Sensors and Actuators B 182 (2013) 706–710

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A simple and fast colorimetric method for detection of hydrazine in water samples based on formation of gold nanoparticles as a colorimetric probe

Behrooz Zargar, Amir Hatamie*

Department of Chemistry, Faculty of Sciences, Shahid Chamran University, Ahvaz, Iran

ARTICLE INFO

Article history:
Received 1 October 2012
Received in revised form 16 February 2013
Accepted 13 March 2013
Available online 26 March 2013

Keywords:
Surface plasmon resonance
Hydrazine
Gold nanoparticles
Probe
Spectrophotometric determination

ABSTRACT

It is critical to be able to detect and quantify hydrazine under aqueous conditions with high sensitivity and selectivity. A colorimetric sensor for hydrazine with high selectivity and sensitivity by gold nanoparticles (AuNPs) within about 4–5 min at room temperature is presented. In this paper, the reduction of $AuCl_4^-$ to gold nanoparticles by hydrazine compound produced very intense surface plasmon resonance peak of AuNPs. The formation of gold nanoparticles as a result of the redox reaction in water samples was identified by measuring the localized surface plasmon resonance (LSPR) absorption. With increasing hydrazine concentration, the LSPR intensity displays linear response with the hydrazine content over the range from 6.0 to 40.0×10^{-6} M, with a detection limit of 1.1×10^{-6} M. The relative standard deviation (R.S.D.) for determination of 10×10^{-6} M and 28×10^{-6} M of hydrazine was 3.2% and 0.68% ($n = 6$), respectively. The proposed method is convenient, low-cost and free of complex equipment, making it possible to successfully analyze hydrazine in industrial water samples (boiler and cooling water) and river water.

1. Introduction

Hydrazine (N_2H_4) is a toxic material and it is widely used in industrial applications. Its primary uses are as high-energy rocket propellant, reactant in military fuel cells, in nickel plating, for removal of halogens from wastewater, oxygen scavenger in boiler feed water to inhibit corrosion, in organic reactions as a reducing agent and in photographic development. However, hydrazine is a toxic and harmful material and Environmental Protection Agency (EPA) has reported hydrazine and its derivatives as environmental pollutants and classified hydrazine as a group B2 (human carcinogen) although it is used more and more [1,2]. It has been known to be harmful for human life, acute exposure can also damage the liver, kidneys, and central nervous system in human, which must be treated with care. Due to the reasons above, fabricate a reliable and sensitive analytical tool for the effective detection of hydrazine is still a challenging research in analytical chemistry. So, development of sensitive and selective analytical methods for the determination of trace levels of hydrazine especially in environmental samples and industry is necessary [3]. Several methods have been proposed for the determination of hydrazine and all of them depend on its basic character or reducing property. Several methods have been proposed for the determination of hydrazine including titrimetric [4] spectrophotometric [5–8], chromatographic [9] and electrochemical methods [10–12]. Although each method has its own advantages, some defects are still existed. Operation of some techniques such as HPLC is complex and required expensive apparatus and complicated procedures for pretreatment of samples. Titrimetry is only suitable for macro analysis. Electrochemical techniques have been more popular because of reducing ability of the hydrazine but spectroscopic analyses in comparison with electrochemical techniques are simpler and faster. Also, colorimetric methods are still important methods, generally inexpensive, safe, with simplicity of analysis which does not require highly skilled staff and needs simple pretreatment and apparatus.

In this paper, we introduce a simple and fast colorimetric method for detection of hydrazine in water samples based on reducing property of hydrazine. This compound can reduce gold ions to gold nanoparitcles in a few seconds. In this condition, a change in color of solution which is a result of AuNPs formation by hydrazine can monitored spectrophotometrically. Change in color of solution can be easily observed with the naked eye in the presence of sub ppm level of hydrazine in water samples and is directly related to the hydrazine concentration such as a sensor.

Nanoparticles, which have unique physical and chemical properties, are promising materials in our overall strategies to detect and remediate environmental pollutants [13–15]. Among these, gold nanoparticles (AuNPs) are the most extensively investigated due to their unique optical property which is known as localized surface plasmon resonance (LSPR) and has obtained extensive applications in the fabrication of optical sensors [16]. The field of research that built on light metal interaction is known as

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* Corresponding author. Tel.: +98 916 604 8367; fax: +98 611 333104223.
E-mail address: amirhatchem@yahoo.com (A. Hatamie).

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http://dx.doi.org/10.1016/j.snb.2013.03.036

plasmonics. The solution of AuNPs shows distinctive color (red or blue) arising from their small sizes and exhibits a strong UV–vis extinction band. Surface plasmon resonance (SPR) band of AuNPs are typically located in the visible region and is strongly depended on the nanoparticle size, shape, composition, crystallinity, and interparticle spacing [17]. Relying on the color change and UV–vis spectrum response, colorimetric sensors have been established. AuNPs based sensing methods have attracted more and more attention due to their intrinsically high sensitivity and easy colorimetric read-out. AuNPs based colorimetric probes have been established to analyze thiamazole [18], sugar [19], glucose [20], resorcinol [21], As^{3+} [22], Hg^{2+} [23], Ca^{2+} and Mg^{2+} ions [24] and dopamine [25].

In this paper, the use of LSPR band of AuNPs for the rapid, simple, and selective determination of hydrazine reported. The changes of SPR band which were a result of gold ions reduction in solution by hydrazine as reducing agent were monitored spectrophotometrically at a maximum wavelength of AuNPs (580 nm) vs. time.

2. Experimental

2.1. Apparatus

UV–vis absorbance spectra were recorded by a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia) and 1.0 cm plastic cells were used. Measurements of pH were made with a Denver Instrument Model 270 pH meter equipped with a Metrohm glass electrode. Image of nanoparticles was obtained by a transmission electron microscope (TEM) (Zeiss EM 10C (Carl Zeiss Inc., Oberkochen, Germany) 80 kV).

2.2. Reagents

All chemicals were of analytical reagent grade purity. Hydrazine hydrate (80%), sodium dodecyl sulfate (SDS), NaOH and gold standard (H $(AuCl_4)$, $3H_2O$) in 12.7% HCl; were purchased from Merck (Darmstadt, Germany). Phosphoric acid (84–85%) was purchased from Fluka (Fluka, Buchs, Switzerland). All of the solutions were prepared with doubly distilled water. Stock solutions of gold $(AuCl_4^-)$ were prepared after adjusting pH of the gold standard solution to 7 with NaOH and diluting to the required volume. Also, a solution of 0.2% SDS (w/v) (0.2 g SDS in 100 mL) was prepared and used as stabilizer. Phosphate buffer was prepared by dissolving appropriate amounts of phosphoric acid, and NaOH solution in water to adjust the desired pH value. Also, Britton–Robinson (B–R) buffer was prepared by dissolving appropriate amounts of boric acid, phosphoric acid and acetic acid in water and adjusting the desired pH value with NaOH (pH 4–10). All experiments were performed at ambient temperature ($25 \pm 3\,^{\circ}C$).

2.3. General procedure

In to a 10 mL volumetric flask different concentrations of hydrazine, 1 mL of 0.1 M phosphate buffer (pH 7), 0.5 mL of 0.2% SDS solution, and 2 mL of 100 $\mu g\,mL^{-1}$ gold $(AuCl_4^-)$ solution were added. The mixture was diluted to the mark with distilled water. Afterward, within 4–5 min a portion of mixture was transferred into a spectrophotometric cell to record the absorbance. The absorbances were measured at 580 nm (λ_{max} of AuNPs surface plasmon resonance peak) against a blank solution. It should be noted that the order of addition of reagents is very critical. Fig. 1 shows the schematic mechanism for the formation of AuNPs in the presence of hydrazine.

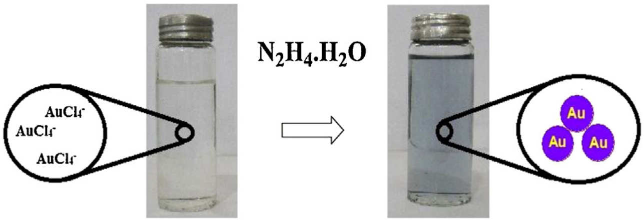

Fig. 1. Schematic mechanism of colorimetric detection of hydrazine hydrated.

3. Results and discussion

It is well known that hydrazine is thermodynamically capable of reducing $AuCl_4^-$ to bulk metal. The principle of colorimetric detection of hydrazine is based on the formation of AuNPs in the presence of hydrazine. The rate of changes in color is increased with concentration of hydrazine. UV–vis spectrums resulted from changes in intensity of mixture color in the presence of various concentrations of hydrazine are shown in Fig. 2. Based on this phenomenon, a colorimetric method for determination of hydrazine in water samples is developed, which is simple, rapid, quantitative, and inexpensive. In order to establish optimal conditions for the direct colorimetric detection of hydrazine, several parameters including time, pH, and concentration of buffer and the concentration of $HAuCl_4$ were systematically investigated and optimized.

3.1. Effect of reaction time

Fig. 3 shows the changes of the absorbance at 580 nm vs. time. The rate of particle growth is highly dependent on and is proportional to the initial concentration of hydrazine. During the first few seconds from addition of gold $(AuCl_4^-)$ solution, color of the solution changes to blue due to AuNPs formation and the absorbance changes slowly to reaches a maximum after about 3–4 min and remains nearly constant afterwards. Therefore, all absorbance measurements were performed within 3–4 min from addition of gold $(AuCl_4^-)$ solution.

3.2. Effect of pH of solution

It is well known that hydrazine has reducing ability and the reaction between hydrazine and gold ion $(AuCl_4^-)$ is a redox reaction. So, hydrazine can reduce $AuCl_4^-$ ion at room temperature in solution. Since H^+ was produced from the reaction between hydrazine and $AuCl_4^-$ ions, consumption of H^+ can accelerate gold ion reduction and low pH media is not suitable for the reaction. Also, a pH

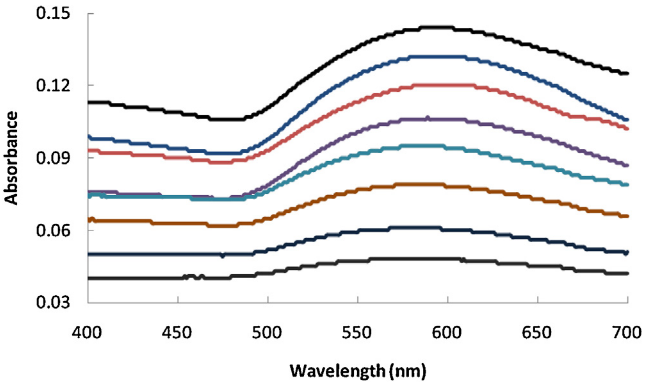

Fig. 2. UV–vis absorption spectrum of AuNPs at different concentrations of hydrazine. From bottom to top hydrazine concentrations are 6, 10, 14, 20, 24, 28, and 32 ($\times 10^{-6}$) M, respectively.