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COMMUNICATION

Investigating the Mechanism of Catalytic Reduction of Silver Nitrate on the Surface of Barium Titanate at Room Temperature: Oxygen Vacancies Play a Key Role

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Suibin Luo,^a Shuhui Yu,^{a*} Fang Fang,^a Maobai Lai,^a Rong Sun^{a*} and Ching-Ping Wong^b

In this study, the formation mechanism of Ag nanoparticles deposited on Barium Titanate (BT) surface was investigated. The surface oxygen vacancies of BT linked with the hydroxyl oxygen of ethylene glycol and catalyzed the reduction of silver nitrate, leading to promoted deposition of Ag nano particles on the BT surface.

Noble metal nanoparticles have received increasing interest because their optical,¹ electrical,² and catalytic³ properties can be tailored by controlling the size, shape, crystalline phase and chemical status of the particle surface. The particles with specific microstructure have found applications in surface-enhanced Raman spectroscopy,⁴ catalysts,³ anti-bacterial⁵ and electronic packaging materials⁶, etc.

A single homostructure nanoparticle displays advanced properties in some respects over its bulk counterpart owing to the nano-meter effect. Consequently, the multi-component heterostructure nanoparticles, which combine the function of different components, are expected to exhibit more distinguished properties. Recently, metal particles depositing on the surface of metal-oxide or carbon materials to form hybrid nanoparticles were reported, which displayed superior electrical or catalytic properties.⁷ For instance, the hybrids of discrete silver nanoparticles depositing on BT surface were used to fill polyvinylidene fluoride. The obtained composites exhibited enhanced dielectric constant and suppressed dielectric loss, or improved electrical breakdown strength.^{7a, 7b}

Silver nanoparticles have been studied in detail because of their good chemical stability and relatively low cost. Numerous literatures reported the principles of synthesis of silver particles with controlled size and morphology, including chemical reduction,⁸ photochemical reduction,⁹ and Pulse sonochemical methods.¹⁰ Among these methods, the common chemical reduction is the polyol process assisted with capping agent.¹¹ In a typical chemical reduction or photochemical reduction process, external energy such as heat, was necessary to promote the reaction. So, it is surprising that we have found silver nanoparticles can be spontaneously deposited on the

surface of BT particles in the ethylene glycol (EG) medium at room temperature without imposing external energy.

The aim of this study is to clarify the formation mechanism of silver nanoparticles on BT surface. The findings could be applicable to the synthesis of other metal hybrid particles.

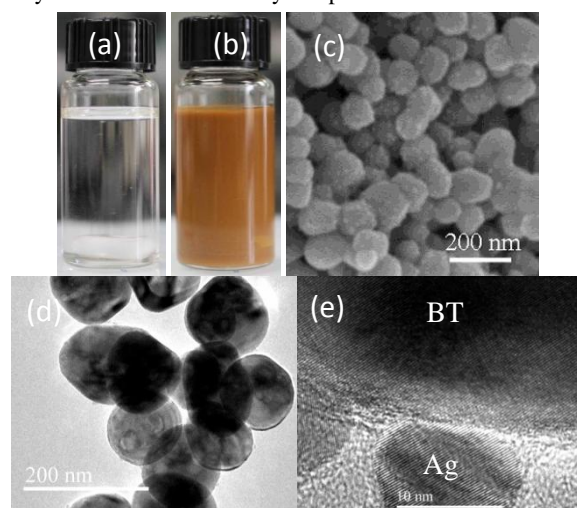


Figure 1. Photographs of (a) AgNO₃/EG and (b) AgNO₃/EG/BT (100 nm) suspensions after magnetically stirred for 2 h at room temperature, and (c) SEM image of resultant particles from the suspension of (b). (d) TEM image of pure BT and (e) HRTEM image of an individual hybrid from the suspension of (b).

In the polyol process to synthesize silver nanoparticles, capping agent like poly(vinylpyrrolidone) (PVP) was usually adopted and the reaction occurred at an elevated temperature ranging from 120 °C to 180 °C.¹² Ag⁺ was not reduced at room temperature due to the low reduction activity of EG. As shown in Figure 1a, the color of AgNO₃/EG solution was always transparent and no change was observed after being magnetically stirred for a couple of hours at room temperature. Magically, the color of the solution turned to

brownish red in a few minutes after adding 100 nm untreated BT particles (Figure 1b). The change of the color indicated that some of the Ag^+ was reduced and silver seeds were formed. After magnetically stirred for 2h at room temperature, the suspension of $\text{AgNO}_3/\text{EG}/\text{BT}$ was analyzed through a scanning electron microscope (SEM). As revealed by the SEM images in Figure 1c, a large amount of nano particles with the size of about 10~20 nm are distributed on the surface of BT particles. The TEM image of BT (Figure 1d) shows that the surface of BT was smooth with the size about 100 nm. The HRTEM image of an individual hybrid from the resultant suspension (Figure 1e) shows that the small particles have a lattice spacing of 2.40 Å, characteristic of the (1 1 1) planes of Ag particles. The BT grain shows a lattice spacing of 2.33 Å, characteristic of the (1 1 1) planes.^{7a} Besides, the EDS analysis (See Figure S4) further confirms that the small particles on BT surface are Ag. The above results indicate that BT nanoparticles perform catalytic effect on the reduction of Ag^+ in EG solution.

During the reducing process, it was the surface of BT that was in contact with the Ag^+ solution. Therefore, it needs to clarify how the chemical state of BT surface promoted the reducing rate of Ag^+ . The commercial BT nanoparticles were fabricated through hydrothermal process (confirmed by the supplier), and it is likely that hydroxyl groups (-OHs) are left on the particle surface. In order to investigate the effect of -OH attached to BT surface on the reduction of Ag^+ , two other samples were prepared for comparison. The as-received BT was heat-treated at 350°C for 10h in order to remove the -OHs on its surface, denoted as BT-T. And the other sample was treated with H_2O_2 in order to attach more -OHs to the BT surface which is denoted as BT-H. The as-received BT was marked with BT-U.

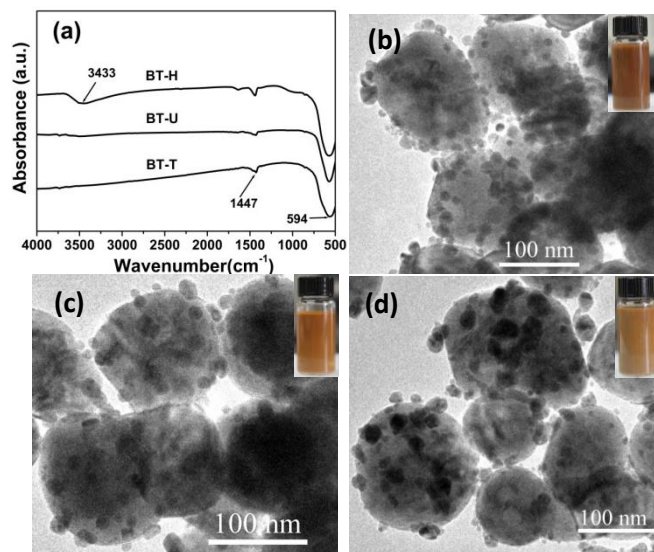


Figure 2. (a) FTIR spectra of BT-T, BT-U and BT-H. (b-d) TEM images of BT-Ag hybrids prepared from BT-T, BT-U, and BT-H, respectively. The insets shows the photographs of suspensions after magnetically stirred for 2 h at room temperature.

The surface chemistry of the three samples was characterized with Fourier-transform infrared (FTIR) spectroscopy. As shown in Figure 2a, the as-received BT-U shows two conspicuous absorption bands at 1447 cm^{-1} and 594 cm^{-1} . The two bands correspond to the stretching vibration of CO_3^{2-} from the residual barium carbonate (BaCO_3) in the BT and the Ti-O vibration in BT, respectively.¹³ A broad band at 3433 cm^{-1} was detected in BT-H which is assigned to the stretching mode of O-H. The -OH contents on the surface of the three types of BT were estimated using Chang's method¹³ which compares the relative intensity of O-H and Ti-O bands from the

FTIR results. The calculated concentration ratios of O-H to Ti-O for BT-T, BT-U and BT-H were 0.01, 0.14 and 0.77, respectively. The content of -OHs in BT-T is 77 folds (BT-H) and 14 folds (BT-U) of BT-T, respectively. The results indicate that the content of -OHs was reduced after 350 °C thermal treatment and increased after H_2O_2 treatment.

Then, the BT-T and BT-H were added into the AgNO_3/EG solution respectively at room temperature, and the color changing progress was recorded with a camera. Photographs were gathered every 10 min from 0 min to 120 min (See Figure S1-3). The color of both suspensions changed after adding the treated BT, but the terminated color and time were different. As shown in Figure 2b-d insets, the terminated colors of BT-T and BT-H suspension were crimson and yellowish-brown, respectively. With the increasing content of -OHs, the terminated color became pale and the terminated time (20 min, 40 min and 60 min for BT-T, BT-U and BT-H, respectively) at which the color stops changing was prolonged. The results suggest that the existence of -OHs on BT surface retarded the reducing rate of Ag^+ and the more -OHs, the lower the reducing rate. TEM images (Figure 2b-d) of these three BT-Ag hybrids show that a large number of Ag nano particles were discretely grown on the surface of BT in granular shape. The size of Ag particles was 8~20 nm, 8~23 nm and 8~30 nm for BT-T, BT-U and BT-H, respectively. The size of larger particles increased with the increasing content of -OHs.

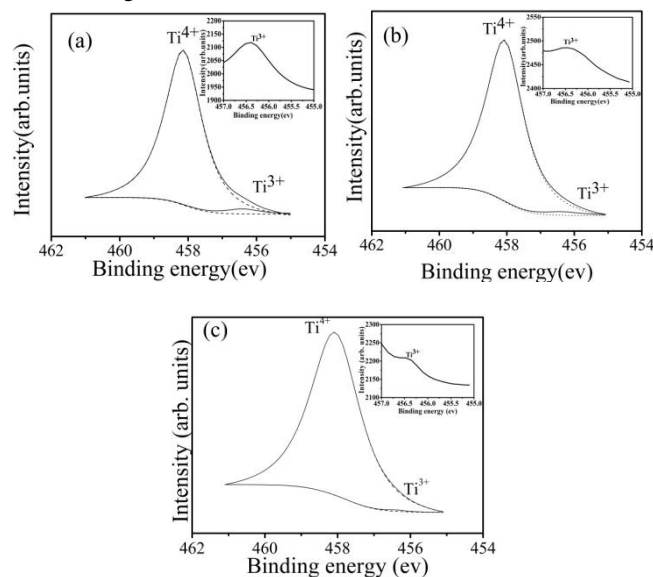
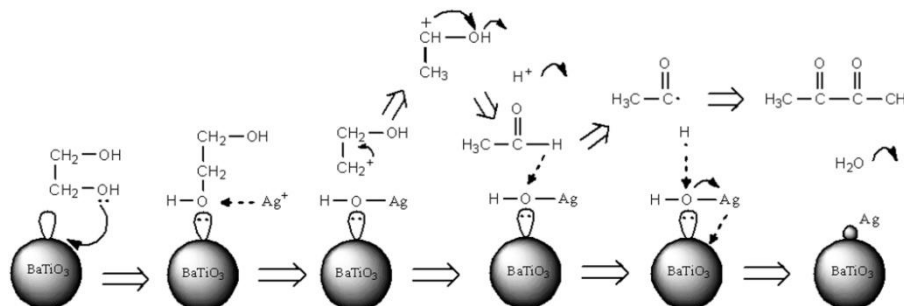
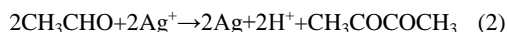
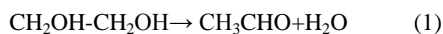


Figure 3. Ti $2\text{P}_{2/3}$ XPS peak for (a) BT-T, (b) BT-U, and (c) BT-H. The insets show the enlarged Ti^{3+} peaks.

The above results revealed that the -OHs delayed the reducing reaction rate of Ag^+ and not acted as catalyst. Since the EG also has -OHs and the reducing reaction needs the -OHs to turn to acetaldehyde, so we consider that the surface -OHs of BT might impede the contact of the -OHs of EG with BT. The oxygen atom of -OHs was apt to occupy the surface oxygen vacancies (Vo) of BT. Thus, it is necessary to analyze the variation of the Vo concentration of the three types of BT. The surface Vo of BT was characterized with X-ray photoelectron spectroscopy (XPS). The XPS results of Ti $2\text{P}_{2/3}$ are presented in Figure 3. The spectra consist of a main component of Ti^{4+} (BE=458 eV) as in the perovskite structure of BT and a very weak component that shifts to low binding energy by 1.6 eV which corresponds to Ti^{3+} .¹⁴ The FWHM of Ti^{4+} XPS profiles increased from 1.34 (BT-T) and 1.4 (BT-U) to 1.7 (BT-H), which

suggests increase of the number of Ti^{4+} species. The relative intensities of Ti^{3+} decrease from 2.81% (BT-T) and 2.35% (BT-U) to 0.33% (BT-H). For the BT grains, reduction of two Ti^{4+} results in two Ti^{3+} and one Vo. Therefore, the surface Vo concentration decreased as the amounts of $-\text{OH}$ s on BT surface increased.

The typical mechanism of the reduction of silver ions by ethylene glycol can be represented by the following reactions:¹⁵



Scheme 1. Schematic illustration of the proposed mechanism of catalytic reducing process of Ag^+ for preparing Ag deposited BT hybrids at room temperature

normal condition. With the addition of BT particles, Ag nanoparticles formed on the BT surface at room temperature and the reaction rate can be controlled by the surface Vo concentration of BT. Based on the above results, we propose the mechanism of the catalytic reducing process of Ag^+ , as illustrated in Scheme 1. The reaction process involves four steps as described belows.

1. The hydroxyl group of EG was dislodged under the catalytic effect of BT. The surface Vo of BT with two positive charges appeals to the center of negative charges of oxygen in EG, which reduces the active energy for reaction and is beneficial for the Ag^+ to attack the hydroxyl group of EG. The resultants were $\text{C}_2\text{H}_5\text{O}^-$ and $\text{BT}-\text{OH}(\text{Ag})$.
2. $\text{C}_2\text{H}_5\text{O}^-$ was re-arranged and meanwhile acetaldehyde and hydrogen ion were produced.
3. Then the silver ion of $\text{BT}-\text{OH}(\text{Ag})$ was reduced by the acetaldehyde to produce acetyl and silver atom.
4. The combination of acetyls forms 2,3-Butanedione. As the reactions proceeded, the concentration of silver atoms reached a critical concentration for nucleation, followed by the growth of Ag nanoparticles.

The FTIR spectra (see Figure S5) of the solution after synthesis revealed that the 2,3-Butanedione was produced after the reaction process. The reducing process occurred on the surface of BT, so that Ag nanoparticles easily grew on it. Meanwhile, due to the similar lattice spacing of the (1 1 1) planes of BT ($d=2.33 \text{ \AA}$) and Ag ($d=2.40 \text{ \AA}$), hetero-epitaxial growth of Ag nanoparticles on the BT surface resulted in strong bonding, which cannot be detached from BT even after ultrasonication.^{7a} With the increase of the content of $-\text{OH}$ s on BT surface, the concentration of Vo was reduced which decreased the catalytic reaction rate. So, the terminated time at which the color of BT-H/ AgNO_3 /EG suspension (60 min) stopped changing was longer than BT-U/ AgNO_3 /EG (40 min) and BT-T/ AgNO_3 /EG (20 min). Simultaneously, the location for silver seed deposition on BT surface was provided by Vo. With the decreasing concentration of Vo on BT surface, the opportunity for silver seeds to deposit on BT surface was reduced, leaving the space for some of the deposited Ag particles to grow to a larger size.

Ethylene glycol is a weak reducing agent and turns to acetaldehyde under external energy to reduce Ag^+ . The reaction ability of EG depends on the formation rate of acetaldehyde. The reducing rate of Ag^+ can be controlled by elevating reaction temperature of the solution which relates to the formation rate of acetaldehyde. Opris et al.¹⁶ pointed out that if the reaction process was carried out without PVP and the temperature was lower than $150 \text{ }^\circ\text{C}$, the reaction could not occur. In this study, the reaction occurred at room temperature at which Ag^+ could not be reduced in

In summary, it is discovered that the BT particles demonstrated catalytic effect for Ag^+ reduction on their surface in EG solution. The reaction activity of EG was enhanced by the surface Vo of BT. The concentration of Vo increased with the decrease of $-\text{OH}$ concentration which resulted in accelerated reducing rate of Ag^+ .

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Notes and references

^a Center for Advanced Materials, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, 518055, China

^b Department of Electronics Engineering, The Chinese University of Hong Kong, Hong Kong, China

† Electronic Supplementary Information (ESI) available: [Details of experimental procedures and characterization were applied.]. See DOI: 10.1039/c000000x/

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COMMUNICATION

Table of Contents (TOC)

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Title: Investigating the Mechanism of Catalytic Reduction of Silver Nitrate on the Surface of Barium Titanate at Room Temperature: Oxygen Vacancies Play a Key Role

The oxygen vacancies on BaTiO_3 surface linked with the hydroxyl oxygen of ethylene glycol and catalyzed the reduction of AgNO_3 .

