Colorimetric Sensor Array: Rapid and Sensitive Approach for Detecting and Identifying Emerging Nanomaterial Contaminants

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ABSTRACT

Emerging contaminants such as nanomaterials and microplastics pose significant environmental risks due to their elusive nature and the limitations of current detection methods. Conventional techniques like UV-Vis spectroscopy and electron microscopy, though effective, are costly, low-throughput, and non-portable, particularly impacting populations in remote areas and less developed countries with increased vulnerability to materials contamination in natural and drinking water. To address this challenge, this study aims to develop a simple, portable, and rapid colorimetric sensor tailored for detecting materials contaminants in drinking water.

The proposed sensor design features an array utilizing chemo-responsive (pH indicator) dyes. The collective color-change response of the array serves as a distinctive "colorimetric fingerprint," enabling the identification of specific materials contaminants. This research focuses on evaluating the sensor array's capability to differentiate nanomaterials contaminants based on their surface charge. Specifically, the efficacy of the array in detecting and quantifying poly electrolyte-coated gold nanoparticles will be systematically evaluated through experimentation.

By leveraging chemo-responsive dyes in a portable sensor design, this study aims to provide a cost-effective and accessible solution for identifying emerging contaminants in drinking water, thereby addressing critical environmental and public health concerns.

BACKGROUND

Material contaminants are tiny particles that have become a significant concern due to their persistence in the environment and potential health impacts. They include microplastics and nanoparticles.[1] While microplastics are small plastics pieces less than 5 mm long that come from the degradation of plastics, nanoparticles are small sized particles of about 1-100nm with numerous applications in medicine, chemistry, materials science and engineering. Due to their very small sizes, nanomaterials move more freely than bulkier molecules giving them the ability to permeate physiological barriers of living organisms causing harmful biological reactions.[2]

The surface chemistry of nanomaterials plays a key role in determining their degree of toxicity. The surface chemistry of nanoparticles can include charge density, hydrophobicity, ligands and so on. For example, positively and negatively charged nanoparticles interact with biological systems through different mechanisms which will influence the level at which cells take them up. Additionally, acutely toxic ligands such as Poly allyl hydrochloride cause significant toxicity when conjugated to nanoparticles.[3]

Engineered nanoparticles and microplastics have found their way into drinking water sources worldwide, contaminating drinking water and causing chronic diseases like cancer, metabolic disorders, and heart diseases. Rapid and cost-effective detection of emerging materials contaminants in drinking water is of paramount importance due to their persistent nature and adverse effects on human health and ecosystems.[4]

To address these issues, a novel colorimetric sensor array is being developed. This sensor array uses chemical sensing principles to detect subtle changes in the chemical environment, using chemo-responsive dyes to probe analytes' chemical reactivity. The design of the sensor array depends on the specific change needed to be detected, such as detecting nanoparticles with different surface chemistries. The criteria for choosing the dyes include affordability, simplicity both in preparation and analysis, similar surface chemistry to proposed analytes to encourage intermolecular attraction.

Previous studies have shown the effectiveness of sensor arrays in detecting nanoparticles with varying sizes and shapes. The proposed research aims to evaluate the sensor array's ability to distinguish between gold nanorods functionalized with different polyelectrolytes at different concentrations.

Figure 1: Image of the different dyes in water solution.[6]

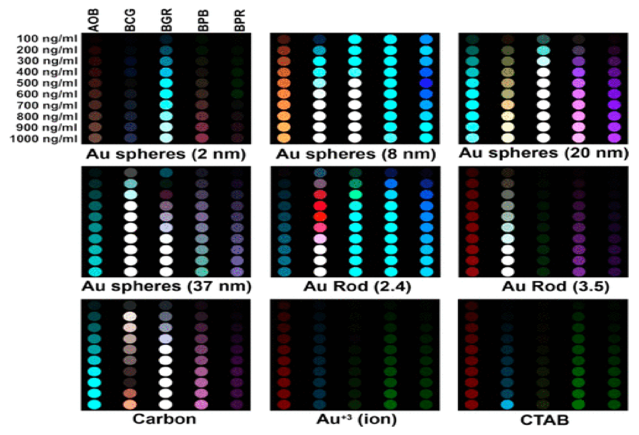

Figure 2: Color difference profiles of dyes after interactions with various NPs at different concentrations.[4]

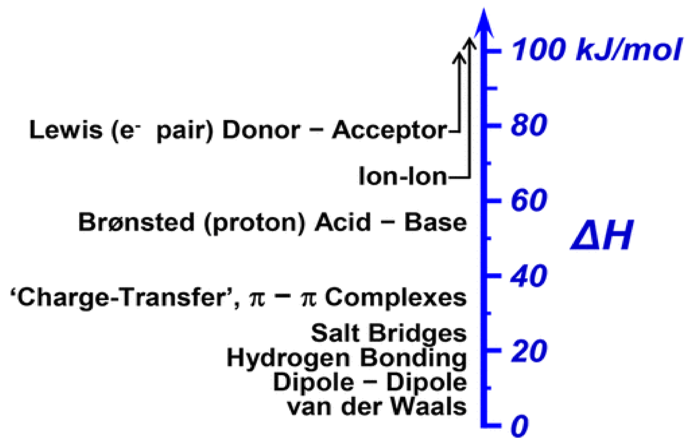

Figure 3: Image showing the strength of intermolecular interactions on a semiquantitative scale of enthalpy change.[5]

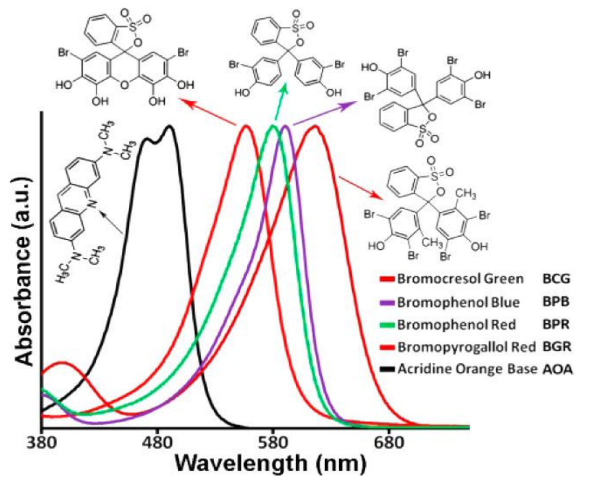

Figure 4: Image showing the structure and absorbance spectra of five different dyes.[4]

GOLD NANOROD SYNTHESIS AND CHARACTERIZATION

CTAB-coated gold nanorods (AuNRs) were synthesized using a previously published seeded growth approach[7]. This involved reducing $HAuCl_4$ in the presence of CTAB and a reducing agent to form gold nanoparticle seeds which were further grown into CTAB capped gold nanorods by adding $AgNO_3$ and excess CTAB. The CTAB-AuNRs were purified by centrifugation and then functionalized with one of the polyelectrolytes shown below using a previously published layer-by-layer wrapping approach[8]. The complete library of functionalized AuNRs will be characterized to confirm the AuNR's shape and surface chemistry using UV-vis absorbance spectroscopy, SEM, DLS, and ζ-potential analysis.

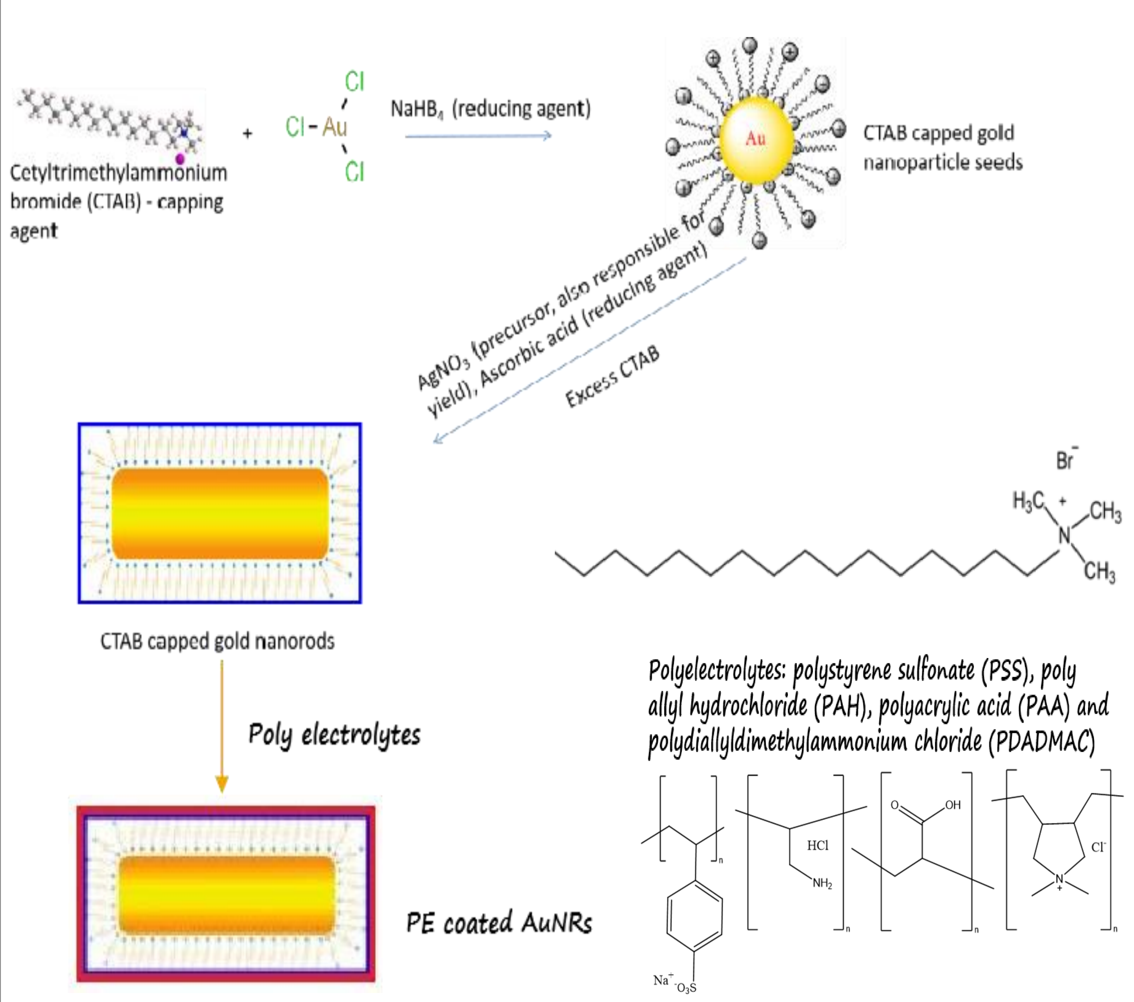

Figure 5: Illustration of the seeded growth synthesis and functionalization of nanorods.

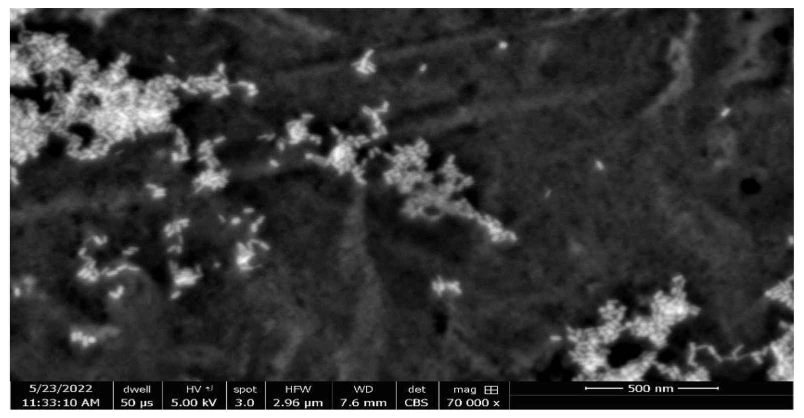

Figure 6: Scanning electron micrograph of gold nanorods (AR ~ 3.5)

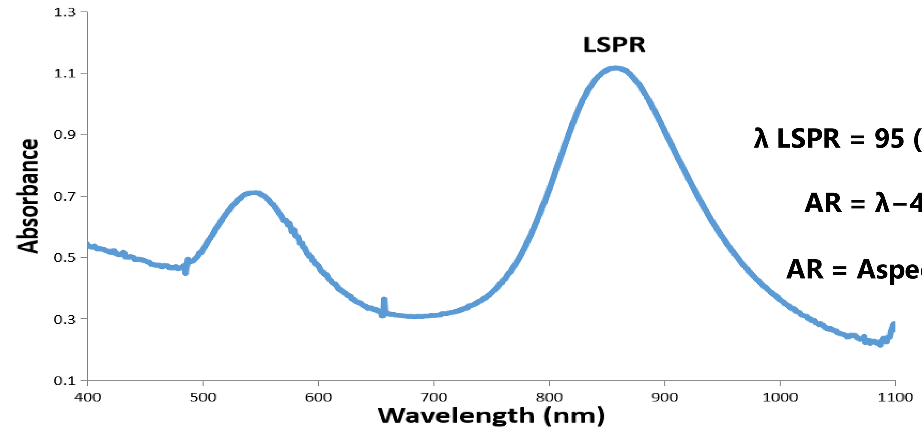

Figure 7: UV-vis absorbance spectrum of nanorods with aspect ratio of 4.5

DYE RESPONSE TO CTAB-NANORODS

The sensor's ability to discriminate between AuNRs' surfaces was quantified. The change in each dye's absorbance will be quantified using both UV-Vis absorbance spectroscopy and digital imaging. Principal component analysis of the data, performed in R, will be used to analyze the sensor's selectivity. The sensitivity of the sensor array will also be measured by interacting the dyes with varying concentrations of the nanoparticles until the point where the array cannot detect the presence of the nanoparticles (LOD/LOQ).

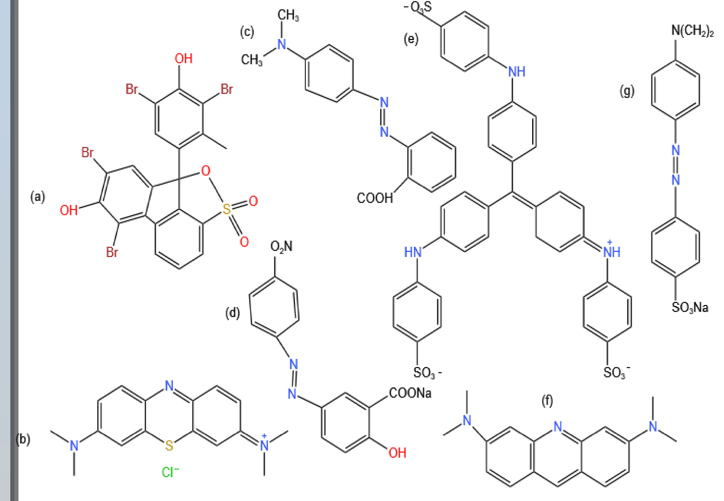

Figure 8: Structures of possible dye to be used in this research: (a) bromocresol green, (b) methylene blue, (c) methyl red, (d) mordant orange, (e) methyl blue, (f) acridine orange, (g) methyl orange

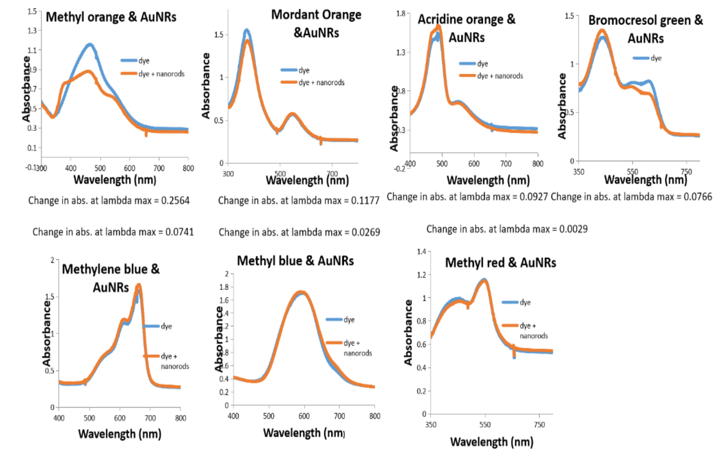

Figure 9: Initial interactions of dyes with nanorods in reactivity order with methyl orange being the most reactive and the least being methyl red (Methy orange > Mordant orange > Acridine orange > Bromocresol green > Methylene blue > methyl blue > Methyl red).

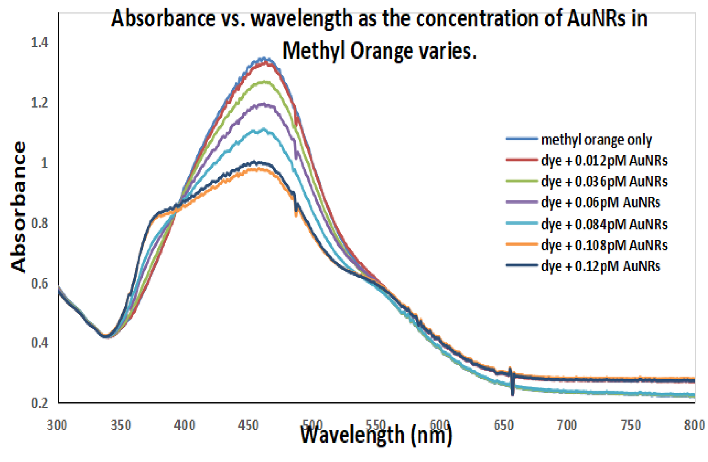

Figure 10: Methyl orange interaction with nanorods as concentration of nanorods vary. As concentration of nanorods increases, change in absorbance at lambda max increases and the peak height at lambda max decreases.

CONCLUSIONS AND FUTURE WORK

- pH dyes show unique responses to nanoparticle exposure.
- Methyl Orange is the most reactive out of the seven dyes chosen to CTAB-AuNRs.
- **Future Work:** Synthesize polyelectrolyte-coated nanorods and interact them with the dyes.
- **Future Work:** Reaction of the dyes with different concentrations of the functionalized AuNRs will also be studied.
- **Future Work:** Figures of merit such as limit of detection (LOD), limit of quantitation (LOQ) to ascertain sensitivity

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