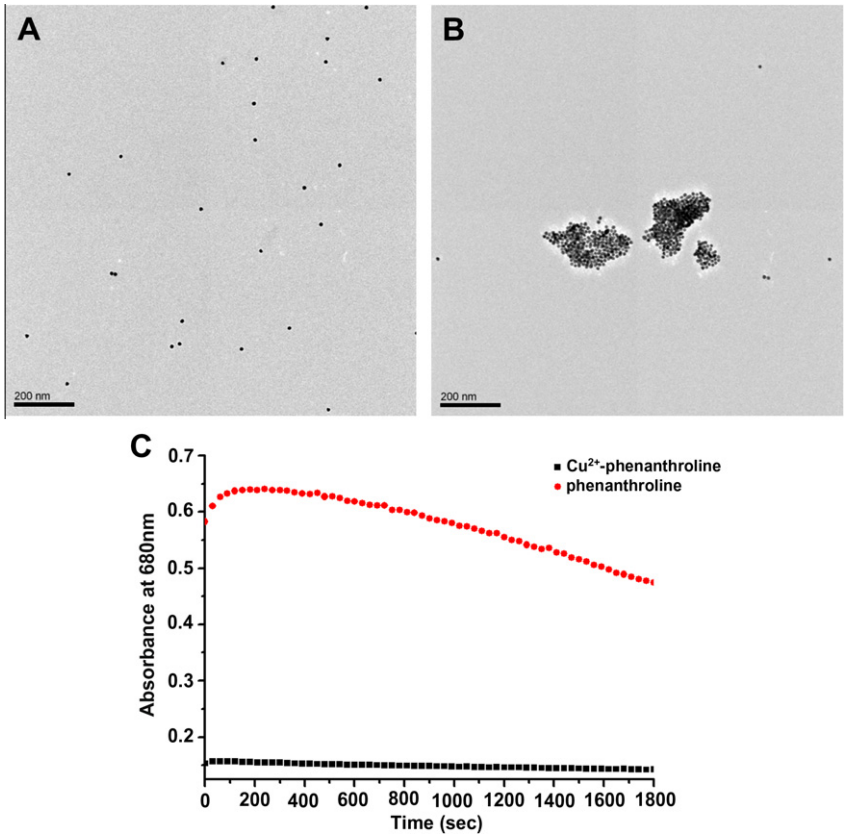

Figure 2. (A) TEM image of a mixture of ATP-stabilized 13 nm AuNPs (3 nM) and Cu^{2+}–phenanthroline (10 μM) at pH 7.0. (B) TEM image of the mixture after the addition of cyanide (20 μM). The scale bar represents 200 nm. (C) Stability of the sAuNPs stabilized with ATP (3 μM) to phenanthroline and Cu^{2+}–phenanthroline.

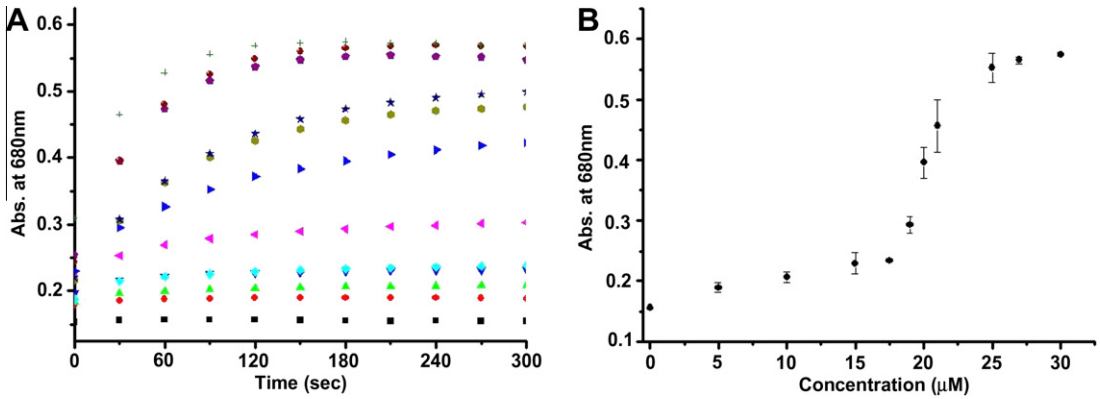

Figure 3. (A) Absorbance changes of the ensemble solution after the addition of cyanide anion versus time. (B) Plot of absorbance intensities of assay solutions recorded 3 min at 680 nm after the addition of cyanide anion versus CN^- concentration.

Cu^{2+}–phenanthroline. In the presence of Cu^{2+}–phenanthroline, the dispersion of the sAuNPs was confirmed by transmission electron microscopy (TEM; Fig. 2A) and by the appearance of a surface plasmon resonance (SPR) band at 520 nm in the UV–vis spectrum. However, the sAuNPs aggregated upon the addition of cyanide (Fig. 2B) with a concomitant SPR band red shift from 520 nm to 680 nm. Also, free phenanthroline induced an immediate red to blue color change in the sAuNPs despite the sAuNPs being stabilized with 3 μM ATP (Fig. 2C). This indicates that free phenanthroline, generated from cyanide removing Cu^{2+} from the Cu^{2+}–phenanthroline complex, forms more stable $[Cu^{2+}(CN^-)_x]$ complexes with sAuNPs. This reaction caused the aggregation of sAuNPs and induced a color change to blue, which is observed in the SPR as a band red shift. This red shift is a well-known phenomenon and is used to confirm the formation of nanoparticle aggregates.[39–41] On the other hand, cyanide is capable of dissolving metals, such as Au and Ag, in the presence of oxygen through the formation of soluble metal–cyanide complexes.[57–60] Therefore, it is possible that cyanide induces a color change in the sAuNP solution simply by dissolving the sAuNPs. However, the color in the sAuNP solution in the absence of Cu^{2+}–phenanthroline did not change, even after 30 min in the presence of cyanide anions (30 μM) (see Supplementary data).

The sensitivity of the ensemble for cyanide was evaluated. A stock solution of cyanide ions was added to the assay mixture containing sAuNPs (3 nM) and Cu^{2+}–phenanthroline (10 μM) in a pH 7.0 buffer solution (10 mM phosphate buffered saline (PBS) + 0.1 M NaCl), such that the final concentration was between

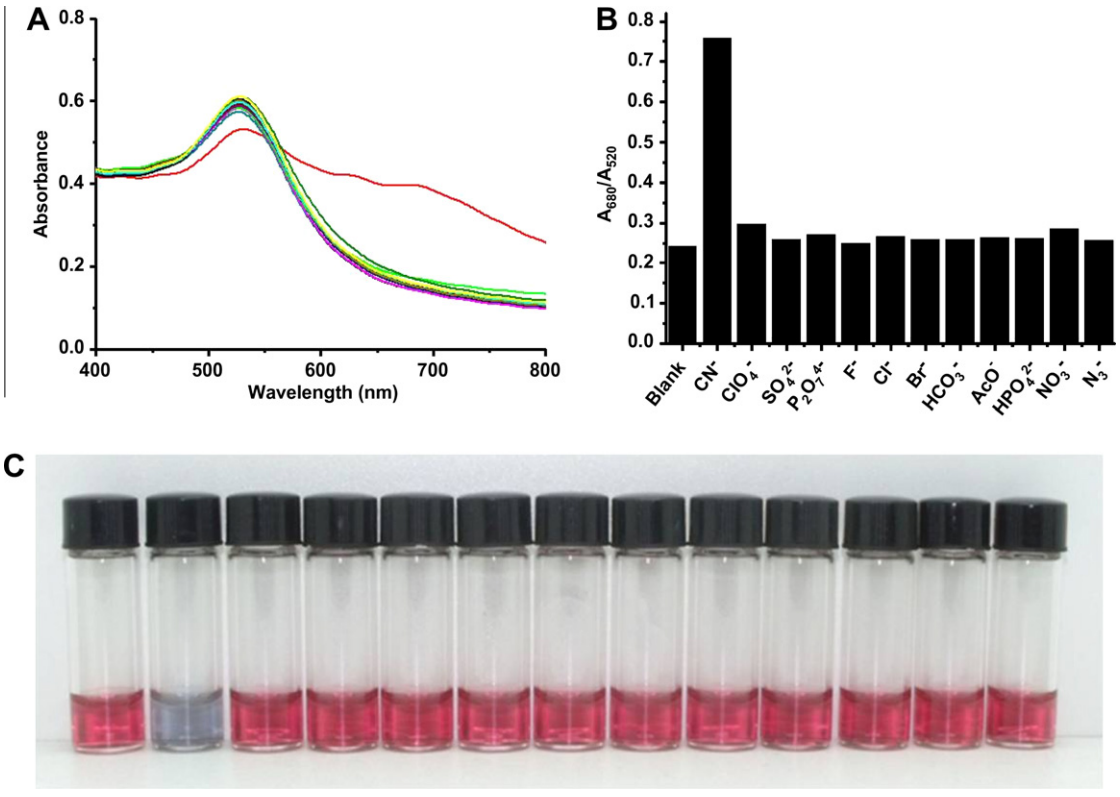

Figure 4. (A) UV–vis spectra obtained after the addition of various anions (30 μM) to pH 7.0 buffer solution (10 mM phosphate buffered saline (PBS) + 0.1 M NaCl) containing sAuNPs (3 nM) and Cu^{2+}–phenanthroline (10 μM). (B) Plot of absorbance intensities of the assay solution at 680 nm versus anions. (C) The color of the solution in the absence and presence of anions (30 μM): from left to right; no anion, CN^-, F^-, Cl^-, Br^-, ClO_4^-, SO_4^{2-}, HCO_3^-, AcO^-, HPO_4^{2-}, NO_3^-, N_3^-, $P_2O_7^{4-}$.

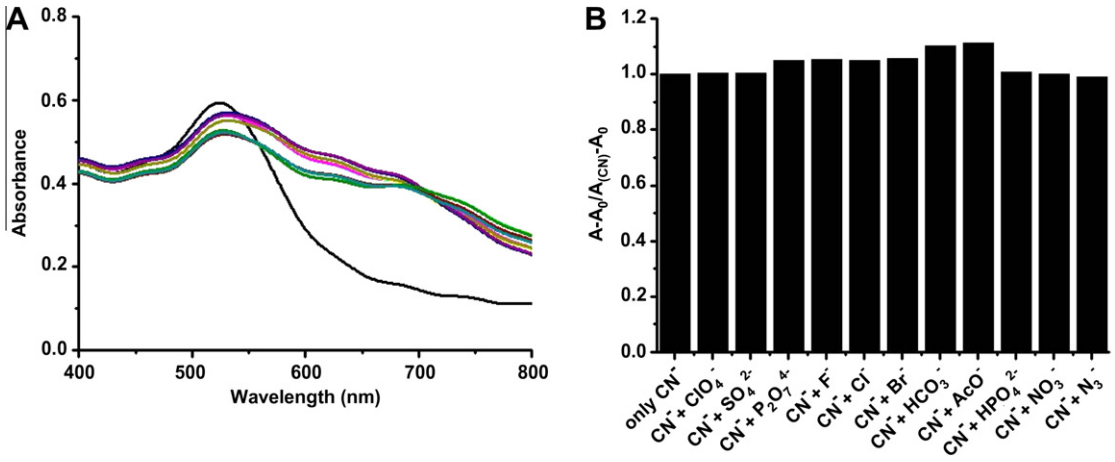

Figure 5. (A) UV–vis spectra obtained by the addition of CN^- (30 μM) to a pH 7.0 buffer solution (10 mM phosphate buffered saline (PBS) + 0.1 M NaCl) containing sAuNPs (3 nM), Cu^{2+}–phenanthroline (10 μM), and other anions (300 μM). (B) Absorbance intensities of the sensing ensemble (10 μM) in the presence of CN^- (30 μM) and other anions (100 μM).

0 μM and 30 μM. The changes in absorbance of the assay mixtures were recorded at 680 nm after adding the cyanide anions. Figure 3A shows the changes in the absorbance of the assay mixtures in the presence of various concentrations of cyanide ions. As shown in Figure 3B, the observed absorbance intensity at 680 nm was almost proportional to the cyanide concentration. From the results, the detection limit for the ensemble with cyanide was estimated to be 1.4×10^{-5} M (see Supplementary data).

Another important property of the ensemble is its high selectivity for cyanide over other anions. Figure 4A shows the UV–vis spectra of the solutions of the ensemble recorded 3 min after adding 3 equiv of each of the anions. The ensemble showed high selectivity for cyanide over the other anions. No significant change in the absorbance of the ensemble was observed upon the addition of other anions.

In particular, acetate and fluoride did not affect the absorbance of the sensing ensemble. This is important because many previously reported sensors for cyanide suffered from low selectivity over fluoride and acetate. Moreover, only limited colorimetric chemosensors have been reported to detect cyanide selectively in a pure aqueous solution.[35,36]

The practical applicability of the developed colorimetric sensing ensemble to the analysis of cyanide was also investigated. The possible interference by other anions was assessed by measuring the cyanide-induced changes in absorbance in the sensing ensemble in the presence of background anions. Figure 5 shows the UV–vis spectra of solutions of the ensemble, which were recorded 3 min after the addition of cyanide anions (30 μM) to a buffer solution containing the ensemble and 10 equiv (300 μM) of other anions. The changes in absorbance caused by the addition of cyanide anions were almost unaffected by the presence of the other anions, which may be due to two factors. First, cyanide ions have a higher affinity to copper ions than other anions. Second, despite the other anions being able to strongly bind to copper ions, only cyanide ions have the ability to abstract copper ions from the Cu^{2+}–phenanthroline complex.

In conclusion, a colorimetric sensing ensemble for cyanide anions was prepared by simply mixing a readily prepared sAuNPs and Cu^{2+}–phenanthroline complex in water at neutral pH. The probe can detect cyanide ions in an aqueous solution at physiological pH, either spectrophotometrically or visually, with unprecedented high selectivity toward cyanide anions over a range of other mono- and di-anions. This sensing ensemble also allows a quantitative assay of the analyte, in a neutral aqueous solution, down to a concentration of 10^{-5} M. In addition, this method can, in principle, be used to detect other molecules by substituting Cu^{2+} in the Cu^{2+}–phenanthroline complex with the other metal ions that can be exchanged selectively with anions or molecular ligands.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.07.002.

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