Effect of Nanoparticles Shape on Conductivity of Ag nanoparticle PVA composite films

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Abstract

In this article, shape effect of silver nanoparticles on photocatalysis and electrical conductivity has been investigated. Different shapes of silver nanoparticles (AgNPs) achieved by varying concentration of NaBH₄ were characterized using particle size, UV-Vis spectroscopy and high-resolution transmission electron microscope. Colors of colloidal solutions were found to be influenced by shape of nanoparticles. The yellow and blue AgNPs were spherical and triangular in shape respectively. Whereas, distorted spherical particles resulted red color and presence of both particles in one solution resulted a green color colloidal solution. All the AgNPs were used to prepare Ag/PVA composite films and their electrical conductivity was investigated. Owing to their better charge carrier generation, uniform distribution in PVA matrix and enhanced surface plasmon resonance blue AgNPs (triangular shaped) exhibited superior conductivity performance

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compared to other nanoparticles. The values for maximum conductivity for blue and yellow AgNPs obtained were $3.45 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ and $2.67 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ respectively.

Keywords: Nano-structures; Polymer nanocomposites; Multifunctional composites; Electrical conductivity;

1. Introduction

Noble metal nanoparticles have recently been recognized as a new class of materials applied in different domains¹⁻². Some noble metals nanoparticles, such as silver (Ag)/Gold (Au) are reported to possess superior optical properties as a function of their particle size and shape³. For certain applications Silver nanoparticles (AgNPs) are preferred over their Au counterpart because of their spectral properties and cost⁴⁻⁵. Nanoparticles of Ag also exhibit brilliant colors and spectral properties of AgNPs can be chemically optimized for yellow, green, red, blue and near IR excitation. Such properties of silver nanoparticles are used for efficient light harvesting and enhanced optical spectroscopies including surface-enhanced Raman scattering (SERS)⁶, molecular detection⁷ and photo thermal cancer therapy⁸. AgNPs also exhibit large absorbing as well as scattering spectrum owing to their Surface Plasmon Resonance (SPR)⁹. Additionally, AgNPs exhibits novel physical, chemical and biological properties, making them suitable candidates in the field of electronics, medicine, photovoltaic, plasmonics, conductive composites and surface coatings.

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Extensive research is pursued in different application domains of Ag nanocomposites and conductive composite is one of such areas. Conductive composites find application in smart, protective coatings and conductive inks. There are various parameters affect conductivity of a nanocomposites and affect structure property relationships¹⁰⁻¹³. One such parameter is the particle shape. Recently, AgNPs have been proposed as a novel photocatalyst for degradation of organic pollutants due to their surface plasmon resonance (SPR) absorption in the visible range¹⁴ which is a function of its particle size and shape. In our previous study, role of particle shape on photocatalytic activity is already reported showing better activity in case of triangular AgNP¹⁵⁻¹⁶. However, effect of shape of AgNPs on the conductivity of Ag/polymer composite films need to be explored.

In the present work, we have made an attempt to tune the morphology of AgNPs by varying the concentration of NaBH₄. AgNPs of different morphology were used to prepare Ag/Poly (vinyl alcohol) (PVA) composite films. PVA was chosen as the matrix because of its easy film forming ability and adhesive characteristics. Additionally, pedant hydroxyl groups of PVA interact with nanoparticles and facilitate the formation of well dispersed polymer nanocomposites¹⁷. Moreover, these composites are commercially used as hydrogels¹⁸, electrospun scaffolds¹⁹, conductive ink²⁰, adhesive²¹, sealants for microchip and antimicrobial smart packaging systems²². It is also known that, conductivity of nanoparticles is a function of size as well as oxidation state of Ag as it slowly oxidizes to form AgO²³⁻²⁴. Therefore, extensive care was taken to maintain the similar oxidation level in different composite films.

2. Materials and method

2.1 Materials

Poly (vinyl pyrrolidone) (SRL, M_w 40,000 g mol^{-1}), tribasic sodium citrate (SRL, $\geq 99\%$), silver nitrate (Loba, $\geq 99\%$), hydrogen peroxide (Thomas Baker, 30% solution), sodium borohydride (CDH, $\geq 98\%$), PVA (Merck, M_w 9000-10,000 g mol^{-1}) and sodium dodecylsulfate (Merck) were used as received. All solutions were prepared using double distilled water (HPLC grade, Merck).

2.2 Methods

Synthesis of silver nanoparticles

Silver nanoparticles were synthesized using Silver nitrate (AgNO_3) as precursor²⁵⁻²⁶. In a typical synthesis, 0.005 mmol AgNO_3 , 0.002 mmol PVP and 0.0067 mmol sodium dodecyl sulphate were dissolved in 10 mL water at ambient temperature. The solution was continuously stirred at 500 rpm for 15 min. 120 μL of 30% H_2O_2 and 0.13 mmol of tribasic sodium citrate were added to the solution and stirred for another 30 min. Freshly prepared borohydride stock solution (35 mM solution) was used to achieve different concentration of sodium borohydride (220 μL (1.54 mmol), 520 μL (3.64 mmol), 990 μL (6.94 mmol), and 1.5 mL (10.5 mmol) in the silver nitrate

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solution. The solution was stirred at 60 °C for 1 h and observed for the color change. The obtained silver nanoparticles were characterized using UV spectrophotometer (Lambda 35, Perkin elmer, USA), particle size analyzer (Malvern Zetasizer Nano ZS, USA), X-ray photoelectron spectroscopy (XPS) (ESCA+Omicron Nanotechnology, Oxford Instruments, Germany) and high resolution transmission electron microscope (HRTEM) (JEM 2100F, JEOL, Japan). Diameter of the nanoparticles was determined as an average of 100 readings using ImageJ software.

Photocatalysis of methylene blue

AgNPs were compared for their photocatalysis behavior using 200 mg/L methylene blue. For the study, 10 µL of AgNPs colloid solution were dispersed in methylene blue solution. The methylene blue solution consisting of nanoparticles was kept in dark for 60 min to attain the adsorption/desorption equilibrium and then exposed to the sunlight for photodegradation. The photocatalytic behavior was analyzed using UV-Vis spectrophotometer.

Preparation of Ag/PVA nanocomposite film

2% (w/v) PVA solution was prepared in DI water. 10-100% v/v of AgNPs colloidal solution were added into the PVA solution and stirred for 30 min at 500 rpm to obtain uniform distribution of AgNPs in PVA. Solution casting was used to prepare the Ag/PVA nanocomposite film. The films were coded as 10-Ag/PVA, 20-Ag/PVA, 50-Ag/PVA and 100-Ag/PVA for 10, 20, 50 and 100% of AgNPs respectively. The obtained films were analyzed for resistivity and

conductivity using an Electrometer (Keithley 6517 B, USA). Dispersion of AgNPs in polymer films was analyzed using field emission scanning electron microscope (FE-SEM) (FEI Quanta 200F, Netherland).

3. Results and Discussion

Synthesis of AgNPs

AgNPs were synthesized by using silver nitrate as precursor and Sodium borohydride as the reducing agent in the presence of polyvinyl pyrrolidone (PVP), hydrogen peroxide, tribasic sodium citrate and sodium dodecyl sulphate. High viscosity of PVP solution not only facilitates viscosity stabilization of colloid, but also controls the rate of reduction and thereby the size and shape of nanoparticle²⁷⁻²⁸. The role of the citrate is to stabilize the Ag^+ cluster and acts as capping agent.

As the NaBH_4 was added into precursor solution, color of solution changed to pale yellow confirming formation of silver nanoparticles²⁹. The growth rate was controlled by varying the concentration of NaBH_4 . Further increase in the concentration of NaBH_4 from 220 to 550, 990 and 1150 μL resulted in change in the color of the colloid from yellow to red, blue and green respectively as shown in Scheme 1. The samples were named according to their color as $\text{Ag}_{\text{yellow}}$, Ag_{red} , Ag_{blue} and Ag_{green} .

Scheme 1. Scheme showing different steps in synthesis of AgNPs and formation of AgNP colloidal solution with different colors at different concentration of NaBH_4 . Where, (a) $\text{Ag}_{\text{yellow}}$, (b) Ag_{red} , (c) Ag_{blue} and (d) Ag_{green} . Note: Duration of each step in nanoparticle synthesis was 15 min and reagents were added under constant stirring maintained at a speed of 500 rpm.

Obtained AgNPs were characterized for their size and shape using particle size analyser and HRTEM respectively. Particle size analysis of AgNPs are shown in **Figure 1 and S1 (Supporting information)**. The $\text{Ag}_{\text{yellow}}$ were found to have a narrow and small peak at 28 ± 8 nm and a broad peak at 154 ± 50 nm. The peak corresponding to 154 nm may be attributed to the aggregated AgNPs. The high surface energy in case of smaller size nanoparticles could result in aggregates. Increasing the NaBH_4 concentration from 220 to 550 μL resulted Ag_{red} , and was found to have a narrow peak at 29 ± 9 nm and a broad peak at 225 ± 75 nm. Further increasing

concentration of NaBH_4 to 990 μL resulted a blue colloidal solution (Ag_{blue}) in single peak corresponding to 56 ± 20 nm for Ag_{blue} . However, a green colloidal solution of AgNPs was obtained when concentration of NaBH_4 was 1150 μL . This green solution of Ag_{green} is due to presence of both $\text{Ag}_{\text{yellow}}$ and Ag_{blue} . The size of Ag_{green} was found to be 159 ± 21 nm. It may therefore be inferred from the results that at low NaBH_4 concentration nucleation is favoured over growth resulting in small spherical nanoparticles. On increasing the NaBH_4 concentration, the growth will be prominent and the size of nanoparticles was found to be increased.

Figure 1. Particle size of (a) $\text{Ag}_{\text{yellow}}$ (b) Ag_{red} (c) Ag_{blue} and (d) Ag_{green} determined by DLS.

HRTEM analysis was performed to confirm the size and morphology of AgNPs. As shown in **Figure 2**, Ag_{yellow} were found to have spherical in shape with an average diameter of 25 ± 10 nm. The Ag_{red} were found to have an average size of 30 ± 15 nm. However, the shape of these nanoparticles was oval/distorted triangular instead of spherical. This indicates transition of spherical to triangular with increasing concentration of NaBH₄. In case of Ag_{blue} well defined triangular shaped AgNPs were observed with average size of 60 ± 25 nm. Although, some distorted spherical and triangular can be seen in the TEM image (Figure 2c) but proportion of such particles were low.

Figure 2. HRTEM micrographs of (a) Ag_{yellow} (b) Ag_{red} (c) Ag_{blue} and (d) Ag_{green}. From TEM images it is evident that AgNP size is increasing with increase in concentration of NaBH₄.

As inferred from particle size analysis and color of colloidal solution, Ag_{green} was found to be a mixture of spherical as well as triangular nanoparticles with an average size of 90 ± 30 nm. It is quite evident from HRTEM analysis that, shape and size of AgNPs can be controlled with the concentration of NaBH₄. However, after certain concentration (990 μ l) further increase in

NaBH₄ concentration (1150 μ L) can lead to uncontrolled growth and mixture particles having different shape and sizes (Figure 2d).

UV-Vis spectra of the particles resemble fairly well with literature³. Ag_{yellow} and Ag_{blue} were observed to have absorption maxima at 395 and 800 nm respectively (**Figure 3**). Ag_{yellow}, being spherical in shape, were found to have single peak in visible spectra corresponding in-plane dipole plasmon resonance peak at 395 nm. In Ag_{red}, the peak for SPR was shifted from 395 to 404 nm. As reported in literature the in-plane dipole plasmon resonance of Ag_{blue} was observed at 600-800 nm³. An additional peak at 330 nm and 398 nm can be attributed to out-of-plane quadrupole and in-plane quadrupole plasmon resonance of triangular nanoparticles, respectively. Anisotropic triangular silver nanoparticles are reported to have high SERS intensity owing to their three surface plasmon resonance (SPR) bands corresponding to dipole and quadrupole plasmon resonance, while only one SPR band is reported for spherical silver nanoparticles. Ag_{green} being mixture of spherical and triangular AgNPs showed SPR matching with yellow as well as blue AgNPs.

Figure 3. UV- Vis spectra of (a) Ag_{yellow} (b) Ag_{red} (c) Ag_{blue} and (d) Ag_{green}.

XPS analysis of AgNPs

It is already reported in literature that, different oxidation states of Ag (Ag^0 or Ag^{+2}) in nanoparticle can influence their conductivity³⁰⁻³¹. To evaluate the state of Ag in nanoparticles, XPS analysis of PVP stabilized Ag nanoparticles were carried out. To nullify charging effect, all XPS spectra were corrected by taking binding energy (BE) of C1s peak (285.0 eV) as reference³²⁻³³. **Figure 4** shows the high resolution XPS scans in Ag 3d_{5/2} region of Ag_{yellow} and

Ag_{blue}. BE of Yellow and Blue Ag nanoparticles were found to be 368.3 eV and 368.0 eV respectively (See Table S1). Depleted valence electrons and higher lattice strain in case of small particles contribute to such positive shift ($\Delta E = +0.3$ eV) in core level binding energy of Ag_{yellow}³⁴⁻³⁶. Additionally, similar contour of high resolution scans in Ag 3d region of both Ag nanoparticles indicates the composition of Ag⁰ is (71% in Ag_{yellow} and 67% in Ag_{Blue}) similar in both nanoparticle samples.

Figure 4. (a) High resolution XPS scan in Ag3d region of Ag_{yellow} and Ag_{blue} showing the change in binding energy arising due to size of nanoparticle, (b) Higher binding energy of O1s spectra in case of Ag_{yellow} suggest the adsorption of PVP in this case is predominantly by carboxyl Oxygen (C=O) of PVP, (c) High resolution XPS scan in N1s region of Ag_{yellow} and Ag_{blue}. Positive shift in BE of Ag_{blue} nanoparticle is an indication that more number of vinyl pyrrolidone moieties interact with Ag nanoparticle surface via N atom.

More insight on chemisorption of PVP on different Ag nanoparticles emerged when BE of O1s and N1s of both nanoparticle samples were compared. Positive shift in BE ($\Delta E = + 4$ eV) of O1s spectra was observed in case of Ag_{yellow} compared to Ag_{blue} (Figure 4b). Such changes in binding energy may arise due to chemisorption of PVP on Ag nanoparticle surface predominantly via carboxyl O atom (C=O)³⁷⁻³⁸. On contrary, higher binding energy ($\Delta E = + 3$ eV) of N1s spectra in case Ag_{blue} is may be due to adsorption of PVP by N atom (Figure 4c and Figure S3)³⁹⁻⁴⁰. It is worth mentioning here that, shape of nanoparticle is the major contributing factor for such difference in adsorption mechanism of PVP.

Photocatalytic activity of AgNPs

Photodegradation of methylene blue in presence of AgNPs carried out to evaluate the catalytic activity of different nanoparticles. The nanoparticles were dispersed in dye solution (0.02 % w/v) and placed in dark for 60 min to achieve adsorption-desorption equilibrium followed by exposure to sunlight and analysis of their photocatalytic behavior.

The dye degradation behavior of $\text{Ag}_{\text{yellow}}$ and Ag_{blue} is shown in **Figure 5**. Ag_{blue} exhibited ~18% higher degradation as compared to $\text{Ag}_{\text{yellow}}$. As confirmed by XPS analysis, both the NPs contains similar proportion of Ag^0 , suggesting the extent of dye degradation is a function of morphology of nanoparticles. The triangular nanoparticles had two peaks in UV spectra indicating efficient SPR, resulting more active sites on nanoparticles and leading to better dye degradation. The k_d value for $\text{Ag}_{\text{yellow}}$ and Ag_{blue} were estimated to be 16.3×10^{-3} and $19.3 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ respectively. It may therefore be deduced from the results that enhanced SPR of triangular AgNPs make them efficient photocatalyst compared to spherical nanoparticles.

Figure 5. Degradation of methylene blue in presence of (a) $\text{Ag}_{\text{yellow}}$ and (b) Ag_{blue} under sunlight. C_0 and C are the initial concentration and concentration at a given time respectively.

Ag/PVA composite films and their conductivity

The morphology of 20-Ag/PVA composite films was analyzed using FESEM. As shown in **Figure 6**, uniform distribution of AgNPs was observed in PVA in triangular silver nanoparticles (Ag_{blue}). $\text{Ag}_{\text{yellow}}$ incorporated PVA composite films although exhibited good dispersion but the distribution of AgNPs was not uniform.

Figure 6. FESEM micrographs of (a) only PVA film, (b) 20- $\text{Ag}_{\text{yellow}}$ /PVA nanocomposite film showing limited distribution of AgNPs in PVA matrix (c) 20- Ag_{blue} /PVA nanocomposite film indicating a uniform distribution of AgNPs.

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Difference in AgNPs distribution in PVA matrix can be attributed to mode of interaction between PVP with AgNPs. As it was found from XPS analysis that, in case of Ag_{yellow}, PVP interacts with Ag preferably through oxygen atoms. In such situation, oxygen atom of PVP is no longer be available for Hydrogen bonding with PVA matrix (Scheme 2a). This restricted interaction between supported AgNPs and matrix can hinder the uniform distribution of AgNPs in PVA matrix. In contrary, triangular shaped Ag_{blue} facilitates PVP and AgNP interaction via N atom, enabling oxygen atom of PVP to form H-bonding with PVA matrix (Scheme 2b) and achieve uniform distribution of nanoparticles. Influence of different mode PVP-AgNP interaction became more pronounced when AgNP loading was increased (i.e. 50-Ag/PVA). Though, cluster formation was observed (see Figure S2) in both 50-Ag_{yellow}/PVA and 50-Ag_{blue}/PVA, size of clusters remained much smaller in case 50-Ag_{blue}/PVA. This confirms better distribution of Ag_{blue} NPs in PVA matrix, as a result of improved Ag-PVP-PVA interaction in presence of triangular AgNPs. The presence of Ag inside composite films was confirmed by Energy dispersive X-ray spectroscopy (EDX). Both yellow and blue AgNPs incorporated PVA composite films showed the presence of Ag (**Figure S2**)

Scheme 2. Schematic representation of interaction between AgNP-PVP-PVA when particle shape is (a) Spherical (Ag_{yellow}) and (b) Triangular (Ag_{blue}). In case of spherical particles formation of H-bond between PVP and PVA is limited due to the interaction of PVP with AgNPs via Oxygen atom. On the other hand, in triangular nanoparticles interaction of PVP via N atom facilitates H-bond formation between PVA and PVP.

The influence of concentration as well as shape of silver nanoparticles on conductivity of Ag/PVA composite films was analyzed and is shown in **Figure 7**. The conductivity of PVA film without any AgNPs was found to be $0.0199 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$. Incorporation of AgNPs resulted in increased conductivity of all Ag/PVA composite films. The observed conductivity values for 10-Ag/PVA composite films were 0.85 , 0.915 , 0.977 and $1.07 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ for Ag_{yellow}, Ag_{red}, Ag_{blue} and Ag_{green} respectively. On increasing AgNPs concentration from 10 to 20 and 50 %

proportional increase in the conductivity was observed. Interestingly, in case of 100-Ag/PVA composite films, the effect of shape became more prominent. 100-Ag_{blue}/PVA(triangular AgNPs) exhibited maximum conductivity value of $3.45 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$. 100-Ag_{yellow}/PVA (spherical AgNPs) on the other hand, showed minimum conductivity of $2.67 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$. As XPS analysis clearly indicates that the extent of oxidation of Ag to AgO is same in both Ag_{yellow} and Ag_{blue}. Such difference in conductivity can arise from enhanced surface plasmon resonance and uniform distribution of AgNPs in case of Ag_{Blue}

Figure 7. Conductivity of Ag/PVA composite films at different loading of (a) Ag_{yellow} (b) Ag_{red} (c) Ag_{blue} and (d) Ag_{green}. Note: 100-Ag/PVA means, no PVA was to prepare composites, As prepared PVP stabilized NPs were used for analysis.

Conclusions

Silver nanoparticles of different shape and size were successfully synthesized by changing the concentration of NaBH₄. Depending on shape and size, AgNP colloidal solution were of yellow, red, blue and green color. The particle size and HRTEM analysis confirmed the increase in size of AgNPs with rise in NaBH₄ concentration. HRTEM analysis also confirmed the spherical and triangular shape of yellow AgNPs and blue AgNPs respectively. UV analysis confirmed the enhanced SPR of blue AgNPs showing three peaks as compared to single SPR for yellow AgNPs. Composite Ag/PVA films (10, 20, 50 and 100%) were investigated for their electrical conductivity. A proportional increase in the conductivity was observed by increasing AgNPs concentration to 10, 20 and upto 50%. Further increase in concentration to 100 %, led to significant increase in the conductivity of triangular AgNPs as compared to yellow AgNPs. The values for maximum conductivity for AgNP-PVA nanocomposites having Ag_{blue} and Ag_{yellow} were found to be $3.45 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ and $2.67 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ respectively. XPS analysis indicated the influence of particle shape on distribution in PVA matrix. In spherical AgNPs interaction of PVP and Ag is preferably via O atom while in anisotropic triangular AgNPs PVA

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interacts with Ag preferably via N atom. The O atom of PVP available for H-bonding with PVA is likely to facilitate uniform distribution of blue AgNPs in PVA matrix. Blue AgNPs, owing to their uniform distribution in PVA, better charge carrier generation and enhanced surface plasmon resonance exhibited superior conductivity as compared to Yellow AgNPs.

Supporting Information (SI)

Electronic Supporting Information (ESI): Particle size analysis of AgNPs, EDX spectra of Ag/PVA composite films and XPS Spectra for yellow and blue AgNPs.

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