



## Review

# Gold nanoparticles as sensors in the colorimetric and fluorescence detection of chemical warfare agents



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## ABSTRACT

A short overview of colorimetric and fluorescence detection with gold nanoparticle (AuNP) sensors of chemical warfare agents (CWAs) is provided. This review of CWA sensing includes nerve agents, vesicant agents, pulmonary agents, cytotoxic proteins, suffocating/blood agents, incapacitating agents, and lachrymatory. The sensing methods are based on the optical (surface plasmon band) and other physico-chemical properties of appropriately functionalized AuNPs.

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## 1. Introduction

Chemical threat agents such as chemical warfare agents (CWAs) [1], heavy metals ions [2], halide ions [3], explosive compounds [4],

and radioactive compounds [5] have nowadays become a key problem for the protection of our society and environment. Among these risks and dangers, CWAs are probably the major one. The increasingly critical aspect of this area has provoked a growing interest in the scientific literature mainly focusing on chemical and biological sensors [6,7]. The key problem of chemical and biological sensors in this field, however, is the rapid detection of CWAs. This problem plays an important role in homeland security in terms of responding to or recovering from unexpected situations (e.g. terrorist attacks or incidents) [8]. In addition, this field also has great

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importance in tracing pollutants in the environment [9]. Therefore, the development of highly sensitive, cost-effective and small-sized sensors has been recalled in chemistry and biology especially during the last decade [6]. The emergence of nano-sized sensors is currently offering a possible solution, because of their high sensitivity and selectivity [10,11]. Indeed, nanomaterials, particularly AuNPs are considered as the preferred candidates for the production of nano sensors towards detection of chemical threat agents for the following reasons: (i) AuNPs can be prepared according to a straightforward method involving stability and biocompatibility in the presence of appropriate capping ligands; (ii) they possess unique optical and electronic properties that quickly respond to small compounds or metal ions; (iii) AuNPs provide high surface area to volume ratios and serve as an excellent scaffold to immobilize large amounts of recognition elements, thus dramatically increasing the possibility of their interaction with the target analytes [12–15].

Owing to their optical and electronic properties [16], AuNPs offer a multiple platform for the detection of chemical threat agents with a series of methodologies, including spectroscopic (i.e. Surface Enhanced Raman Scattering, SERS) [17], colorimetric [18], fluorimetric [19] and electrochemical methods [20]. However, the detection of chemical threat agents by spectroscopic and electrochemical methods needs specific instruments that are costly and pre-prepared samples that are practicable for these instruments. Thus, the investigation of an alternative safe and simple method is urgently called for [7].

A key property of AuNPs is their plasmon absorption in the visible or near-infrared region. The surface plasmon resonance (SPR) stems from the free electrons at the metal surface collectively resonating with the incident photons. When the AuNPs are irradiated by light at wavelength much larger than the AuNP size, the surface electron cloud is displaced with respect to the AuNP nuclei. This generates a restoring force arising from Coulomb attraction between electrons and nuclei, leading to oscillation of the surface electrons. At a specific frequency the surface electrons are oscillating coherently with the incident light, resulting in localized surface plasmonic resonance (LSPR). With non-spherical AuNPs such as nanowires, however, one dimension of the AuNPs approaches the light wavelength. Then, the electron field is not uniform, and the nanoparticle is subjected to propagating surface plasmons (PSPs).

This plasmonic phenomenon is extremely sensible to substrates that are very close to the AuNP surface [21,22]. Hence, the major application of AuNPs for chemical threat agents is colorimetric and fluorescence sensing, a field that has been well established with high sensitivities and low detection limits [23–25]. The simplicity of the visible-light absorption is a clear advantage over other techniques that require fragile and sophisticated instrumentation and time-consuming manipulations [26].

Therefore, in this review, the design and mechanism of several colorimetric and fluorescence-based AuNP sensors will be highlighted, and the recent advances in the detection of a variety of CWAs based on AuNPs will be discussed.

## 2. Mechanism and properties of AuNPs in colorimetric and fluorescence sensing

### 2.1. Colorimetric based AuNP sensors

Well-dispersed AuNPs with particle size between 3 nm and 10 nm exhibit red-colored solution, due to their strong SPR near 520 nm [27]. However, as shown in Fig. 1, the agglomeration of these AuNPs always more or less induces interparticle surface plasmon coupling. This results in surface plasmon band shifts from the visible region toward the near-infrared region and color changes

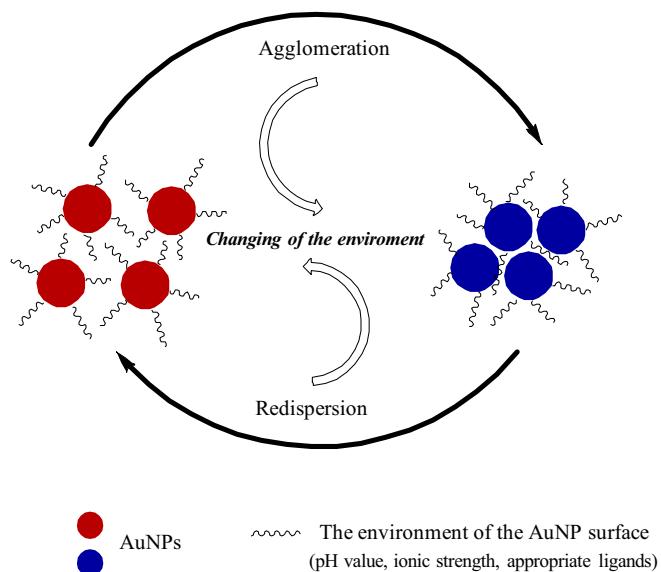


Fig. 1. Possible mechanism for the colorimetric AuNP sensors.

from red to blue. On the opposite, the redispersion of agglomerated AuNPs causes color change from blue to red. In both cases, AuNPs provide the practical platform for absorption-base colorimetric sensors [28–30]. Generally, the agglomeration or redispersion of AuNPs is induced by the change of the environment of the AuNPs surface, including the alteration of the pH value or ionic strength of the solution and the functionalization of the AuNPs with appropriate ligands [31–34].

### 2.2. Fluorescence-based AuNP sensors

The fluorescence-based AuNP detection strategy relies on the fluorescence change when the system meets the target because of the surface modified fluorescence (SMF) or the fluorescence resonance energy transfer (FRET). The SMF is the modification of fluorescence by an electromagnetic environment, whereas the FRET is based on the resonant energy transfer occurring between an excited donor fluorophore and an acceptor fluorophore via induced dipole–dipole interactions.

The strategy of the SMF method uses the modification and control by the surrounding electromagnetic environment of the fluorescence emitted by a fluorophore. This fluorescence is affected by the nearby presence of a metal particle or metal surface [35]. SMF has been applied to measure the fluorescence changes caused by excited fluorophores. For example, if the distance between the fluorophore and the metal surface is less than 10 nm, the latter absorbs the energy and cause a change of the fluorescence signal [36,37].

The most popular and widely used strategy is FRET, however. It is a non-radiative process involving an excited state donor (usually a fluorophore) that transfers energy to a proximal ground state acceptor through long-range dipole–dipole interactions (Fig. 2). The acceptor must absorb energy at the emission wavelength(s) of the donor but does not necessarily have to re-emit itself the absorbed energy fluorescently. The rate of energy transfer is dependent on many factors among which the most important one is the distance between the donor and acceptor. Normally, FRET occurs when the distance is between 1 nm to 10 nm [38,39]. Due to their extraordinary high molar extinction coefficients and broad energy bandwidth, AuNPs serve as excellent fluorescence quenchers for FRET-based assays. Semiconductor quantum dots (QDs) have many advantages such as high efficiency and stability [40]. The inner

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