



# One-pot synthesis of silver nanoparticles using folic acid as a reagent for colorimetric and fluorimetric detections of 6-mercaptopurine at nanomolar concentration



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## ABSTRACT

A simple and versatile strategy was developed for dual detection (colorimetric and fluorimetric) of 6-mercaptopurine (6-MP) using folic acid (FA) fabricated silver nanoparticles (Ag NPs) as a probe. The optical properties (surface plasmon resonance (SPR) band and fluorescence) of FA-Ag NPs were strongly influenced by the addition of 6-MP. The abrupt change in absorbance of FA-Ag NPs was observed with increasing concentration of 6-MP, resulting a slight blue-shift in the SPR band and a color change from yellow to colorless, which confirms the oxidation of Ag<sup>0</sup> NPs to Ag<sup>+</sup> ion. Advantage is taken of the fact that FA is displaced from the surface of the Ag NPs, which progressively enhanced the fluorescence intensity of FA with increasing concentration of 6-MP. The perfect linear variations of absorbance at 399 nm and emission peak at 448 nm with 6-MP concentration was observed in range of 20–1000 and 5–300 nM by UV–vis and fluorescence spectrometric methods, enabling the use of probe as a dual probe for quantification of 6-MP. Moreover, the probe shows excellent anti-disturbance ability when exposed to a series of interfering other organic, inorganic and biomolecules and can be applied to the determination of 6-MP in real samples with the detection limits of 13.2 and 2.3 nM by colorimetric and fluorimetric methods, which suggests that the present method has a great potential of application for assay of 6-MP in pharmaceutical and biological samples.

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## 1. Introduction

With the features of organic framework on metal nanoparticles surfaces, research interest in fabricating metal NPs with various organic ligands and their integrations with various analytical techniques for assaying of wide variety chemical species have been growing unabated [1–5]. Recent years, metal NPs-based dual optical (colorimetric and fluorimetric) sensing assays have sparked significant excitement in analytical sciences due to high surface to volume ratio with the realization of supramolecular assemblies, allowing them to act as versatile and selective portable platforms for the implementation of different sensing schemes for assay of various analytes with more convincing results [6–8]. As a result, silver (Ag) and gold (Au) NPs have been brought to the forefront of UV–vis and fluorescence-based analytical research because of their

tunable optical properties, facile synthesis and surface modification for the development of portable optical analytical tools.

For example, Zhao's functionalized carbon dots on the surfaces of Au NPs for colorimetric and fluorimetric detection of thiocyanate in tap water and saliva samples [9]. Cheng and co-workers modified Au NPs with fluorescein isothiocyanate for assay of cyanide by colorimetric and fluorimetric methods [10]. Zuber's team developed a portable sensing platform for the detection of gold nanoparticles based on the absorption and fluorescence mechanisms [11]. Tao et al. developed fluorescence turn-on and colorimetric dual channel probe for the detection of Hg<sup>2+</sup> ion using poly(acrylic acid)-template Ag nanoclusters as a probe [12]. Mi's group synthesized chitosan capped Ag NPs for fluorescence and colorimetric detections of Hg<sup>2+</sup> ion in water samples [13]. Unmodified Ag NPs were used as sensors for dual functional colorimetric assays of both Hg<sup>2+</sup> ion and H<sub>2</sub>O<sub>2</sub> via Ag NPs catalyzed reaction [14]. Similarly, Su et al. developed FA-Ag NPs-based colorimetric and "turn-on" fluorescent sensor for the detection of Hg<sup>2+</sup> ion in water samples [15]. Cui's group modified Ag NPs with Rhodamine B for the fabrication of dual probe for highly selective and sensitive detection of fenamithion in

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food samples [16]. The colorimetric and phosphorimetric signaling strategies were developed for sensitive assay of organophosphorus pesticides using Mn-ZnS quantum dots-Au NPs through the inner filter effect and the activity of acetylcholinesterase [17]. Zheng and co-workers fabricated Au NPs with triazolylcoumarin for the colorimetric and fluorimetric detections of lysozyme *via* fluorescence resonance energy transfer (FRET) mechanism [18]. Furthermore, fluorescent carbon dots were functionalized on the surfaces of Au NPs for dual readouts of glutathione [19] and bromelain [20] in biological samples. These reports illustrate that the advancements in fabricating of metal NPs with organic network allowed to act them as a dual probe for both colorimetric and fluorimetric assays of target analytes with high selectivity and sensitivity. Furthermore, these organic ligands have only been recognized as the stabilizers in the synthesis of metal NPs where they can be acted as specific analyte recognition *via* large shifts in their optical properties (red/blue shift and fluorescence turn- off/on). Therefore, one-step synthesis of metal NPs with the specific recognition is an attractive but challenging target to pursue.

6-Mercaptopurine is a sulfur analogue of adenine that was used as an anticancer and an immunosuppressive agent [21]. It also acts as an anti-metabolic purine antineoplastic agent for the treatment of acute lymphoid leukemia [22,23]. It was observed that 6-MP and its metabolites inhibit the function of RNaseH in DNA-RNA heteroduplex molecules through incorporation of deoxythioguanosine into DNA [24]. It shows serious side effects due to its cytotoxicity nature towards various cells [25], which confirms that its activity was also different with the change of its concentration in plasma [26]. Therefore, it is important to develop a simple and sensing analytical tool for the accurate identification and quantification of 6-MP in pharmaceutical and biological samples.

In this connection, several analytical methods have been reported for the determination of 6-MP, such as high-performance liquid chromatography (HPLC) [27], multi-walled carbon nanotube (MWCN) and nanocomposite-based voltammetry [28,29], liquid chromatography-mass spectrometry [30,31], capillary electrophoresis [32], Raman spectroscopy [33], UV-vis [34] and fluorescence [35] spectroscopic techniques, respectively. These techniques suffer from poor sensitivity [34], entails time-consuming and tedious sample preparations (drug extraction and purification of analytical samples prior to its identification). In order to minimize sample preparations with improved sensitivity, few methods have been described the integration of nanomaterials with UV-vis and fluorescence spectroscopic techniques for analysis of 6-MP in pharmaceutical and biological samples. For example, Chen's group synthesized bovine serum albumin capped Au NPs for the development of logical switch fluorescent sensor for the detection of 6-MP in human serum samples [36]. Shen et al. analyzed 6-MP in human urine samples by fluorescence spectrometry using Au NPs as a fluorescent probe [37]. Cuin and co-workers synthesized Ag(I) and Au(I) complexes with 6-MP and studied their biological activities [38]. The Ag NPs were decorated with  $\beta$ -cyclodextrin and used as a substrate for the detection of 6-MP by surface-enhanced Raman spectroscopy (SERS) [39]. Recently, Yuan's group synthesized fluorescent carbon dots (CDs) and used as probes for detection of 6-MP human serum samples *via* fluorescence quenching mechanism [40]. Although these methods are shown to be promising tools for 6-MP detection, they usually need either complicated procedures or multiple steps for the modifications of metal NPs with organic molecules as well as they require addition of specific reagents in order to interact with 6-MP. Although few nanomaterials were used for assay of 6-MP, no Ag NPs-based dual (colorimetric and fluorimetric) sensor was reported for the assay of 6-MP. Furthermore, there is still a gap of improvement within these reported works especially in the synthesis of Ag NPs with specific ligand for selective and sensitive analysis of

6-MP by UV-vis and fluorescence spectrometric techniques. Consequently, as mentioned above, it is very challenge to develop Ag NPs-based dual sensor (colorimetric and fluorimetric) sensor for selective and sensitive detection of 6-MP in biological samples.

Herein, we report one-step FA mediated synthesis of Ag NPs for the development of logic switch dual sensor for colorimetric and fluorimetric detection of 6-MP in pharmaceutical and biological samples. The addition of 6-MP into FA-Ag NPs causes oxidation of Ag<sup>0</sup> NPs to Ag<sup>+</sup> ion, resulting a blue-shift in the SPR peak and a color change from yellow to colorless. As expected, the emission peak at 448 nm was progressively increased with increasing concentration of 6-MP, indicating that the displacement of FA from Ag NPs, which facilitate to develop colorimetric and 'turn-on' fluorescence probe for the detection of 6-MP in biological samples with high selectivity and sensitivity. This work opens up new perspective for the development of miniaturized dual (colorimetric and fluorimetric) spectrometric methods for selective and sensitive detection of 6-MP without any complicated procedure or instruments.

## 2. Experimental

### 2.1. Chemicals and reagents

All reagents used were of analytical reagent grade. Tris(hydroxymethyl) aminomethane (Tris buffer), and silver nitrate (AgNO<sub>3</sub>) were purchased from Sigma Aldrich, (St. Louis, MO). Folic acid and 6-mercaptopurine were purchased from SRL Pvt. Ltd., India. Milli-Q-pure water was used throughout the experiments. The 6-MP tablet (50 mg 6-MP, Zydus Cadila Pvt. Ltd., India) was purchased from local medical shop, Surat, Gujarat, India. Urine samples were collected from three healthy volunteers in Applied Chemistry Department, S.V. National Institute of Technology, Surat, Gujarat, India and the serum samples were obtained from Iyer's pathological laboratories, Surat, Gujarat, India. The obtained biofluids were diluted to 50 folds with distilled water before further use.

### 2.2. Synthesis of FA functionalized Ag NPs

The FA-mediated synthesis of Ag NPs was carried out by one-step reaction. Standard solutions of FA and AgNO<sub>3</sub> were prepared using water as solvent. Briefly, 1.0 mL of 2.0 mM FA was added drop wise into 10.0 mL of 1.0 mM AgNO<sub>3</sub> under vigorous stirring and then stirred for 60 min at room temperature. The color of solution was changed from colorless to yellow, confirming the formation of FA-Ag NPs. The absorption spectra, size and morphology of FA-Ag NPs were characterized by UV-vis spectrometry, DLS and TEM, respectively.

### 2.3. Dual detection of 6-MP by FA- Ag NPs

The dual detection of 6-MP was carried out by the following procedure using FA-Ag NPs as a dual probe. In a typical procedure, different concentrations of 1.0 mL 6-MP were added separately into 1.0 mL of FA-Ag NPs solutions that were contained 30  $\mu$ L of Tris-HCl buffer (pH 7.0). The above mixtures were equilibrated for 30 min at room temperature. After that, UV-vis and fluorescence spectrometric techniques were used to measure the absorption and emission spectra of the above solutions at room temperature. The color changes of the above solutions were studied at day light and at dark under UV light illumination at 365 nm.

### 2.4. Instrumentation

UV-vis absorption and emission spectra of the solutions were measured by Maya Pro 2000 spectrophotometer (Ocean Optics,

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