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LETTER

Ultrafast synthesis of silver nanoplates in ethanol at room temperature

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Silver nanoplates are found to be facilely synthesized at room temperature in ethanol. It is proposed that silver nanoplates are specifically obtained by using aged $NaBH_4$ due to the presence of $NaBO_2$. The assumption is confirmed by the synthesis of silver nanoplates using $NaBO_2$ and fresh $NaBH_4$ directly.

Silver nanoplates exhibit unique features for their localized surface plasmon resonances (LSPR) properties, which have been applied in various areas. [1-3] Many efforts are attracted for the fabrications of silver nanoplates and they can be prepared using various protocols such as light-mediated or chemical reduction methods. [4-9] However, it remained a challenge to simply design silver nanoplates in the absence of citrate until Yin found that citrate could be replaced with various types of di- and tricarboxylate compounds. [10] On the other hand, in the presence of organic solvent, neither citrate nor carbonxylate compounds are required for the synthesis of silver nanoplates. [11] To the best of our knowledge, high temperatures are required for the preparation of silver nanoplates in all kinds of organic solvents by previous papers. [11-15] For instance, Rong intended to obtain silver nanoplates in various kinds of organic solvents based on microwave assisted method. Though Silver nanoplates were obtained from DMF and NMP solvents, silver nanoplates couldn't be fabricated using pyridine or ethanol. [13] Not until recently, Zhang have obtained silver nanoplates in ethanol by using solvent thermal methods. [11] In ethanol solvent, the colloid of silver nanoplates can be stored in both the cabinet and freezing chamber of a refrigerator, which provides additional options for long-time protection. Nothwithstanding, the use of solvent thermal power requires more complicated conditions compared to the protocols at room temperature. As well as this, it took relatively long time for the synthesis. [11] $NaBH_4$ will decompose in water so fast that most papers related to the synthesis of silver nanoplates have mentioned the application of fresh $NaBH_4$ as their reducing reagents. [16-18] This means aged $NaBH_4$ was mostly trashed. In consideration of the high temperature that has to be required in ethanol for the synthesis, a method was initially found to turn the 'trash' to 'treasure'. It is interesting to find that silver nanoplates can be formed in ethanol by the application of aged $NaBH_4$ at room temperature within two minutes. Though silver nanoplates could be facilely obtained by the employment of aged $NaBH_4$, there was still uncertainty. For instance, the decomposition of $NaBH_4$ will depend on temperature, pressure, humidity, etc. As a result, it is difficult to grantee the composition of aged $NaBH_4$ will be completely same after decomposition at different kinds of weather especially when there is significant difference for the temperature. It is known that the degradation of $NaBH_4$ in water is as follows.

$$NaBH_4 + 2H_2O = NaBO_2 + 4\,H_2$$

Then, it is worth wondering whether the presence of $NaBO_2$ in aged $NaBH_4$ plays a vital role for the assistance of the formation of silver nanoplates since we can't obtain silver nanoplates at the current conditions by just using fresh $NaBH_4$ no matter what kinds of amounts are used. Initially, the growth mechanism for the formation of silver nanoplates using aged $NaBH_4$ is proposed in Scheme 1. Based on the decomposition of $NaBH_4$ in water as a function of time, it is assumed that the silver nanoplates are specially formed at room temperature because both the residual $NaBH_4$ and newly formed $NaBO_2$ are present in aged $NaBH_4$. It can be concluded the silver nanoplates will be possibly obtained when the ratio between $NaBO_2$ and the residual $NaBH_4$ is appropriate at certain aging time if the assumption is true. For the confirmation of this assumption, different conditions are investigated when fresh $NaBH_4$ and $NaBO_2$ are used in the place of aged $NaBH_4$. As is expected, silver nanoplates can finally be directly prepared by the employment of both $NaBO_2$ and fresh $NaBH_4$. Additionally, the as synthesized silver nanoplates can be formed just after the mixing of the required reagents. To the best of our knowledge, this is the first work that reported a method for fabrication of silver nanoplates in ethanol at room temperature. Compared to the complicate

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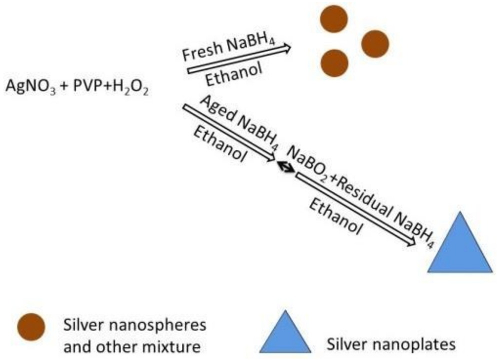
protocols for previous papers, the methods describe great advantages over time, temperature as well as procedures. [11-14]



Scheme 1 Mechanism for formation of silver nanoplates based on aged $NaBH_4$.

Herein, $AgNO_3$, PVP and H_2O_2 are used as precursor, stabilizer and etching reagents (or the formation of seeds) respectively, which play similar roles to previous papers. [3, 5, 19, 20] Thus, they will not be discussed in detail. The typical UV-Vis absorption spectra of silver nanoplates fabricated by using fresh and aged $NaBH_4$ (aged after 3 days at room temperature and 20 minutes at 80 ℃) are shown in Fig. 1. UV-Vis absorption spectra for the silver nanoplates obtained using fresh $NaBH_4$ exhibit a peak at ca. 489 nm, see Fig. 1a. It can be concluded that silver nanoplates are hardly present in the colloid. On the other hand, an absorbance peak is located at ca. 648 nm when aged $NaBH_4$ has been used, which indicates the formation of silver nanoplates based on the absorbance band. Meanwhile, a small peak at around 336 nm nm is attributed to the out-of-plane quadrupole resonance of silver nanoplates. A shoulder peak at ca. 470 nm can be attributed to the in-plane quadrupole resonance of silver nanoplates. [21] The third peak at the longest wavelength side, which is very sensitive to the size and aspect ratio of the particles, is due to the in-plane dipole plasmon resonance of silver nanoplates.

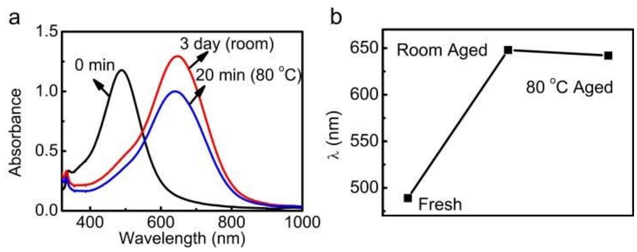


Fig. 1 UV-Vis absorption spectra of silver nanoplates obtained using fresh $NaBH_4$ (0 min, black line), $NaBH_4$ aged at room temperature(3 days, red line), 80 ℃ (20 minutes, blue line) (a) and the corresponding wavelength of maximum absorbance for the colloid of silver nanoplates (b).

Though the method for preparation of silver nanoplates based on the application of aged $NaBH_4$ is facile, we have to wait for about 3 days for the aging of $NaBH_4$. It is worth wondering whether fast aged $NaBH_4$ can be applied for the fabrication of silver nanoplates. Then, $NaBH_4$ that aged at 80 ℃ in water bath was also investigated. UV-Vis absorption spectra of the as prepared silver nanoparticle colloid are demonstrated in Fig. 1 (blue line). No significant difference was described for their absorbance peak at ca. 640 nm. Then, it can be seen that similar silver nanoplates can be obtained by aging $NaBH_4$ at high temperatures with shorter time when the composition after decomposition are fortunate to be similar.

The typical TEM images for the silver nanoplates obtained using 3 day (at room temperature) and 20 minute (80 ℃) aged $NaBH_4$ are described in Fig. 2. It can be evaluated that the average size of nanoplates are ca. 68 nm based on the counting of 50 particles by using $NaBH_4$ that aged for 3 days at room temperature (Fig. 3a). On the other hand, when 20 minute (80 ℃) aged $NaBH_4$ is used, the average size of the silver nanoplates is ca. 62 nm (Fig. 3b). In combination with their UV-Vis spectra in Fig. 1 and Fig. 2, it can be concluded the as formed silver nanoplates are quite similar by using $NaBH_4$ that aged for 3 days (at room temperature) and 20 minutes (80 ℃).

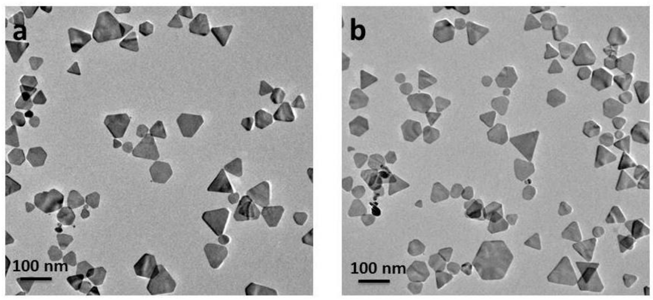


Fig.2 TEM images of the silver nanoplates obtained using $NaBH_4$ that aged for 3 days (room temperature) (a) and 20 minutes (80 ℃) (b).

Furthermore, various conditions are investigated for the preparation of silver nanoplates by just using $NaBO_2$ and fresh $NaBH_4$. Initially, the volumes of $NaBO_2$ and $NaBH_4$ are fixed as 170 µL. The mixtures are used in the place of aged $NaBH_4$. Fig. 3 describes the UV-Vis absorption spectra as well as the wavelength of maximum absorbance for the as formed silver nanoparticle colloid. Initially, the colloids of silver nanoplates are prepared by the application of various ratio of $NaBO_2/NaBH_4$ with the total amounts fixing as 170 µL of 10 mM. It can be seen from Fig. 3a that no significant difference has been observed for the absorbance of all the obtained UV-Vis spectra at 334 nm, which is very sensitive to the thickness of the nanoplates. On the other hand, it is interesting to find in Fig. 3b that the wavelength of maximum absorbance changes linearly as a function of the ratio of $NaBO_2/NaBH_4$ within a range of 0.725 - 0.85. Thus, it can be concluded that the size ({ 111} basal facets) of the silver nanoplates can possibly be tuned by changing the ratio between $NaBO_2$ and $NaBH_4$. For further increasing or decreasing the ratio of $NaBO_2/NaBH_4$, no peak or quite unregularly absorption curves with broad peaks are observed for the UV-Vis spectra. This indicates the mixtures of the aggregated particles are obtained. On the other hand, UV-Vis absorption spectra of silver nanoplates are fabricated by 170 µL of the mixture with different concentration of $NaBO_2$ while that of $NaBH_4$ (3 mM) is kept constant. It can be seen from Fig. 3c that the absorption peak is hardly observed when the concentration of $NaBO_2$ is lower than 3 mM. In the absence of additional $NaBO_2$, $NaBH_4$ will decompose extremely fast with low concentrations. Therefore, it is impossible to grantee absolutely no $NaBO_2$ is present. However, the amounts are not enough to direct the formation of silver nanoplates. When $NaBO_2$ increases to 3 mM, a broad absorption peak around 527 nm is observed. It indicates silver nanoplates with excellent purity have not been obtained at this stage. Furthermore, it can be observed the wavelength of maximum absorbance red shifts as function of the concentration of $NaBO_2$ within the range of 5 - 9 mM (Fig.3 d). In the absence of additional $NaBO_2$, just the aggregates or silver nanospheres can be formed (depending on the amounts and the decomposition of $NaBH_4$, see Fig. 1a). On the other hand, silver nanoplates can be obtained in the presence of certain amounts of $NaBO_2$. Furthermore, based on the red shift of the wavelength by using relatively high concentration of $NaBO_2$, it can be concluded that $NaBO_2$ may serve as the capping agent to the {111} basal facets of the Ag nanoplates. Thus, the size will increase as a function of $NaBO_2$ at certain range. Meanwhile, by using the linear curve equation (see Fig. 3d, inset), it will enlighten us to fabricate silver nanoplates with an expected size. On the other hand, based on the linear equation, we can expect that it is possible to evaluate the decomposition ratio of $NaBH_4$ based on the spectra of the as prepared silver nanoplates in the future.

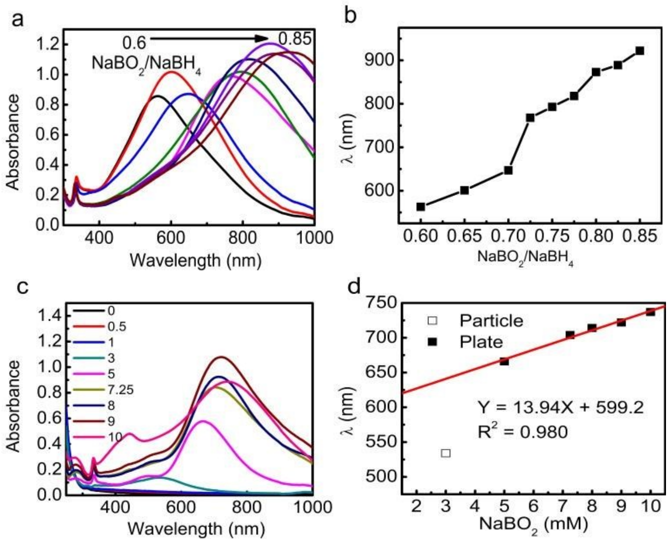


Fig. 3 UV-Vis absorption spectra of silver nanoplates by using different ratio of $NaBO_2/NaBH_4$ while the total amounts are fixed (170 µL, 10 mM) (a) and the wavelength of maximum absorbance as a function of the ratio (b); UV-Vis absorption spectra of silver nanoplates by using different concentration of $NaBO_2$ while that of $NaBH_4$ (3 mM) is kept constant (c) and the wavelength of maximum absorbance as a function of the ratio (d).

In addition, it is well acknowledged that H_2O_2 is a key ingredient on the formation of seeds or the etching reagent that is essential for the growth of silver nanoplates. [5, 20, 22] Thus, the change of H_2O_2 (30%) are investigated to find out the required amounts for the synthesis of silver nanoplates by the employment of $NaBO_2/NaBH_4$ with ratios of 0.725 and 0.700 respectively, see Fig. 4. It can be seen from Fig. 4a and Fig. 4c that no silver nanoplates are formed in the absence of H_2O_2 since the absorption peaks are located at ca. 410 nm. As well as this, the peaks at ca. 410 nm decrease when the amounts of H_2O_2 increase to a certain extent, which reveals less ratio of silver nanoshperes are present. Additionally, the peaks almost 、disappear when the amounts of H_2O_2 are higher than 16 µL, which indicates that more than 16 µL of H_2O_2 are required in our case for the preparation of silver nanoplates with high purity. However, when the amounts of H_2O_2 are more than 28 µL, both the absorbance decrease when the ratios of $NaBO_2/NaBH_4$ are 0.725 and 0.700, which possibly reveals the dissolution of silver nanoplates (see Fig. 4b and Fig. 4d). As a result, 16 - 28 µL can be applied for the formation of silver nanoplates with high yield and purity.

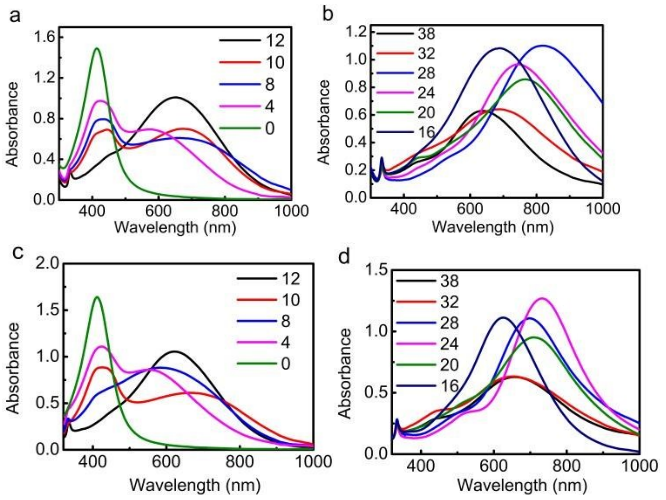


Fig. 4 UV-Vis absorption spectra of silver nanoplates by using various amounts of H_2O_2 (30%) from 0 - 12 µL (a, c) and 16 – 38 µL (b, d) by the employment of different ratio for $NaBO_2/NaBH_4$ including 0.725 (a, b) and 0.700 (c, d).

The properties of silver nanoplates depend on all the ingredients and various kinds of conditions including $AgNO_3$, PVP, H_2O_2, $NaBO_2$ and $NaBH_4$, temperature, stirring, etc. The studies in detail for the influence of the concentration of each ingredient or other conditions are beyond the investigation of this work, but it will enlighten further synthesis of silver nanoplates with various properties based on our method. It is noted in Fig. 3 that the wavelength doesn't change gradually as a function of the ratio. There is sharp increase for the red shift when the ratio changes from 0.700 to 0.725. Then, for the characterization of typical silver nanoplates, 28 µL of H_2O_2 (30%) are used. Meanwhile, 0.700 and 0.725 were selected as the ratio of $NaBO_2/NaBH_4$ (total amount, 170 µL, 10 mM). The TEM images for the as prepared silver nanoplates are described in Fig. 5. It can be seen from Fig. 5a that the average size is ca. 52 nm when the ratio of $NaBO_2/NaBH_4$ is 0.700. At the same time, the thicknesses of the silver nanoplates are evaluated as 3 - 5 nm based on the inset picture for side evaluation. When the ratio of $NaBO_2/NaBH_4$ is 0.725, the area sizes of the silver nanoplates increase to ca. 81 nm, see Fig. 5b. In combination with the UV-Vis spectra of the colloids of silver nanoplates in Fig. 3, it can be further confirmed that the size of silver nanoplates ({111} basal facets) will be tuned by controlling the ingredient such as $NaBO_2$.

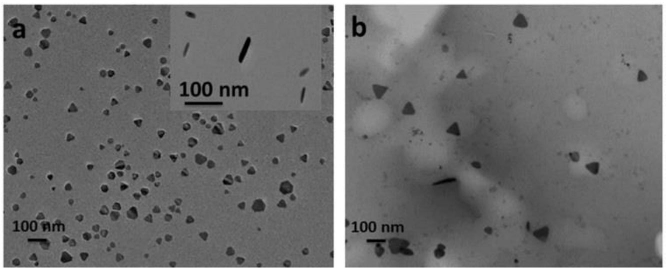


Fig. 5 TEM image of silver nanplates prepared by using 28 μL of H_2O_2 (30%) when the ratios of $NaBO_2/NaBH_4$ are 0.700 (a) and 0.725 (b) respectively.

In summary, we have demonstrated a strategy for facile synthesis of silver nanoplates in ethanol at room temperature. A linear relationship was found between the wavelength of maximum absorbance and the concentration of $NaBO_2$ and $NaBO_2$ may serve as the capping agent to the {111} basal facets of the Ag nanoplates. It will enlighten the preparation of silver nanoplates with desired size. Meanwhile, based on the linear equation, it is possible to evaluate the decomposition of $NaBH_4$ based on the formation of silver nanoplates in the future.

Experimental section

Reagents and characterization

All the reagents were of analytical grades and used as received without further purification. Transmission electron microscopy (TEM) images and (Energy-dispersive X-ray spectroscopy) EDS were taken using a JEM-1400 microscope (JEOL, Tokyo, Japan) operated at 120 kV. The Ultra Violet-Visible Spectroscopy (UV–Vis) spectra were recorded using a Cary 50 UV−1600 spectrometer.

Synthesis of silver nanoplates based on aged $NaBH_4$

In a typical procedure, 250 μL of 15 mM of $AgNO_3$ solution was added to 25 mL of ethanol (absolute). After that, 750 μL of 0.7 mM Poly(vinylpyrrolidinone) (PVP) (30000 MW) was combined, followed by the addition of 70 μL of H_2O_2 (30%). Then, 40 μL of aged $NaBH_4$ (106.25 mM) was injected. After that, the colour of the mixture turned to blue within two minutes.

Preparation of the silver nanoplates by using fresh $NaBH_4$

In a typical procedure, 150 μL of 10 mM of $AgNO_3$ solution was added to 10 mL of ethanol. After that, 300 μL of 0.7 mM Poly(vinylpyrrolidinone) (PVP) (30000 MW) was combined, followed by the addition of 28 μL of H_2O_2. Then, 170 μL of the mixture of fresh $NaBH_4$ and $NaBO_2$ (total concentration, 10 mM) was injected. After that, the colour of the mixture turned to blue within two minutes.

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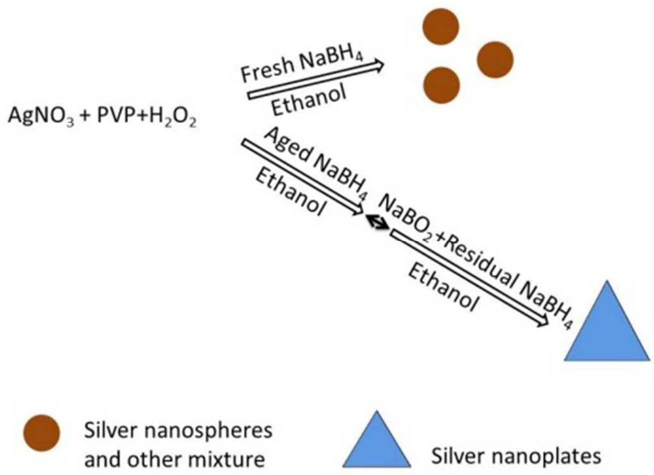

Formation of silver nanoplates based on aged $NaBH_4$ due to the production of $NaBO_2$