



In-situ colorimetric recognition of arylamine based on chemodosimeter-functionalized gold nanoparticle

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ABSTRACT

Aniline, a typical example of arylamines, is one of most important raw materials in many industries. However, arylamine-related pollution in waters threatens the public health and environment along with their wide applications. In this work, a simple, fast, and convenient colorimetric sensing system was presented for the arylamine (e.g. aniline) recognition in aqueous media. The system was presented using diazonium salt (DS) decorated gold nanoparticles (AuNPs), based on the classic coupling reaction of arylamine with diazonium salt. DS-AuNPs showed an excellent response and a good sensitivity to aniline, and the limit of detection reached 0.5 μM for aniline in this work. There was a good linear relationship ($R^2 = 0.997$) between the values of $A_{640\text{ nm}}/A_{520\text{ nm}}$ and aniline concentrations over a range of 5–60 μM , which covered the Chinese standard of the maximum permissible pollutant emission concentration for aniline. The introduction of arylamine (e.g. aniline) caused a rapid and obvious red-to-blue color change, so the arylamine-polluted water could be qualitatively recognized by our naked-eyes and quantitatively measured by absorbance changes.

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1. Introduction

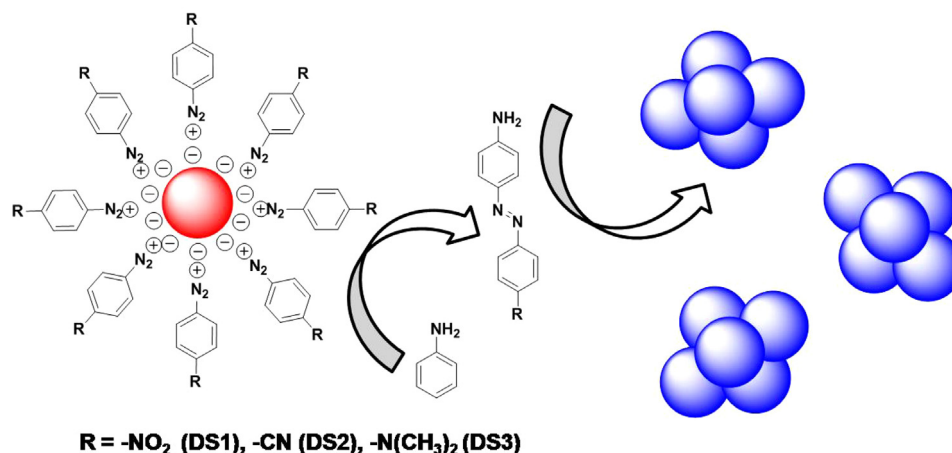
Aromatic amines, aniline and its related derivatives, are most ubiquitous and important building blocks used as raw materials on a large scale for extensive industrial products in the industry of rubber, dyes and pigments, agricultural chemicals, and pharmaceuticals. The aniline, discovered in 1826, is the parent molecule of a vast family of aromatic amines, such as nitroaniline, chlorinated anilines and so on. They are considered as the priority pollutants in environmental risk assessment (e.g. surface water) as the degradation product of certain pesticides, azo-dyes or pharmaceuticals besides the illegal discharge of industrial effluents [1–4]. For example, early effects of aniline can trigger the methemoglobin formation and damage to erythrocytes when absorbed into organisms accidentally [5,6]. Besides damage to erythrocytes, the aniline exposure also causes a damage to the spleen, leading to the congestion, fatty infiltration, capsular hyperplasia, fibrosis, and a variety of sarcomas [7]. In the face of escalating concerns over its environmental exposure and subsequent deleterious effects on human health, therefore, rapid, specific and cost-effective tools have been

developed to provide a rapid and sensitive recognition of aniline and its derivatives.

Numerous methods/techniques, such as the spectrophotometry, surface enhanced Raman scattering (SERS), electrochemistry, high performance liquid chromatography (HPLC), gas chromatograph (GC), capillary electrophoresis, micellar electrokinetic chromatography, and fluorescent probe, can qualitatively and/or quantitatively determinate the aniline and its derivatives in different matrixes [8–22]. However, these instrument-based analytic approaches/techniques are ill-suited for an on-site or *in situ* analyses because of their complicated sample-preparation and professional operation. Considering the cost, response time, as well as the convenient operation, the colorimetric assay is one best choice, though the selectivity and sensitivity are still main puzzling problems for those based on organic chromophores [23]. In recent, gold nanoparticle (AuNP) has become a great colorimetric platform, based on its fascinating surface plasmon resonance (SPR) [24–28]. The SPR of AuNPs, for instance, exhibits a colorimetric behavior (red-purple-blue), which is directly tuned by altering the inter-particle distance and the size, shape, or composition of particles. Therefore, the AuNP system becomes an ideal colorimetric platform suited for naked eye assays, [29–34] because the molar extinction coefficient (ca. $10^8\text{ cm}^{-1}\text{ M}^{-1}$) of AuNPs is much higher than those of common organic dyes (ca. $10^5\text{ cm}^{-1}\text{ M}^{-1}$) in aqueous media. Together with nano-effect, gold nanoparticles can make the

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Scheme 1. Schematic illustration of the DS-AuNPs based colorimetric system for the aniline detection.

colorimetric signal magnified greatly with a much better sensitivity. Besides better solubility in aqueous media, a more sensitive color change of AuNP solution renders itself excellent properties for the colorimetric assay rather than organic chromophore-based colorimetric system. It has been revealed by various excellent examples (e.g. DNA, enzyme activity, proteins, biomolecules, and cations/anions) as well as our previously published works, combined with strategies of the coordination chemistry, host-guest interaction, and chemical reaction [35–40].

For target sensing, the supramolecular interaction and chemodosimeter are two main mechanisms in usual [41–45]. Aniline exhibits little supramolecular activity with other molecules selectively. Therefore, a proper arylamine-participant reaction, i.e. chemodosimeter strategy, is a viable option. For a chemodosimeter-AuNP system, moreover, it needs the product to exhibit a conspicuous differing behavior toward AuNPs from raw materials of the reaction in aqueous media.

Most of arylamine-involved reactions, however, usually occur in organic solvents. Then inspired from a classic approach to manufacture an azo compound in the dyestuff industry [46,47], the azo-coupling reaction becomes a good candidate. The diazonium compound could react with an arylamine or phenol in aqueous media at room temperature [48,49]. Furthermore, we chose this reaction to effectuate our design also because: (1) the reactions of diazonium salt with aniline or phenol are the acid- and base-catalyzed respectively, which could be distinguished by pH values easily; and (2) the diazonium is positively charged and highly soluble in water, so it could be decorated on the surface of AuNP due to the electrostatic effect without mixing organic solvents in the system [50], while the neutral azo product shows a poor solubility in water. Typically, this azo-coupling reaction is accompanied by a faint yellow-to-red color change, but it is invisible by naked eyes unless in a prohibitively high concentration (nearly millimole level) which far exceeds the standard of aniline in waters. In our system, AuNPs amplified the color change at a much lower concentration of the reactant by a two-stage magnification: the nano effect and SPR effect, which makes it a competitive tool compared with other methods/techniques as shown in Table 1 [51,52].

Scheme 1 illustrated the working principle of our system. The AuNPs solution (13 nm) exhibited a red color with a typical SPR band at 520 nm, wherein particles were stabilized by citrate ions through the electrostatic effect. When a positive aromatic diazonium salt was introduced, it could decorate on the surface of AuNPs and keep particles stable owing to the steric repulsion in a media of high salinity. However, in the presence of aniline, for example, the diazonium salts reacted with the aniline. Then the

produced insoluble natural azo dye was released and resulted in particles' aggregation along with a red-to-blue color change. As a proof-of-concept, a series of aromatic diazonium salts **DS1** (4-nitrobenzenediazonium), **DS2** (4-cyanobenzenediazonium), and **DS3** (4-(dimethylamino)benzenediazonium) were synthesized and fabricated on AuNPs for the aniline recognition (Scheme S1).

2. Experimental section

2.1. Chemicals

Gold (III) chloride trihydrate (99.9+%), sodium citrate dehydrate (>99%), and 4-aminobenzonitrile were purchased from Sigma-Aldrich. Tetrafluoroboric acid (50%, w/w) and sodium nitrite was obtained from Aladdin company. The solutions of anions and metal ions were prepared from NaCl, LiBr, KNO₃, Na₂CO₃, Na₂SO₄, NaNO₂, Na₂HPO₄, Na₃PO₄, Zn(NO₃)₂·6H₂O, CaCl₂, Na₂SO₄, KNO₃, and MgCl₂ by separately dissolving each metal ions in distilled water. All other chemicals were supplied by Sigma-Aldrich and were used as received. Solutions of amine acids were prepared from lysine, arginine, histidine, glycine, asparagine, glutamine, serine, and tryptophan by separately dissolving each molecule in DI water.

2.2. Characterization

UV-vis spectra were recorded by using a UV-vis Spectrophotometer (UV-vis 2501 PC) with the baseline correction. Nanoparticles dispersion and aggregation were characterized by a transmission electron microscopy (TEM, JEM2010). The zeta potentials of AuNPs before and after modification were measured with a Zetasizer Nano-ZS90 instrument.

2.3. Synthetic procedure

2.3.1. Synthesis of 13 nm AuNP

AuNPs (13 nm) was prepared by sodium citrate reduction of a HAuCl₄ solution as described in the literature [53].

2.3.2. Synthesis of DS1-3

A cold solution of NaNO₂ (45 mg, 0.65 mmol) in Milli-Q water (0.25 ml) was added slowly to a cold solution (over an ice bath) of *p*-nitroaniline (81 mg, 0.59 mmol) in 1 M HCl (1 ml). The mixture was left to react at 4 °C for 1 h, and then 0.6 ml of a saturated solution of NaBF₄ in Milli-Q water was added. The off-white precipitate was filtered and rinsed twice with cold ether (10 ml). The crude product was purified by the reprecipitation from acetonitrile in the presence

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