

# Advancing Chloride Ion Detection in Edible Oils: Enhanced Sensitivity with NCQD/Ag Nanotriangles via Localized Surface Plasmon Resonance

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**Abstract:** Chloride ion detection in edible oil is crucial for food safety and preventing harmful compounds like 3-MCPD during refining. This study presents a novel method utilizing Nitrogen-Doped Carbon Quantum Dots (NCQDs) combined with Silver Nanotriangles (AgNTs) through Localized Surface Plasmon Resonance (LSPR) for chloride ion detection. The chemical properties of AgNT-NCQD enhance sensor performance by improving stability and biocompatibility while providing new binding sites for chloride ions. LSPR allows precise monitoring of the interaction between AgNT-NCQD and chloride ions, resulting in a distinct LSPR peak for accurate detection. The synergy between surface plasmon resonance and NCQDs increases sensitivity, with significant LSPR peak shifts upon chloride exposure. This technology offers a wider dynamic range and lower detection limits, demonstrating excellent selectivity for chloride ions in edible oil. The enhanced properties of NCQDs make this sensing platform vital for food quality assurance and consumer health protection.

## 1 INTRODUCTION

The discovery of various contaminants in edible oils that pose health risks has raised significant concerns about their quality and safety. Contaminants like 3-monochloropropane- 1,2-diol (3-MCPD) esters are particularly concerning due to their potential carcinogenicity (Jong-Sun et al., 2020). 3-MCPD are byproducts formed as impurities during high-temperature oil refining. 3- MCPD was classified as a possible human carcinogen (Group 2B) by The International Agency for Research on Cancer (IARC) (Panel & Chain, 2016). These compounds are produced during the deodorization process of oils and have been linked to tumor development in animal studies. According to EFSA (2016), palm oil contains significantly higher levels of 3- MCPD than regular fat margarine (Panel & Chain, 2016). 3-MCPD has

been known to form as a contaminant in processed foods, including refined oils, since the 1980s (Cheng et al., 2017). The presence of 3-MCPD has raised global safety concerns especially in refined edible oils. The synthesis of 3-MCPD esters is primarily influenced by chloride, acylglycerols, pH, temperature, and time (Kuntom et al., 2006).

Frequency depends on the nanoparticles' material, shape, and surrounding environment (Bakar et al., 2022) (Abdullah et al., 2018). Moreover, gold and silver are popular choices for these nanoparticles, which can come in various shapes. Gold nanoparticles (AuNPs) are favored for their stability and biocompatibility. However, triangular silver nanotriangles (AgNTs), with their sharp edges, are particularly useful for enhancing electric fields in surface-based spectroscopic techniques (Zannotti et al., 2020) that offer greater sensitivity. Yet, to

selectively detect low concentrations of target molecules, these nanoparticles often require additional modifications with specific materials (Azeman et al., 2020) (Rahman et al., 2019) (Abu Bakar et al., 2020).

Carbon quantum dots (CQDs) are tiny (less than 10 nm) fluorescent particles made of carbon with unique properties. Their core is carbon, but their surface has elements such as oxygen, hydrogen, and nitrogen. CQDs can be improved by attaching specific chemical groups (amino, hydroxyl, carboxyl) to their surface, making them more reactive and water-soluble (Nazri et al., 2022). Different materials such as chitosan or branched polyethyleneimine can be used for this. By attaching certain groups like polyamines, CQDs can be made to selectively bind to specific ions (Yoo et al., 2019). For instance, Nazri et al. in 2022, used CQDs with amino groups and silver nanoparticles to detect chlorophyll in water. The author's study showed that improved CQDs (NCQDs) were much better at detecting chlorophyll (Nazri, 2022).

In this study, we evaluate the potential of functionalized carbon quantum dots (CQDs) for chloride ion detection using a localized surface plasmon resonance (LSPR)-based optical sensor. Amino-functionalized CQDs (NCQDs) were synthesized via a two-step hydrothermal method employing polyethyleneimine as the amino group precursor. The composite film comprised of these functionalized CQDs and triangular silver nanotriangles (AgNTs) served to enhance the sensitivity of the LSPR sensor. The introduction of amine groups on the CQD surface facilitated improved chloride ion interaction through electrostatic interactions. The performance of the sensor was assessed by monitoring the wavelength shift of the LSPR spectrum across varying chloride ion concentrations. This analysis aimed to establish the sensor's linearity, range, sensitivity, and detection limit.

## 2 EXPERIMENTAL SECTION

### 2.1 Materials

Citric acid, polyethyleneimine, silver nitrate, sulfuric acid (98%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), trisodium citrate, sodium borohydride (NaBH<sub>4</sub>), 3-aminopropyltrimethoxysilane (97%) (APTES), polyvinyl alcohol, ethanol, and acetone were purchased from Sigma Aldrich. Ethylenediamine, heavy metals, iso-propyl, and ammonia solution

(30%) were purchased from R&M Chemicals, and edible oil was purchased from the local market.

### 2.2 Experimental Setup

Building on prior research, this work utilizes triangular silver nanoparticles (AgNT) synthesized via a room-temperature chemical reduction process. The synthesis utilizes readily available chemicals such as silver nitrate, trisodium citrate, sodium borohydride, and water. The composite sensing material AgNT-NCQD morphology was characterized by HRTEM and FESEM. Figure 1(a) shows triangular-shaped nanoparticles with a scale bar for 50nm. Conversely, Figure 1(b) obtained using FESEM demonstrates that the NCQDs possess a spherical morphology and are smaller than 10 nanometers.

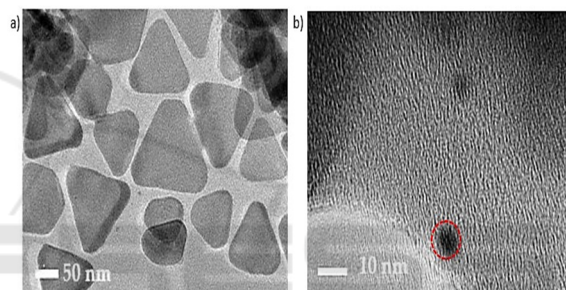


Figure 1: Surface morphology using HRTEM and FESEM showing the structure of a) AgNT b) NCQD.

Experimental setup comprised an HR4000CG-UV-NIR spectrometer from Ocean Optics interfaced with a reflection probe boasting a numerical aperture of 0.22. This configuration facilitated the

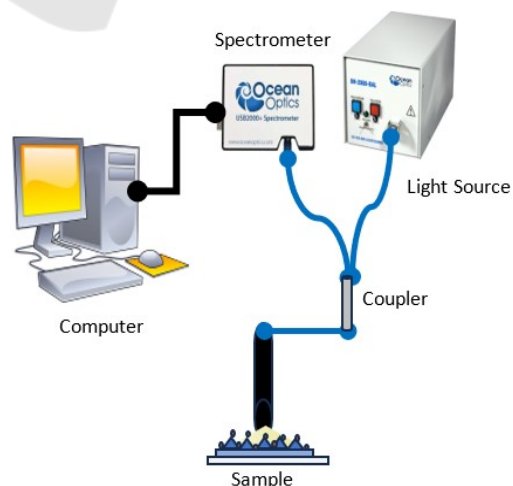


Figure 2: Detection of chloride ion using localized surface plasmon resonance (LSPR) setup.

measurement of the reflectivity spectra of both AgNTs and AgNT-NCQDs in edible oil containing 10 ppm chloride ions. The measurements encompassed a wavelength range of 350-850 nm and were swiftly captured following spectra acquisition. To ensure optimal signal acquisition, the probe was meticulously positioned above the sample as illustrated in Figure 2.

### 3 RESULT AND DISCUSSION

The study evaluated the fabricated AgNT-NCQD film sensor's ability to quantitatively detect chloride ions in edible oil by compared its efficiency and sensitivity to AgNT alone, using edible oil as the baseline for all sensor materials. Figure 3(a) shows when AgNTs were exposed to chloride ion, the wavelength value was shifted from baseline (450 nm) to 448.37, 447.06,

453.09, 448.11, and 447.32 nm for 2, 6, 10, 20, and 50 ppm of chloride ion concentrations, respectively. The wavelength shift ( $\Delta\lambda$ ) values change to 2.10, 3.41, 2.62, 2.36, and 3.15 nm. In contrast, Figure 3(b) shows the response of AgNT-NCQD to different chloride concentrations. Here, we observed a distinct trend: a narrow peak with increasing intensity as the chloride concentration rises.

Figure 3(b) reveals a critical observation as the concentration of chloride ions in edible oil increases, the reflectance peak associated with AgNT-NCQD film undergoes a noticeable shift. At the outset, with edible oil as the baseline, the peak is measured at 343.45 nm and exhibits minimal reflectance. Interestingly, a positive correlation between the concentration of chloride ions and the peak's spectral position were observed. In simpler terms, the higher the chloride ion concentration, the greater the shift towards higher wavelengths observed in the reflectance peak. Thus, the measured  $\Delta\lambda$  values for 2, 6, 10, 20, and 50 ppm of chloride ion are 0.79, 5.30, 7.68, 11.92, and 12.98 nm, respectively. The observed wavelength shift can conclude that it is through plausible electrostatic interaction due to positively-charged NCQD and negatively-charged Cl.

Traditionally, oppositely charged molecules experience stronger attraction due to electrostatic forces, leading to faster diffusion and interaction. The reversibility of the AgNT-NCQD sensor is supported by the non-covalent nature of electrostatic interactions, where chloride ions bind to the functional groups on the NCQD surface. These interactions are relatively weak and temporary, allowing chloride ions to detach when rinsed or exposed to a neutralizing environment, and subsequently reattach during reuse. However, in our study, the LSPR sensor using AgNTs displayed an unexpected result where the wavelength shift wasn't consistent. This finding challenges our understanding of how the shape and size of AgNTs affect the sensor's response. As reported by previous studies by Azeman and co. in 2022, the sharp corners of triangular AgNTs typically cause a redshift (longer wavelength) in reflectance peaks compared to spherical shapes. Multiple arrangements within the triangular AgNT might weaken this effect, leading to less pronounced redshift peaks (Bakar et al., 2022).

Figure 4 depicts the calibration plots for both AgNT and AgNT-NCQD across three separate experiments, all encompassing chloride ion concentrations ranging from 2 ppm to 50 ppm. The graph clearly illustrates that the  $\Delta\lambda$  for AgNT exhibits a gradual rise proportional to increasing chloride ion concentrations. In contrast, the  $\Delta\lambda$  for the AgNT-NCQD composite shows a significantly steeper rise.

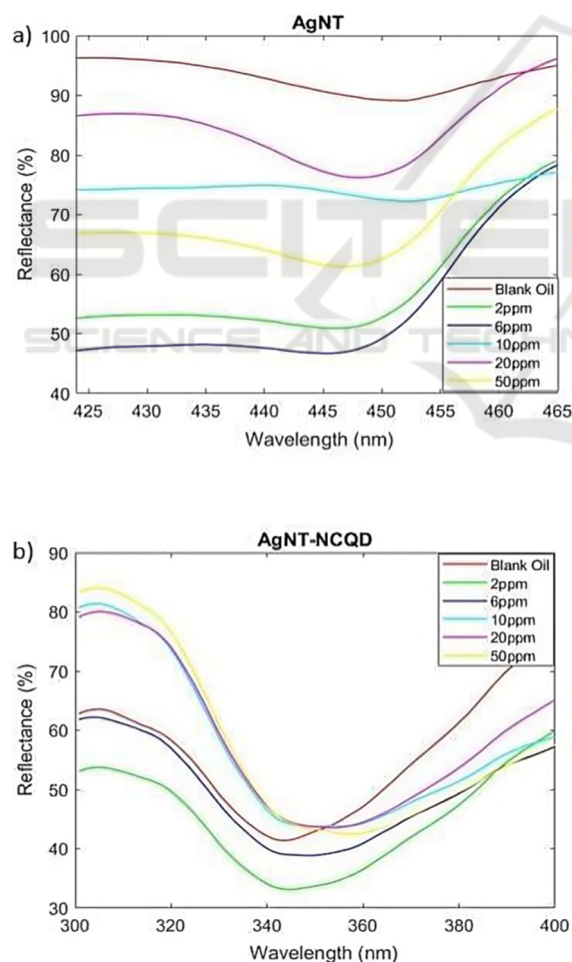


Figure 3: The reflectance spectra of the LSPR sensor in the presence of chloride ion with different concentrations ranging from 2-50 ppm of (a) AgNT, (b) AgNT-NCQD.

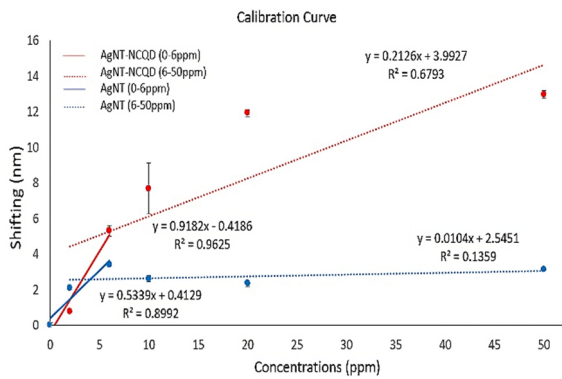


Figure 4: Calibration curve AgNT and AgNT-NCQD.

Furthermore, Figure 4 shows a graph comparing the linear regressions of AgNT and AgNT-NCQD. Notably, when detecting varying chloride ion concentrations, the linear regression for AgNT-NCQD appears to consist of two distinct lines. These two lines correspond to concentration ranges: 0-6 ppm and 6-50 ppm. It shows a high correlation coefficient ( $R^2 = 0.9625$ ) for 0-6ppm and AgNT-NCQD range 6-50ppm correlation coefficient ( $R^2 = 0.6793$ ) compared to the AgNT range 0-6ppm and 6-50ppm for  $R^2 = 0.8992$  and  $0.1359$ , respectively. The sensitivity of the sensor can be determined by analyzing the slope of the lines in Figure 4. The steeper the slope, the higher the sensitivity. The film sensors exhibits optimal sensitivity up to 20 ppm of chloride concentration, beyond which the sensor's binding sites become saturated, leading to a plateau in the response curve and reduced sensitivity. In this case, the slope of the AgNT-NCQD composite's calibration line is significantly steeper compared to AgNT, indicating a greater increase in  $\Delta\lambda$  for each increment in chloride ion concentration. This translates to a higher detection accuracy for the AgNT-NCQD composite, signifying its superior performance as an LSPR sensor for chloride ion detection in edible oil.

The analysis confirms that the AgNT-NCQD sensor is remarkably more sensitive than the AgNT sensor for detecting chloride ions in edible oil. The sensitivity of AgNT-NCQD was measured to be  $0.92 \text{ nm ppm}^{-1}$  (0-6ppm) and  $0.21 \text{ nm ppm}^{-1}$  (6-50ppm), whereas AgNT's sensitivity was only  $0.53 \text{ nm ppm}^{-1}$  (0-6ppm) and  $0.01 \text{ nm ppm}^{-1}$  (6-50ppm). This significant improvement can be attributed to the NCQDs in the composite sensor. NCQDs likely provide more binding sites for chloride ions, allowing for a greater response from the sensor and a more precise measurement. The performance of AgNT-NCQD compared to AgNT strongly suggests that

incorporating NCQDs significantly enhances the sensitivity of LSPR sensors for chloride ion detection.

This work obtained a high sensitivity with the detection range (0-6ppm), primarily due to the addition of NCQDs as the sensor layer of chloride ion detection compared to pure AgNT. However, the AgNT-NCQD range (6-50ppm) has lower sensitivity than the AgNT-NCQD range (0-6ppm). The readily available positively charged sites on the NCQD surface might be limited at higher chloride concentrations, hindering their interaction with the chloride ions. This findings demonstrated that AgNT-NCQD outperforms AgNT as a sensing material for chloride ion detection. It is important to note that this sensor is designed for use with vegetable oils that have properties similar to palm oil, such as olive oil and canola oil.

## 4 CONCLUSIONS

This study investigated a sensor for detecting chloride ions using triangular silver nanoparticles (AgNTs) film and nitrogen-doped carbon quantum dots (NCQDs). It compared the performance of this AgNT-NCQD film sensor to the sensors using only AgNTs. It analyzed the sensors by measuring the shift in reflected light wavelength as the chloride ion concentration increased. Presence of amino in the NCQDs creates more active sites for chloride ions to bind, enhancing the sensor's capability. This binding likely occurs through electrostatic interactions. The AgNT-NCQD film sensor positively responds to increasing chloride ion concentrations within a specific range (potentially 0 to 6 ppm). The sensor demonstrated a value of  $0.92 \text{ nm ppm}^{-1}$ . Additionally, it showed a strong linear relationship between the reflected light shift and chloride concentration ( $R^2 = 0.9625$ ). However, the Limit of Detection (LOD) was calculated to be  $4.12 \text{ ppm}$ , suggesting room for improvement in detecting very low chloride concentrations. In addition, considering the potential of LSPR, this simple and efficient detection technique could be applied to total chlorine in edible oil where it provides a potential real-time detection for total chlorine utilizing AgNT-NCQD films on LSPR to achieve easy and fast detection in the food safety fields.

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