

# The study of antireflection coatings doped with Ag nanoparticles utilized in solar cells

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## ABSTRACT

In this work ,We demonstrate a method for producing Ag nanoparticles (AgNPs) with homogeneous size-distribution ,then combine the AgNPs with SiO<sub>2</sub> antireflection(AR) coatings to enhance the transmittance of solar cell glass in visible region. In order to utilize the metal nanoparticles special size and shape effects,especially the localized surface Plasmon effect which can be used to enhance the light transmission efficiency.AgNO<sub>3</sub> and PVP are used to prepare noble particles. The AgNPs have been fabricated by hydrothermal process.AgNO<sub>3</sub> solution added with PVP which plays a role of reductant and surfactant.We obtained relatively homogeneous silver nanoparticles with a approximate size of 160nm by changing the reaction temperature and time.This one step synthesise process is convenient and stable.The SEM image shows the metal particles' growing at five different conditions. The particle has morphology of approximate sphere and triangular plate at the temperature 150°C.As the temperature increasing to 180°C,the sum of triangular plate reduced and polyhedron particles were well shaped and distributed in etanol solution.UV-Vis absorption spectrum of AgNPs shows the single peak at 420nm and multistage peak at a range from 410nm to 600nm. After optimized with AgNPs co-doped into SiO<sub>2</sub> coating,the transmittance of glass were improved to 95% at most. The measurement shows the transmittance of glass coated with different antireflection collosol.

**Keywords:** antireflection coatings ; Ag nanoparticles; localized surface Plasmon resonance; solar cells

## 1 INTRODUCTION

The Ag nanoparticles(AgNPs) exhibit excellent properties such as electrical conductivity, antibacterial activity, chromaticity and the most attractive phenolmenon of local surface Plasmon resonance(LSPR).Those properties make AgNPs have promising applications in electronics, optical labeling,solar cells,catalysis, and biosensing .For example,amorphous Ag stack with Pt protection layer were coated on Alq3 as top electrode to be used for detection unit in test device<sup>[1]</sup>. Ag crystallites were used in the conductive pastes and thin film solar cells to

make the solar cells work stably and efficiently<sup>[2]</sup>. As Feern reported ,Ag nanoparticles is used to color wool fibers composite materials for its antimicrobial an antistatic properties<sup>[3]</sup>.For the antibacterial property, M.I.Mejia use magnetron sputtering method to produce Ag particles with sizes about 4.7nm on textile to prevent bacterial growth in cotton<sup>[4]</sup>. On the surface of Ag nanoparticles ,an obvious increase in the fluorescence emission appears for the metal-enhanced fluorescence phenomenon.In Kwan's report ,Ag nanoparticle was used for the PEI-capped Ag nanoparticles in detecting charged dye molecules by this phenomena<sup>[5]</sup>.The morphology and size of Ag nanostructures have an important effect on its function. In order to utilize AgNPs, researchers have been searched plenty of methods to prepare AgNPs such as citrate reduction, silver mirror reaction and poly process<sup>[6]</sup>. In those chemical methods polyvinylpyrrolidone(PVP) is often used for surface modification agent to accommodate the silver crystal growth<sup>[7-9]</sup>.In this work ,a kind of uniformed AgNPs were doped into AR coatings to enhance the transparency of solar cell glass.A quite convenient method to prepare AgNPs was introduced in this report.The most frequently-used synthesized method is that Keeping the Ag<sup>+</sup> with reductant and surface modification agent in a solution system with a particular reaction condition.The Ag<sup>+</sup> was transformed into Ag by the reductant ,meanwhile, the Ag crystal growing into various shape for the limit of modification agent on the particular crystal face. And in this experiment we conducted, the reductant and surface modification agent was just one subject-PVP,which played two important roles in the reaction. The SiO<sub>2</sub> AR coatings collosol was synthetized by sol-gel method.In the AR coating prepared process AgNPs were invited into the collosol.Long time stirring made the AgNPs dispersing homogeneously.Then the solar cell glass was coated with this SiO<sub>2</sub> AR coatings with AgNPs in it.

## 2 EXPERIMENT:

This type of AgNPs were prepared via hydrothermal process .Analytical grade of AgNO<sub>3</sub>,PVP were purchased by Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China ). First,0.0678 g of silver nitrate was dissolved in 45ml deionized water and the solution was stirred for 30 minutes.Then polyvinylpyrrolidone(PVP,M<sub>w</sub>=10 000) was

added into the solution. After being stirred for 30 minutes the silver nitrate and PVP was well-distributed in the mixed solution. The above process was at room temperature. The homogeneous solution was transfused into Teflon tank which wrapped up with reaction still. The mixed solution was heated to 180 °C and keep reaction at this temperature for 24 hours. The colour of mixed solution changed into faint yellow after 24hours. The resultant solution was washed via ethylalcohol for three times in order to remove the unreacted organic and metal salts. After centrifugation the AgNPs were collected as precipitate. The morphology of AgNPs were examined by scanning electrons microscope (JSM-6390A,JEOL).The UV-Vis absorption properties was characterized by UV-vis spectrophotometer(U-3900,Hitachi).

The antireflection coatings doped with Ag nanoparticles were synthetized through the sol-gel method<sup>[10]</sup>. Precursor solution was prepared by tetraethyl orthosilicate (TEOS) , ethylalcohol (ETOH) and deionized water.Molar ratio of TEOS:ETOH:H<sub>2</sub>O is 1:60:4.The solution of EtOH was divided into two part A and B.Solution A was added with TEOS.Solution B was added with H<sub>2</sub>O. Two solution were stirred for 30 minutes respectively and then solution B was quickly added to solution A.The prepared AgNPs was interfused into mixed

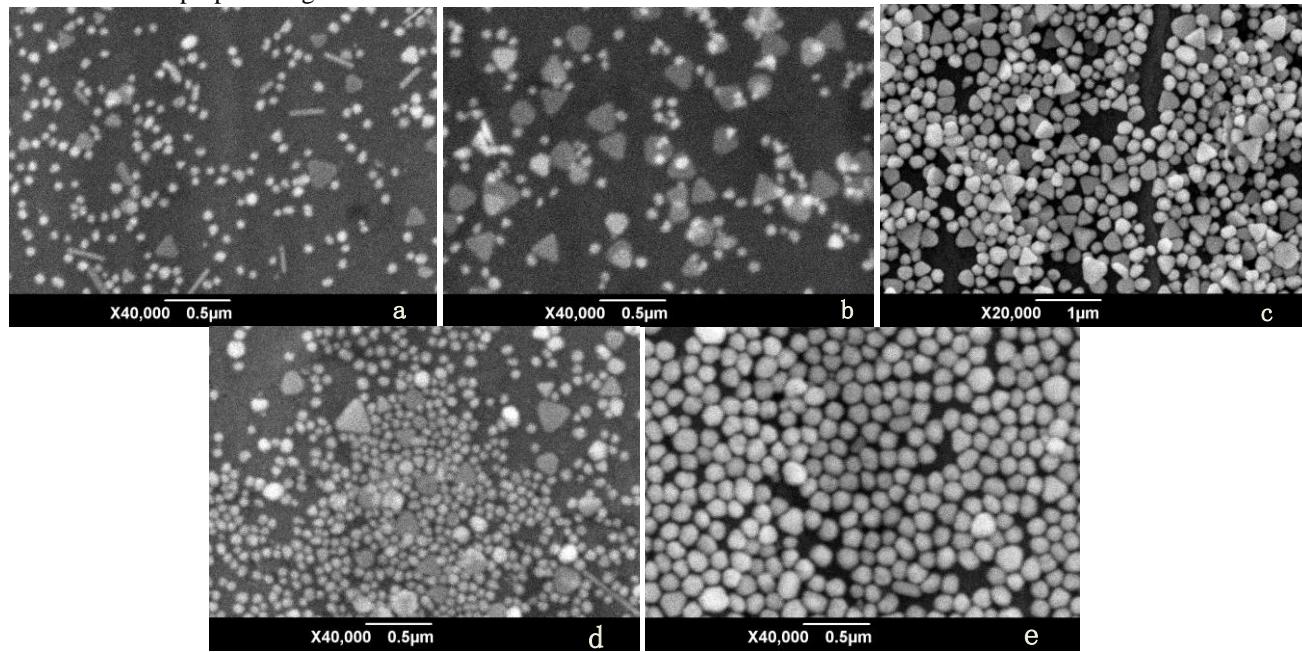


Fig . 1 SEM images of AgNPs prepared at different hydrothermal conditions

Sample a--- 150 °C,6 hours; Sample b---150 °C,12 hours; Sample c---150 °C,18 hours;

Sample d--- 180 °C,6 hours; Sample e --- 180 °C,12 hours

resultant.However,by keeping the temperature at 150°C and increasing the reaction time to 18 hours, the resultant contained more nanoparticles and less other nanostructure. To get relatively homogeneous nanoparticles is the first step in this work.According to the tendency of the three resultant'morphology,we increased the reaction temperature from 150°C to 180°C.The SEM figure 1(d) show that the

solution when it was stirred for 2 hours and then the solution was continually stirred to form collids. The Ag/SiO<sub>2</sub> collid aging was kept for 3 days and coated the collid on the glass substrate by czochralski method to form antireflection coatings(AR-coatings). The transmittance of AR-coatings was measured via UV-vis spectrophotometer(U-3900,Hitachi).

### 3 RESULTS AND DISCUSSION

In many report the surface modification agent plays an important role in shaping the nanostructures .However , in this work changing the reaction temperature and time lead to diverse shape and size of AgNPs when the molar ratio was constant .The morphology of synthesized AgNPs was observed by SEM.Fig 1 shows the various shape and size of AgNPs at different reaction conditions. First ,when the reaction temperature was 150 °C and as the reaction time was controlled for 6hours, there were both particles and a little trilateral plate and nanorod in the product(Fig 1 a).As the reaction time increasing to 12 hours at 150 °C,the trilateral plate became more and there was no nanorods in

major product were polygonal nanoparticles but there also appeared some trilateral plates.When the reaction condition were adjusted to 180°C for 12 hours,the final products were homogeneous nanoparticles. The everage diameter of the uniformed particles was 160nm.The molecule of PVP contains polar lactam and nonpolar methylene, the two functional group make the PVP molecule incline to paste

on the surface of silver. The electron configuration of Ag is  $4d^{10}5s^1$  and this structure is easy to form  $sp^3$  orbital hybridization. In the mixed solution of PVP and  $AgNO_3$ ,  $Ag^+$  combined with the nitrogen atom in the acylamino of PVP to form a complex. As the  $Ag^+$  was reduced for it obtains an electron from nitrogen atom and a nitrogen radical was generated. The nitrogen radical leads to degradation of deuterioxide which generates hydrogen ion ( $H^+$ ) and hydroxyl radical ( $OH \cdot$ ). The nitrogen radical capture an electron from the hydroxyl radical to regain the normal state. The hydroxyl radical became hydroxide ion which combined with  $H^+$  to form  $H_2O$ .

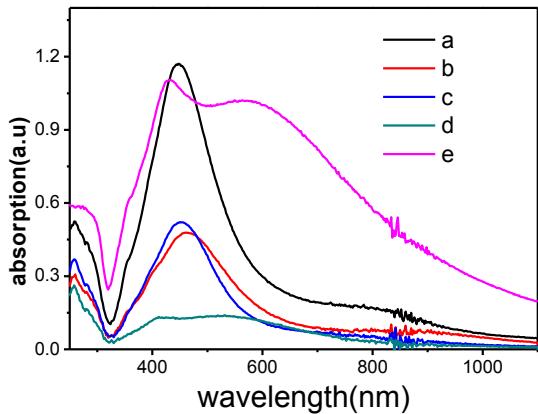


Fig.2 The UV-Vis absorption spectrum of AgNPs

a— $150^\circ C$ , 6 hours. b— $150^\circ C$ , 12 hours.  
c— $150^\circ C$ , 18 hours. d— $180^\circ C$ , 6 hours.  
e— $180^\circ C$ , 12 hours.

Fig 2 shows the result of UV-vis absorption properties. AgNPs was dispersed in ethanol for the absorption tests. It can be concluded from the absorption spectrum that the maximum in the spectrum a and c was both at 450nm. Spectrum b indicates that the maximum has a little shift to 460nm. The product a and c had the similar particles which mainly was AgNPs with a size of 70nm and a small numbers of trigonal plate. The product b contains much more trigonal plate with a length of a side for 270nm. The size of nanostructure has a critical effect on the LSPR of nanoparticles. When change the reaction temperature and time double peak appeared in the absorption spectrum.

The transmittance of AR coatings doped with five different kinds of AgNPs shows in figure 4. In figure 4(a,b,c,d,e) represent five  $SiO_2$  AR coatings collosol doped with five different kinds of AgNPs sample which were shown as figure 1 respectively. N represents AR coating collosol with no Ag doped. According to the measurement, it obviously proves that AgNPs is indeed benefit for the transmittance of AR films based on the glass. Sample e is the most homogeneous particles with a diameter of 160 nm and the result indicates that the AR collosol with this sample exhibits the most excellent transmittance for light. The scattering theory of Mie and Gan have been

calculated for a suitable explanation according to this phenomenon.

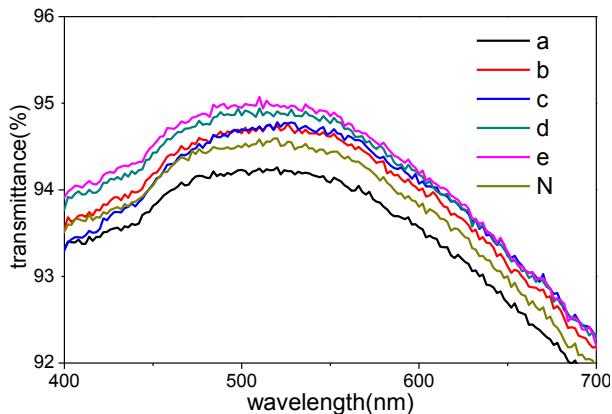


Fig 3. Transmission spectra of AR coatings with AgNPs sample a(a),sample b (b),sample c(c), sample d (d),sample e (e), and no AgNPs sample (N).

The exciting field can be regarded as homogeneous when the size of nanoparticles less than the exciting light in the quasi-static approximation.

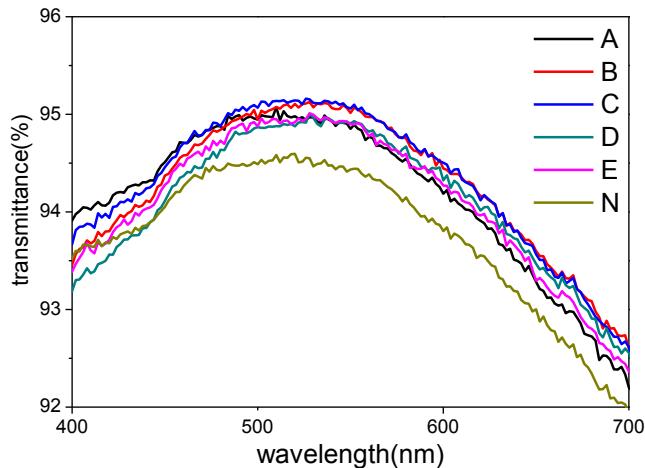


Fig 4. Transmission spectra of AR coatings with AgNPs concentration of 0.004wt.% (A), 0.001wt.% (B), 0.003wt.% (C), 0.005wt.% (D), 0.006wt.% (E), and 0.000wt.% (N)

The simply explanation about optical waveguide in medium of nanosphere can be expressed by equation<sup>[11]</sup>:

$$C_{ext} = \frac{24\pi^2 R^3 \epsilon_m^{3/2}}{\lambda} \left[ \frac{\epsilon_i}{(\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2} \right] \quad \text{where}$$

$C_{ext}$  is the extinction cross section,  $R$  is the radius, and  $\epsilon_m$  is the relative dielectric constant of the medium surrounding the nanosphere. This equation shows that the interaction between a metal nanoparticle and light depends strongly on its dielectric properties ( $\epsilon_r$  and  $\epsilon_i$ ). When the

denominator of the equation approaches zero,  $C_{ext}$  will become large and the optical absorption and scattering at this frequency would be strong. Among the frequently-used materials Ag has the most suitable  $\epsilon_r$ . Fig 5 shows the transmission of AR coatings doped with different quantity of sample e. The result shows that when the concentration of Ag is 0.003wt%, the AR coating has a relative highest transmittance which reaches 95.16% at 526 nm. The light transmission is enhanced not only for the nanoparticles forming light trapping structure to reduce the reflection but also for the noble metal's localized surface plasmons resonance. When the metal NPs is excited, the intensity of the electric field near nanoparticles increases, and this can lead to the forward scattered light and make transmittance of glass improved.

#### 4 CONCLUSIONS

In this work, a particular reaction condition to prepare uniformed AgNPs was confirmed through five groups of check experiments. The morphology and size of silver particles were torispherical polyhedron with an average diameter 160nm. Then the silver particles successfully enhanced the transmittance of AR coatings from 94% to 95.16% at the maximum peak. Compared with the transmission of five different AR coatings, sample e with the most homogeneous shape was found to be the most beneficial for the light transmission. And the suitable concentration of AgNPs was comfirmed through the testing of AR coatings doped with different quantites of sample e. In a word, the transmittance of AR coatings could be enhanced by the LSPR of AgNPs.

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