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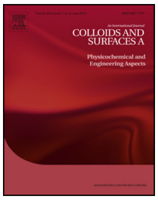


Surfactant stabilized AgNPs as a colorimetric probe for simple and selective detection of hypochlorite anion (ClO^-) in aqueous solution: Environmental sample analysis

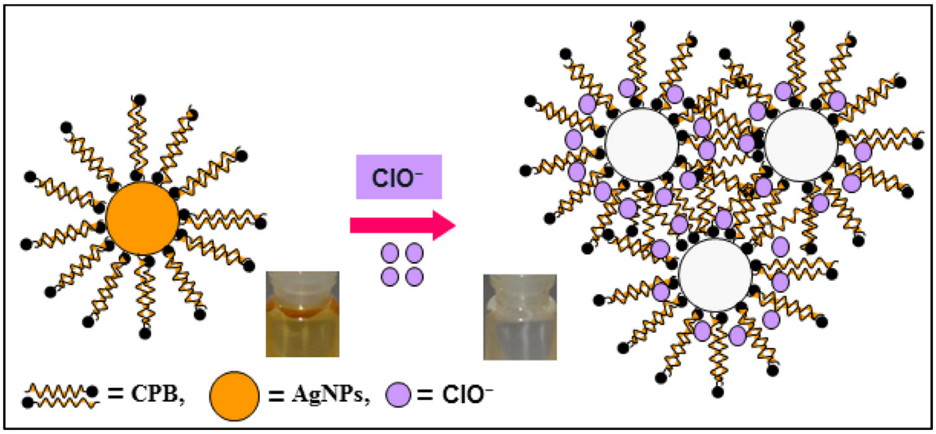
Laxman S. Walekar, Samadhan P. Pawar, Anil H. Gore, Vishwas D. Suryawanshi, Santosh S. Undare, Prashant V. Anbhule, Shivajirao R. Patil, Govind B. Kolekar*

Fluorescence Spectroscopy Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416 004, Maharashtra, India

HIGHLIGHTS

- Simple colorimetric probe for the detection of ClO^- in aqueous media.
- Quenching in the absorbance of CPB-AgNPs with ClO^- due to the inducing aggregation, resulting in the color change from yellowish brown to colorless.
- Straightforward method with LOD (0.4538 μg mL^{-1}).
- The probe successfully applied to determine ClO^- from environmental water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, the development of a colorimetric probe for selective detection of hypochlorite ion (ClO^-) using cetylpyridinium bromide (CPB) capped silver nanoparticles (CPB-AgNPs) in aqueous solution is reported. The absorbance of the CPB-AgNPs was significantly decreased in presence of ClO^- resulting in the color change from yellowish brown to colorless due to inducing aggregation of CPB-AgNPs with ClO^-. The interaction between ClO^- and CPB-AgNPs is studied by some analytical techniques such as UV–vis absorption spectroscopy, Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS) and zeta potential measurements. Under the optimum condition, the calibration plot of (A_0–A) against concentration of ClO^- was linear in the range of 0.5–4.5 μg mL^{-1} with a correlation coefficient of 0.9927. The concentration of ClO^- is quantitatively determined from an UV–vis spectrophotometer with a Limit of Detection (LOD) is 0.45 μg mL^{-1}. This method shows excellent selectivity towards ClO^- checked over other interfering anions. The accuracy and reliability of the methods were further ascertained for the detection of ClO^- from environmental samples via standard-addition method, with percentage recoveries in the range of 98.80–102.94%. The plausible reason for color change is also discussed. The proposed method is simple, rapid, specific and highly selective with good precision.

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* Corresponding author. Fax: +91 231 2692333.
E-mail address: gbkolekar@yahoo.co.in (G.B. Kolekar).

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1. Introduction

Hypochlorite anion abbreviated as (ClO^-) shows strong oxidative property ClO^- is one of the most important Reactive Oxygen Species (ROS). Reactive Oxygen Species play great roles in physiological process [1] as is present around us from body function to water supply. ROS are also present in biological fluids and tissues, both in normal conditions and, particularly, in oxidative stress scenerios, where their rate of production is increased and/or removal rate decreases, leading to an increase in their steady state concentrations. Most of the biomolecules such as Lipids, proteins, DNA [2,3] are the favorite targets of ROS and Reactive Nitrogen Species (RNS) which suffer from oxidative transformations that can modify their structure and capacity of function. ROS can alter the primary structure of proteins both by direct interaction with the oxidant and secondary processes mediated by the initially formed chloramines, lead to fragmentation or oligomerization, and change their capacity of function. In our body, the ClO^- exhibits unique antibacterial properties in the immune system as is produced by hydrogen peroxide and chloride ions in activated neutrophils to defend pathogens invasion. Nowadays, in our daily life ClO^- and hypochlorous acid are extensively used as a disinfectant, as a household bleaching agent, disinfection of drinking water, cooling-water treatment, and cyanide treatment with the concentration in the range of 10^{-5} to 10^{-2} M [4,5]. However, it is proved that, the over-production and excessive intake of ClO^- can be dangerous to human. On the one hand, over-production of ClO^- in organism can cause many diseases like carcinogenesis, inflammation, and cancer [6–9]. On the other hand, disinfected water with residual chlorine may stimulate eye or nose irritation and stomach discomfort, and lead to the production of much toxic organic disinfection byproducts (DBPS) such as trihalomethanes and haloacetic acids [10,11].

The heme enzyme such as myeloperoxidase (MPO) is used to catalyze the reaction of H_2O_2 with Cl^- ions for the production of HOCl which plays a vital role in the ability of the cells to kill a wide range of Pathogens [12]. But excessive production of ClO^- causes variation in the levels of myeloperoxidase enzyme which leads to the various diseases such as including cardiovascular diseases [13], neuron degeneration [14], and arthritis [15]. Therefore, it is very important to develop a sensitive and selective probe for the effective detection of ClO^-. Towards this point, a number of methods, such as colorimetric, luminescent, electrochemical and chromatographic methods [16–28], have been reported. Chemosensors based methods are also proposed for the detection of ClO^- due to the strong oxidation properties of ClO^-. For example, oxidation reactions of *p*-methoxyphenol to benzoquinone, dibenzoylhydrazine to dibenzoyl diimide, thiol tosulfonate derivative, and *p*-alkoxyaniline have been employed as the key reacting components in the design of hypochlorite selective probes [29]. However, most of the chemosensors possesses relatively complicated structures and were not conveniently synthesized. In addition with this, the organic fluorescent probes or chemosensors suffers from intrinsic drawbacks such as narrow excitation spectra, broad emission band and low photo bleaching resistance [30,31]. The excessive production of ClO^- causes adverse effects on human health, so it is very necessary to develop a simple, selective, rapid and cost effective alternative approach to assay it effectively in aqueous media.

Nowadays, both silver and gold nanoparticles have been used for various purposes in the field of nanotechnology. Silver nanoparticles trapped within the gold copolymer nanocomposite have been synthesized by Li et al. and further extended for catalytic activity due to the thermosensitive collapse of the polymer layers [32]. Nanomaterials based colorimetric assays have attracted much attention due to their simplicity, rapidity, high selectivity, can change colors in different conditions and ease of measurement [33,34]. Compared to other assays, colorimetric sensors allow direct and on-site analysis of the samples with the naked eye clarification. Among metal nanoparticles (MNPs), particularly silver nanoparticles (AgNPs) show more advantages as they have more extinction coefficient and lower prices, allowing detection with minimal consumption of material [35]. Shen et al. used the concept of anti-leaching of gold nanoparticles for the assay of iodide ions [36]. Li et al. studied the response of pH on the aggragation of polymer grafted gold nanoparticles [37]. Jin et al. designs the two novel fluorescein-based fluorescent chemosensor probes for ClO^- and its real applications in tap water and biological imaging [38]. Chen et al. have developed simple and rapid colorimetric iodide (I^-) sensor based on the anti-aggregation of gold nanoparticles (AuNPs) [39]. In our proposed approach, we have developed new colorimetric method for direct detection of ClO^- in aqueous solution using CPB capped AgNPs as a nanosensor. Absorbance of CPB-AgNPs is extremely quenched by ClO^- with slight red shift in the λ_{max} without interferences from common ions with color change from yellowish brown to colorless which is easily recognized by naked eye. Furthermore, this proposed method was successfully applied for the determination of ClO^- from environmental samples i.e., water samples collected from different sources in the campus in a complex matrix without pretreatment by standard addition method. This probe offers the advantages of simplicity, rapidity, selectivity, sensitivity and good stability, which makes it a valuable pathway for analytical purposes. The easy synthesis and high stability of the CPB capped AgNPs allow the method to be very simple and easy to implement.

2. Experimental

2.1. Equipment

All the spectroscopic measurements and analysis were carried out using the stable dispersion of the colloidal solution. The absorption spectrum of synthesized CPB-AgNPs was recorded at room temperature on an instrument SPECORD 210 PLUS Analytikjena UV–VIS–NIR spectrophotometer with the use of a 1.0 cm quartz cell. The particle size distribution was measured by dynamic light scattering with zeta sizer Nano ZS (Malvern Instruments Ltd., UK). Transmission electron microscopy (TEM) images were recorded on a Tecnai^{TM} transmission electron microscope (TEM, FEI Tecnai 300). The photographs of samples were taken on Canon digital camera.

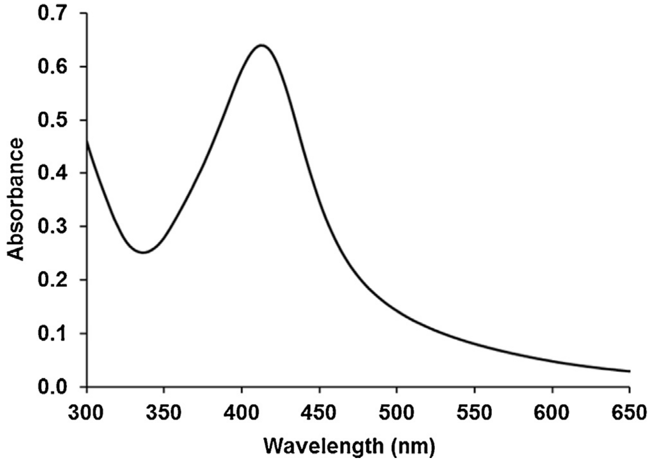

Fig. 1. UV–vis absorption spectrum at $\lambda_{max} = 412$ nm of the CPB-AgNPs (1×10^{-4} mol L^{-1}) ($\varepsilon = 6500$ M^{-1} cm^{-1}) in aqueous colloidal solution.