

COLORIMETRIC DETECTION OF $S_2O_4^{2-}$ USING CTAB FUNCTIONALIZED GOLD NANOPARTICLES
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ABSTRACT

A facile, cost-effective colorimetric detection method for $S_2O_4^{2-}$ has been developed by using CTAB functionalized gold nanoparticles (CTAB-GNPs). The sensitivity and selectivity of detection was investigated in detail. The CTAB-GNPs could be induced to aggregate immediately in the presence of $S_2O_4^{2-}$, especially after the addition of 1M NaCl aqueous solution. The $S_2O_4^{2-}$ could be detected by colorimetric response of GNPs that could be monitored by a UV-Vis spectrophotometer or even naked eyes, and the detection limit could reach 0.02mM. The CTAB-GNPs bound by $S_2O_4^{2-}$ showed excellent selectivity compared to other anions ($S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-} , NO_3^- , NO_2^- , ClO_2^- , Cl^- , Br^-), which lead to prominent color change. This provided a simple and effective colorimetric sensor (no enzyme or DNA) for on-site and real-time detection of $S_2O_4^{2-}$.

KEYWORDS: Gold nanoparticles (GNPs), $S_2O_4^{2-}$ (Dithionite), spectrophotometric detection

INTRODUCTION

Gold nanoparticles (GNPs) are widely used in a range of applications, including electronics, bio sensing, and surface enhanced Raman spectroscopy. GNPs have also received great attention in the development of visual sensing schemes owing to the surface Plasmon resonance (SPR) mechanism based on the binding-induced aggregation of spherical GNPs (Mostafa El-Sayed *et al.*, 2001), (Elisa Hutter *et al.*, 2003). The SPR of the GNPs are extremely sensitive to their nature, size, shape, their inter particle distances, and the nature of their surrounding media (Tokareva Minko *et al.*, 2004). Recently, GNPs have been extensively employed as analytical probes in biotechnological and chemical system. In particular, Mirkin and co-workers demonstrated that the distance-dependent SPR property of GNPs aggregation induced by DNA hybridization was exploited for developing a colorimetric sensor for DNA, Hg^{2+} detection (Liu Huang *et al.*, 2008), (Mirkin Letsinger *et al.*, 1996, Lee Han *et al.*, 2007).

Furthermore, functionalized GNPs become interesting nanomaterials for sensing heavy metal ion (Liu *et al.*, 2009), (Fang Chai *et al.*, 2010). The need for a method to measure and control continuously the concentrations of sodium dithionite has increased over the last 5 years because sodium dithionite is widely used in industry. Sodium dithionite is widely used as a reducing agent in applications such as bleaching of paper pulp (HU Suss *et al.*, 1980), and dyeing of textiles (Baumgarte *et al.*, 1969), (Baumgarte *et al.*, 1987), (Baumgarte *et al.*, 1975), (Hoechst *et al.*, 1993), (Baumgarte *et al.*, 1993), (Feess, 1964). Sodium dithionite is widely used in dyeing processes (Schmidt *et al.*, 1973), (Merck, 1989), (Hubert *et al.*, 2004). as a reducing agent for dyestuffs that are not water soluble in the oxidized form. Other applications can be found in the dyeing of cellulose (Williams *et al.*, 1979), as a reducing agent in biochemical processes (Scaife *et al.*, 1980). and as a bleaching agent (Prior G *et al.*, 1996). Control and reduction of the consumption of sodium dithionite and textile dyes is important for ecological and economical reason. Therefore the search for new methods to determine the concentration of dithionite solution is increasing.

Several methods were described in literature to determine the concentration of sodium dithionite. (Brown *et al.*, 1979), (Kilroy *et al.*, 1979), (Kilroy *et al.*, 1983), (Serjeant, *et al.*, 1984), (Bard *et al.*, 1985).

Other electrochemical methods were used for the detection of dithionite. (Govaert *et al.*, 1998), (Govaert *et al.*, 1999), (Gasana *et al.*, 1999), (Gasana *et al.*, 2000), (Westbroek *et al.*, 1999), (Westbroek *et al.*, 2001), (Camacho *et al.*, 1997), (Shaikh *et al.*, 1993), (Kilroy *et al.*, 1983), (Gasana *et al.*, 2003), (Bockris *et al.*, 1970), (Weissberger *et al.*, 1971), (Horwood *et al.*, 1985). In this study, we present a simple, sensitive, and selective colorimetric probe for the detection of $S_2O_4^{2-}$ based on CTAB-GNPs.

MATERIALS AND METHODS

All chemicals used were of analytical grade or of the highest purity available. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$) were obtained from sigma Aldrich (USA) and used as received. CTAB, NaOH, NaF, NaCl, NaBr, $Na_2 S_2O_3$, $Na_2 SO_4$, $Na_2 SO_3$, $NaNO_3$, $NaNO_2$, $Na_2 C_2O_2H_3$ were purchased from Merc. All glassware was thoroughly cleaned with freshly

prepared aqua regia (3:1v/v) HCl/HNO₃ and rinsed thoroughly with Mill-Q (18MΩ.cm⁻¹ resistance) water prior to use. Mill-Q water was used to prepare all the solution in this study.

The morphology and size of the CTAB-GNPs were characterized by transmission electron microscopy (TEM) using Zice-80Kev transmission electron microscope operated at an accelerating voltage of 80kv. Absorption spectra were recorded on a UV-Vis spectroscopy performed with a Shimadzu spectrophotometer (2550- Shimadzu, Japan) at room temperature.

A. Preparation of GNPs coated with CTAB

Gold nanoparticles (with diameter of 25 nm) were prepared with new method. In a typical preparation, 1.5ml of 1mM aqueous HAuCl₄, 8-10ml of 2 mM aqueous CTAB, 5-10ml of 0.5M aqueous NaOH, were added to a quartz cuvette. The solution was mixed gently for 10 sec and the Ultra sounded for about 45 minutes at room temperature. The color of the resulting solution was purple. Absorbance spectra of the Au nanoparticles dispersions were obtained using a Shimadzu-2550 UV-Vis spectrophotometer. TEM images show average particle diameter of CTAB-capped GNPs in water is 1-10nm.

B. Colorimetric detection of S₂O₄²⁻

Na₂S₂O₄ stock solution was used for the S₂O₄²⁻ sensitivity studies. Various concentration of S₂O₄²⁻ were prepared using serial dilution of the stock solution to test the sensitivity limits of the CTAB-GNPs. Using the stock solution 0.01mM of S₂O₄²⁻ were prepared. The colorimetric detection of aqueous S₂O₄²⁻ was performed at room temperature. Briefly 0.01mM of S₂O₄²⁻ solution with different volumes was added to 2.5mL of CTAB-GNPs solution.

The purple CTAB-GNPs turned gray as they met S₂O₄²⁻ at high ionic strength, indicating formation of aggregation. The addition of enough salt could screen the repulsion between the positively charged GNPs, leading to the aggregation of the GNPs followed by a corresponding color change. So we tested the addition of 20μL 0.1M NaOH in to CTAB-GNPs. Resulting in a color change quickly in the experiments of selectivity and practical assay, all samples were tested in a similar way. We investigated the selectivity of our new approach for S₂O₄²⁻ over other anions (S₂O₃²⁻, SO₄²⁻, SO₃²⁻, NO₃⁻, NO₂⁻, CO₃²⁻, H₂PO₄⁻, F⁻, Cl⁻, Br⁻) under the same conditions.

RESULT AND DISCUSSION

A. Mechanistic Basis for the Sensing System.

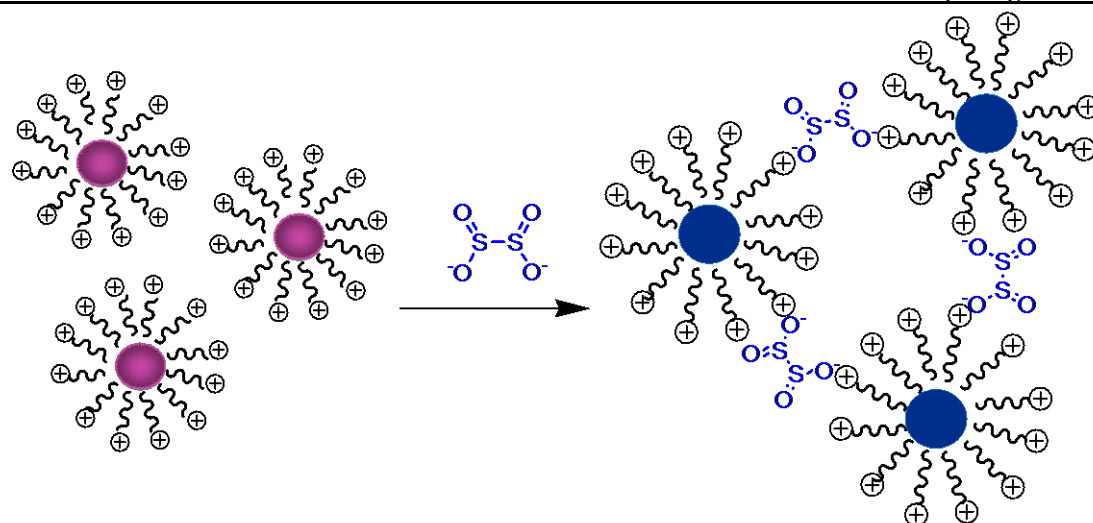
GNPs were used as probes for detecting S₂O₄²⁻. The as-prepared CTAB-GNPs are stable because the CTAB protects the GNPs from aggregation in the presence of a given high concentration of salt. CTAB has -N(CH₃)₃⁺ group to provide a hydrophilic interface and a handle for further reactivity with S₂O₄²⁻. CTAB can capture S₂O₄²⁻ in aqueous solution resulting in the aggregation of GNPs. As shown in schem1.

B. Colorimetric Detection of S₂O₄²⁻

CTAB-GNPs were characterized by UV-Vis spectroscopy and TEM. As shown in Figure 1A, a characteristic SPR band of CTAB-GNPs was observed in the spectrum at approximate 530nm and the color of the solution remain purple (Figure1A, image a) in the absence of S₂O₄²⁻. The corresponding TEM images was shown in Figure 1B, and the as prepared CTAB-GNPs were dispersed with about 20-25nm in diameter. Upon addition of 0.02mM S₂O₄²⁻ to CTAB-GNPs, the solution turned gray owing to the S₂O₄²⁻ stimulated aggregation, with broadening and shifting of the SPR peak.

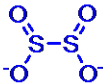


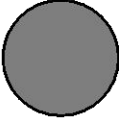
To evaluate the detectable minimum concentration of S₂O₄²⁻ in aqueous solution by color change, we added the S₂O₄²⁻ with concentration of 5-50μM in to CTAB-GNPs solution. When the concentration of S₂O₄²⁻ increased from 0.1 to 20μM, a red shift in wavelength and broadening of the SPR occurred.

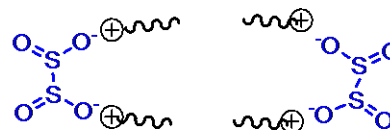
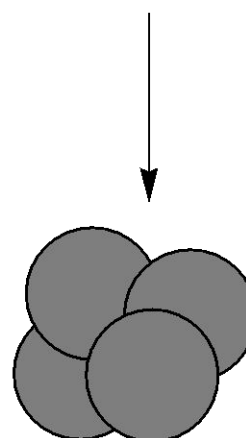
The color changed from purple to gray accompanied with a bathochromic shift, indicating a clear detection result as shown in Figure1A. The changes of SPR band is attributed to the coupled Plasmon absorbance of nanoparticles in close contact. The SPR of the CTAB-GNPs solution at 730 and 530nm are related to the quantities of dispersed and aggregated CTAB-GNPs, respectively.



CTAB capped GNPs

**CTAB capped GNPs
in present of Dithionite**

	Dithionite
	CTAB
	GNP
	Aggregated GNPs



GNPs aggregation

Schem1.Strategy for the Colorimetric Detection of $S_2O_4^{2-}$ Using CTAB-GNPs

Aggregation of CTAB-GNPs in the presence of $S_2O_4^{2-}$ is due to the binding with chelating ligand, yielding both a substantial shift in the Plasmon band energy to longer wavelength and a pink to gray color change.

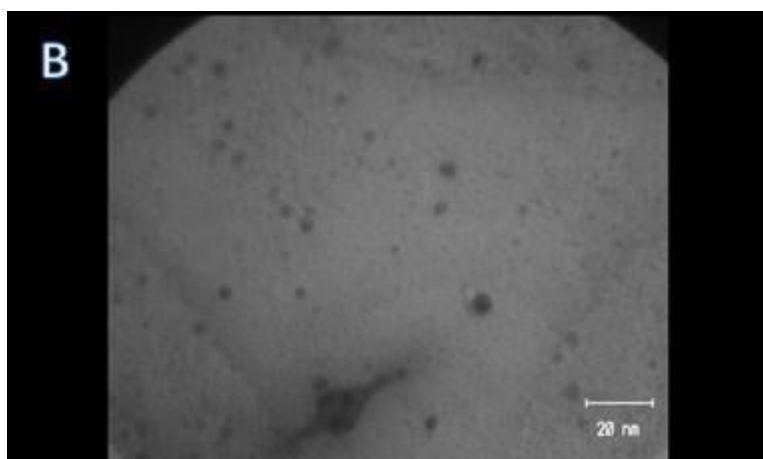
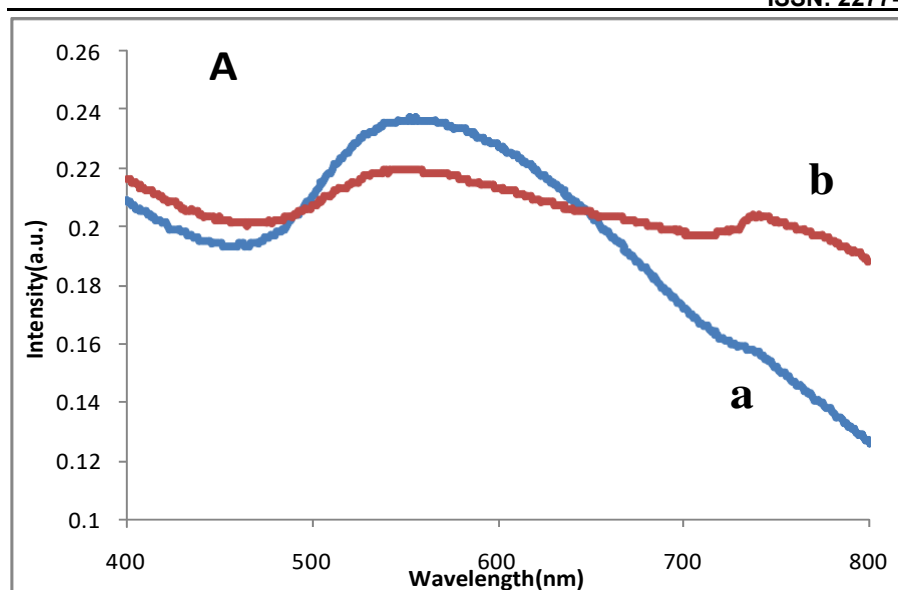


Figure1. (A) UV-Vis spectra of the CTAB-GNPs in the (a) Absent and (b) Presence of 70 μ M S₂O₄²⁻ solution; (B) TEM images of CTAB-GNPs.

A linear relationship between A₇₃₆ and the S₂O₄²⁻ concentration was observed from 0.02-0.12Mm (R²=0.991) as showed in Figure 2. Analytical information of Dithionite determination was presented on table1.

Therefore we suggest that this probe can be used for detecting S₂O₄²⁻ with minimum concentration of 20 μ M. The aggregation of CTAB-GNPs induced by a high concentration of S₂O₄²⁻ resulted a decrease in the intensity of absorption due to the precipitation in solution. This result represents the fast performance of this probe for S₂O₄²⁻.

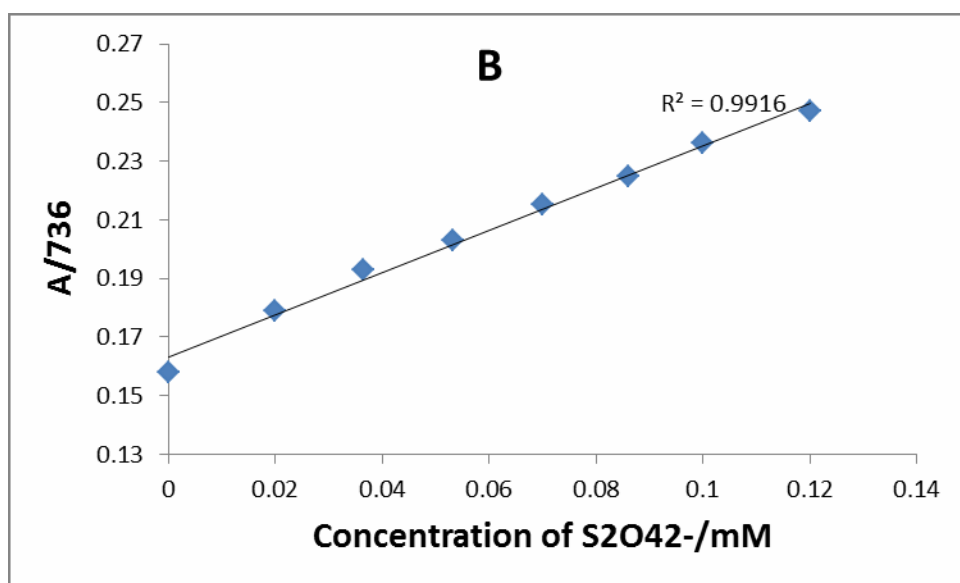
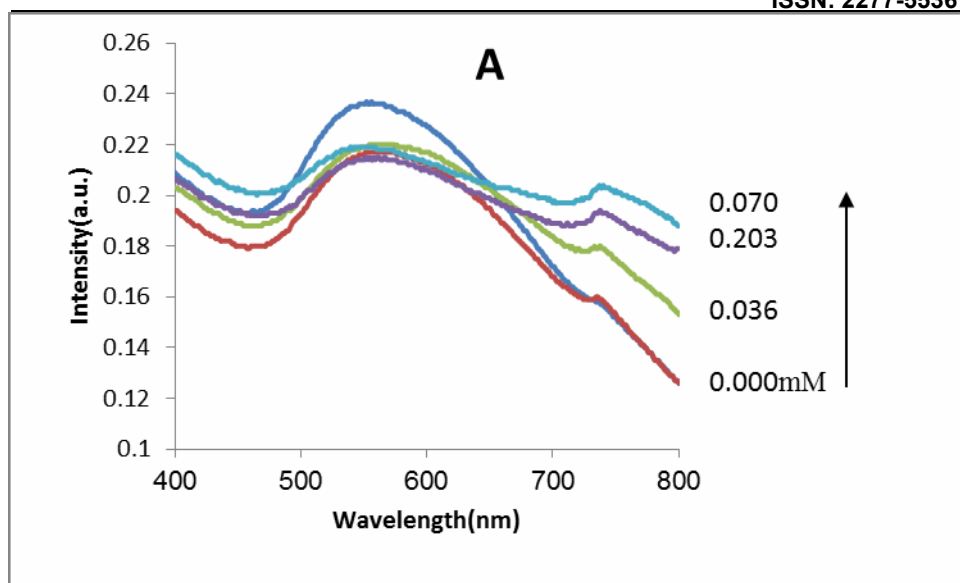


Figure2. A) UV-Vis adsorption spectra of CTAB-GNPs after the addition of different concentration of $S_2O_4^{2-}$ (0.02, 0.0366, 0.0533, 0.07 mM). B) show a plot of A_{736} versus the concentrations of $S_2O_4^{2-}$ in the range of 0.02-0.12mM.

Table 1: Analytical information of Dithionite determination

wave Length (nm)	Calibration equation	LDR(μ M)	LOD(μ M)	R^2
736	$y = 0.724 + 0.163x$	6.54-70	2.18	0.992

LDR: Linear Dynamic Range

LOD: Limit of Detection

C. Selectivity Test

Several commonly existing inions were tested including $S_2O_3^{2-}$, SO_4^{2-} , SO_3^{2-} , NO_3^- , NO_2^- , $C_2O_4^{2-}$, Cl^- , Br^- and $S_2O_8^{2-}$ ions. The SPR band and the corresponding photo images of CTAB-GNPs containing $90\mu M$ other anions and $70\mu M$ $S_2O_4^{2-}$ were shown in Figure 3. The results demonstrate $90\mu M$ $S_2O_3^{2-}$, SO_4^{2-} , SO_3^{2-} , NO_3^- , NO_2^- , $C_2O_4^{2-}$, F^- , Cl^- , Br^- have no obvious effect on the SPR band and color of CTAB-GNPs as compared to $70\mu M$ $S_2O_4^{2-}$, which made the color of solution change from purple to gray under otherwise the same condition, indicating that the assay approach has very high specificity toward $S_2O_4^{2-}$.

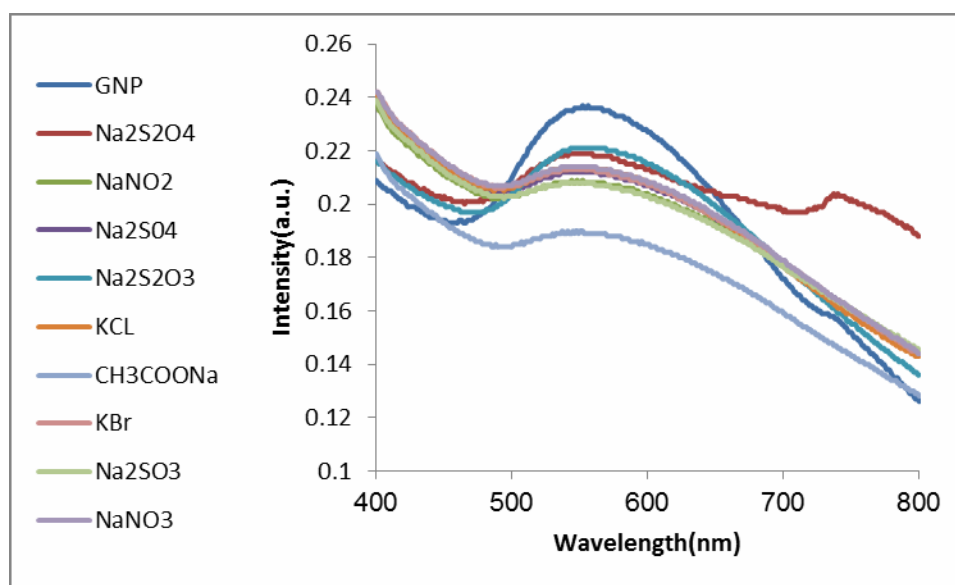


Figure 3. (A) UV-Vis absorption spectra of CTAB-GNPs containing 0.09mM other anions compared with 0.07mM $S_2O_3^{2-}$ (anions were incubated with CTAB-GNPs for 5 min).

D. Determination of Dithionite in real samples

Determination of Dithionite in real samples such as natural water was carried out, and analytical information of that presented in table 2. As shown in table 2, determination of dithionite in natural water is in agreement with deionized water.

Table 2: Analytical information of Dithionite Determination in natural water.

Sample contain Dithionite	Added (mM)	Found (mM)	Recovery %	RSD %
natural water	0	0	---	---
natural water	0.02	0.0198	99	---
natural water	0.04	0.0389	97.25	---
natural water	0.1	0.0988	98.8	---
				1.06

CONCLUSION

In summary, a simple, cost-effective, portable detection method using CTAB-GNPs based colorimetric probe that allows rapid, on-site, real time detection of $S_2O_3^{2-}$ has been developed. The experimental results show that $S_2O_3^{2-}$ can be detected quickly and accurately with high sensitivity and selectivity against other anions. We believed this method may offer a new approach for the detection of $S_2O_3^{2-}$ in aqueous biological and environment samples.

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