

AuAg Nanocage-based Colorimetric Sensor for Silver Detection

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Summary:

Silver ions (Ag^+) are toxic heavy metal pollutants released from industrial wastewater, agricultural runoff, and antimicrobial applications. Existing field-deployable detection tools lack sufficient sensitivity for regulatory thresholds. This work presents a paper-based colorimetric sensor using AuAg nanocages as the sensing material. In the presence of Ag^+ , ascorbic acid catalyzes Ag^0 deposition on the inner walls of the nanocages, causing a blue shift in the localized surface plasmon resonance (LSPR) and a visible color change. Currently optimized on Whatman 3 filter paper at 70% nanocage loading, the sensor now achieves a linear response from 5 to 45 ppm ($R^2 = 0.990$) and a visual detection limit of 1 ppm, without requiring additional reagents, substrates, or instrumentation.

Keywords: AuAg nanocages, colorimetric sensor, silver ion detection, paper-based sensor, LSPR

Background, Motivation and Objective

Silver ions (Ag^+) are toxic heavy metal pollutants released into water systems through industrial wastewater, agricultural runoff, and the widespread use of silver-based antimicrobial agents. Industrial discharge is regulated under frameworks such as the US EPA effluent guidelines and China GB39731-2020 [1,2]. Unlike many contaminants, Ag^+ is particularly concerning because it accumulates in organisms through the food chain [3], making its presence in food and water systems a significant regulatory and public health issue. Drinking water guidelines set a provisional reference value of 100 ppm for Ag^+ [4], while the European Food Safety Authority (EFSA) limits food contact migration to ≤ 50 ppb [5]. Such threshold values demand sensitive and accessible detection tools. Conventional analytical methods such as ICP-MS and atomic absorption spectroscopy offer excellent sensitivity but require expensive instrumentation and centralized laboratory settings making them unsuitable for routine field monitoring [6]. While commercial test strips offer portability, they typically cannot detect Ag^+ below 10 ppm, falling short of the established safety thresholds. Existing colorimetric approaches in literature have shown promise but often rely on complex reagent systems or multi-step procedures that limit practical deployment

[7]. There remains an unmet need for a simple, equipment-free, paper-based colorimetric sensor for naked-eye Ag^+ detection at regulatory thresholds. This work aims to develop such a sensor using AuAg nanocages, targeting performance relevant to food and water safety monitoring.

Description of the New Method or System

This work presents a paper-based colorimetric sensor for Ag^+ detection using AuAg nanocages as the sensing material. As earlier reported [8], the hollow, porous structure of AuAg nanocages gives them a highly tunable LSPR response that is sensitive to changes in their inner cavity. In the presence of ascorbic acid as a reductant, Ag^+ is reduced to Ag^0 , which nucleates and deposits on the inner cavity walls of the nanocages without altering the outer morphology. We confirmed this mechanism by TEM and EDX characterization. This internal deposition causes progressive wall thickening, resulting in a measurable LSPR blue-shift observed as a progressive, distinct, naked-eye color change from blue to purple to orange and then to yellow. To make such sensing platform portable, the nanocages were then deposited onto filter paper strips with an optimal nanocage concentration. Color readout induced by Ag^+ is performed by naked eye or by taking photos and using the CIELAB color system as a

quantitative metric, requiring no instrumentation. Possible interferants, substrate type, and nanocage loading concentration, were systematically screened to optimize reproducibility and selectivity.

Results

Firstly, the selectivity to Ag^+ against seven metal ion interferants were studied with the solution phase reaction. The results revealed that Fe^{3+} , Au^{3+} , and Pt^{4+} caused significant signal distortion in the absence of masking by EDTA, while EDTA chelation effectively suppressed interference from Cu^{2+} , Ni^{2+} , and Zn^{2+} . Au^{3+} and Pt^{4+} remain challenging as they are susceptible to reduction by ascorbic acid, producing interference signals that could not be masked suppressed by EDTA masking alone requiring further investigation. (Fig 1).

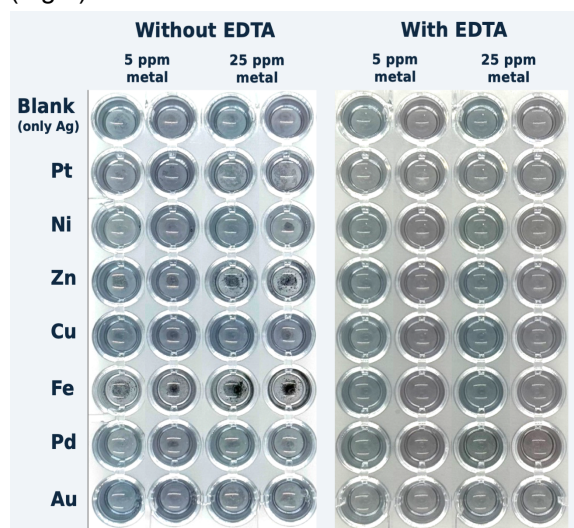


Fig. 1. 96 Well plate images showing colorimetric response of AuAg nanocages to Ag^+ in the presence of seven metal ion interferants at 5 and 25 ppm, without (left) and with (right) EDTA masking.

Systematic optimization of paper substrate and nanocage ink concentration identified Whatman 3 at 70% nanocage loading as the optimal condition, yielding well-defined, uniform sensing spots with a reproducible linear dose-response to Ag^+ from 5 to 45 ppm ($R^2 = 0.990$) based on CIE b^* color analysis (Fig 2). Visual color change was detectable down to 1 ppm, confirmed by statistically significant color difference across replicate measurements. Compared to reported solution-phase colorimetric methods for Ag^+ , this paper-based platform achieves competitive detection performance without requiring enzymatic substrates, oxidizing reagents, or benchtop instruments, highlighting its potential for field-deployable food and water safety monitoring.



Fig 2. Optimization of paper substrate and nanocage ink for Ag^+ detection. (a) Whatman 1 at 70% shows diffuse spots from lateral wicking. (b) Whatman 3 at 70% shows uniform, well-defined spots. (c) R^2 of Δb^* vs. $[\text{Ag}^+]$ for 10–70% nanocage concentrations on both substrates, with Whatman 3 at 70% selected as optimal. (d) Dose-response curve for Whatman 3 at 70% loading with linearity from 5–45 ppm ($R^2 = 0.990$).

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