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# Silver nanoplates: Tetradecyltrimethylammonium ions as additives in seed-growth synthesis and their potential application as catalysts for glucose oxidation reaction

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## ABSTRACT

Tetradecyltrimethyl ammonium ions ($C_{14}TA^+$) were used as trace additives in a seed solution to block the (1 1 1) seed surface so as to govern the growth direction and pathway, leading to the formation of Ag nanoplates. The spectra of the obtained nanoplate solution showed a high intensity peak, attributed to the in-plane dipole resonance, and a low-intensity peak at 400 nm. By decreasing the amount of $C_{14}TA^+$-adsorbed seed amount from 20 μL to 15 μL and 5 μL the mean height of triangular nanoplates was altered from ~96 nm to ~130 nm and ~177 nm. The in-plane dipole resonance peak, which corresponds to the change in the mean height, shifted from 655 nm to 740 nm and 807 nm, respectively. To investigate the feasibility of practical application of the proposed method, the prepared nanoplates were used as an electrocatalyst to sense a glucose oxidation reaction (GOR). A cyclic voltammogram of the nanoplates showed two significant peaks during the cathodic sweep, indicating that the anodic oxides provide active sites and have high GOR activity. Simultaneously, the results measured by potential deposition of Pb show the nanoplates have electrochemical surface areas (ESAs) of 96 nm > 130 nm > 177 nm. The higher activity on the 96 nm sized nanoplates is attributed to the fact they have the largest ESA. Remarkably, the prepared nanoplates show high potential as glucose sensors, in that the 96 nm nanoplates showed 0.527 mA $mM^{-1}$ $cm^{-2}$ sensitivity for glucose.

## 1. Introduction

Applications using metal nanoplates have attracted considerable attention due to the unique chemical and physical properties of the nanoplates. Of the many applications they can be used for, chemical and biological sensing applications are currently the most attractive. These sensing applications are based on the special optical properties from surface plasmon resonance (SPR) the nanoplates possess. For example, Ag nanoplates show potential application for sensing inorganic anions due to their high sensitivity to dipolar in-plane oscillation [1] and rhodamine 6G (R6G), allowed by their unique surface-enhanced Raman scattering properties [2–4]. Additionally, Au nanoplates can be successfully used to electrochemically detect $H_2O_2$, because of their reliable redox behaviour [5]. The shape of catalyst nanoparticles can potentially enhance the rates of catalysis [6–10] and electrocatalysis [11,12]. Crystal faces of various shapes [9,13–15], present on the surface of metallic nanomaterials, play a key role in promoting the reactions where the nanomaterials are employed as catalysts. Recently, it has been reported that Au nanoplates, enclosed with (1 0 0) and (1 1 0) planes, exhibit unique catalytic activities when used as catalysts for the electroxidation of glucose [16], and, further, as a glucose sensor [17].

Recently, cheaper Ag nanoparticles, compared to Au nanomaterials, have been found to have activity with electrochemical GOR [18,19] and further be used as sensor electrode [20,21], showing their potential in reproducibility and long-term stability. Herein, we report a method utilizing a seed additive, tetradecyltrimethyl ammonium ($C_{14}TA^+$) ions, to synthesize Ag nanoplates in a high yield via seed-mediated growth. We determined the effects of $C_{14}TA^+$ and $C_{14}TA^+$-adsorbed seeds on the nanoplate dimensions. Additionally, the practical feasibility of employing the prepared nanoplates as GOR electrocatalysts and sensor was tested.

## 2. Experimental

### 2.1. Synthesis of different-sized Ag nanoplates using $C_{14}TA^+$-adsorbed seeds

The seed growth method of producing Ag nanoplates with $C_{14}TA^+$ was modified from the previous report [22] and carried out

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as follows. First, the $C_{14}TA^+$ ions required for this reaction were prepared. $AgNO_3$ (2 M, 1 mL) was added to a beaker containing 1 mL of an aqueous solution of tetradecyltrimethyl ammonium bromide (2 M) to precipitate AgBr as a grey solid. The grey precipitate was removed with centrifugation (12,000 rpm, 10 min) to obtain 1 M $C_{14}TA^+$.

For seed synthesis 50 μL of 0.05 M $AgNO_3$ was added to 10 mL of a $2.5 \times 10^{-4}$ M sodium citrate solution. Next, 50 μL of the $C_{14}TA^+$ additive, prepared as previously mentioned, was gradually added, with continuous stirring, to the mixed solution of sodium citrate and $AgNO_3$. Finally, 25 μL of as-prepared 0.02 M $NaBH_4$ solution was added to give the Ag seed solution.

Next, 100 μL of 0.05 M $AgNO_3$ was added to 20 mL of 0.1 M hexadecyltrimethyl ammonium bromide ($C_{16}TAB$). Then 1 mL of 0.1 M ascorbic acid and 5 μL of the $CTA^+$-adsorbed Ag seed solution were gradually added to the $C_{16}TAB$ aqueous solution. Ag nanoplates of 177 nm edge-length were obtained after the addition of 80 μL of 2 M NaOH aqueous solution. Using the same method, nanoplates with edge lengths of 130 nm and 96 nm were prepared using 15 μL and 20 μL of the seed solution, respectively.

### 2.2. *Materials analysis of Ag nanoplates*

The prepared nanomaterials were deposited on a copper grid coated with a carbon film and dried naturally. After deposition, the characteristic size, shape, and composition of the nanoplates were observed under a high-resolution transmission electron microscope (JEOL JEM-2100F). Optical properties, such as surface plasmon resonance (SPR), of the as-prepared nanoplate solution were investigated using a UV–vis spectrophotometer (Agilent 8453).

### 2.3. *Electrochemical glucose sensing using Ag nanoplates*

The activity and sensitivity of the prepared Ag nanoplates, for use in a GOR, was evaluated by electrochemical measurement using a computer-controlled CHI potentiostat (611D) with a nanoplate-coated glassy carbon electrode (0.07 $cm^2$). The weight density of the nanoplates, acting as catalysts on the electrode, was 0.48 mg $cm^{-2}$. All electrochemical measurements were conducted in a $N_2$-saturated 0.1 M $NaOH_{(aq)}$ solution, without or with 5 mM glucose, using a three-electrode cell with the nanoplate-covered electrode serving as the working electrode, Pt foil used as the counter electrode, and a Ag/AgCl (3 M KCl) reference electrode. In order to remove any potential interference from $C_{16}TAB$ on the nanoplates during GOR, the Ag catalysts were scanned from −0.2 V to 0.8 V using cyclic voltammetry at a rate of 150 mV $s^{-1}$. The sensitivity of the different-sized Ag nanoplates for glucose was tested using amperometric measurements, where a fixed potential of 0.65 V (vs. Ag/AgCl) was applied. For these measurements, different concentrations of glucose solution (from 4 mM to 11 mM) were added once the background current reached a constant value. To measure the electrochemical surface areas (ESAs), Pb was deposited onto a silver nanoplate modified glassy carbon electrode disc in a 0.1 M HCl solution containing 10 mM of $Pb(NO)_3$.

## 3. Results and discussion

### 3.1. *Characterization of Ag nanoplates prepared by seeds with $C_{14}TA^+$ additives*

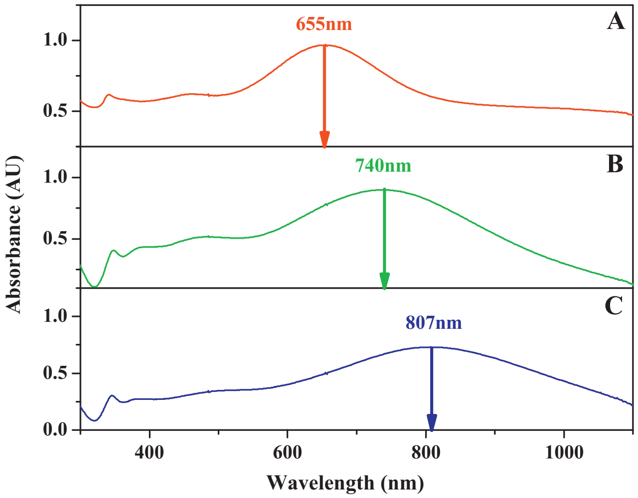

**Fig. 1.** UV–vis (SPR) spectra of as-prepared nanoplate solutions synthesized from various amounts of $C_{14}TA^+$-adsorbed seed solution: (A) 20 μL, (B) 15 μL, and (C) 5 μL.

When 20 μL of Ag seed solution with $C_{14}TA^+$ additives was added to a growth solution, the solution turned blue-green. Fig. 1A shows an SPR spectrum of this solution without any additional purification. The long wavelength peak, located at 655 nm, is assigned to the in-plane dipole resonance. This result is similar to the theoretical spectra of single triangular nanoplates [23,24]. It should be noted that the in-plane dipole peak undergoes a red-shift to 740 nm (Fig. 1B) and 807 nm (Fig. 1C) when the amounts of Ag seed solution mixed with $C_{14}TA^+$ were changed to 15 μL and 5 μL, respectively. The ingenious studies using the chemical seed-growth method for preparing Ag nanoplates [25] and nanocubes [26] observed that decreases in additional seed amounts resulted in a red-shift of SPR peak location and the enlargement of the nanoparticles. Fig. 2A–C show a series of TEM images of nanoparticles whose SPR spectra are shown in Fig. 1A–C, respectively. Obviously, a high-yield of nanoplates can be successfully synthesized by using the seed-mediated growth method and most of the prepared nanoplates are triangular. The size of the Ag nanoplates when using 5 μL of seed solution with $C_{14}TA^+$ is larger than those of nanoplates produced with 15 μL and 20 μL seed solution with $C_{14}TA^+$. Based on the results of TEM, the mean height of the prepared triangular nanoplates are calculated and summarized in Fig. 3. As shown in Fig. 3, the mean height of the nanoplates produced with 5 μL, 15 μL, and 20 μL seed solution with $C_{14}TA^+$ are 177 nm, 130 nm, and 96 nm, respectively. The statistical results revealed the nanoplate size of the seed solutions with 5 μL are the largest followed by 15 μL, which is larger than 20 μL. When using the seed-growth method for preparing metal nanoparticles, the final structure grows based on seed microstructure. At the same concentration of silver ions in a growth solution more seeds can plausibly result in a smaller sized nanoplate.

In order to identify the crystalline structure of different-sized nanoplates, XRD patterns were studied, and the results are shown in Fig. 4. Fig. 4 shows the powder XRD pattern of Ag nanoplates that are 96 nm in height, as shown in the TEM image of Fig. 4A. Two peaks—one strong peak located at 38.07° and one weak peak located at 44.51°—were detected and attributed to the (1 1 1) and (2 0 0) diffraction planes of the face-centred cubic structure, respectively. Similar XRD results (Fig. 4B) are were observed for the 130 nm nanoplates. In agreement with a previous study on the crystal structure of Ag nanoplates [24,27], it was concluded that the Ag nanoplates are essentially composed of the (1 1 1) basal plane. The strong (1 1 1) peak detected in the XRD patterns of Ag nanoplates can be reasonably assigned to the contribution of the basal plane. Note that for large nanoplates, only the (1 1 1) strong peak is detected (Fig. 4C), suggesting that most of planes to enclose the nanoplate are (1 1 1).