Green Synthesis of Silver nanoparticles using piper nigrum extract for Dye Sensitized Solar Cell Applications

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We report a facile green synthesis method for the production of silver nano particles (AgNPs) using the aqueous extract of piper nigrum (commonly known as black pepper) as reducing and capping agent. The as synthesized AgNPs colloid was mixed with titanium dioxide slurry to produce Ag:TiO₂nanocomposite. The green synthesized AgNPs and Ag: TiO₂nanocomposite were characterized using X-ray diffraction (XRD), Fourier Transmission Infra-Red Spectroscopy (FTIR), UV-vis-NIR spectroscopy, Field Emission Scanning Electron Microscopy (FESEM) with Energy Dispersive Spectroscopy (EDS), Scanning Electron Microscopy with Back Scattered Electron (BSE) and Transmission Electron Microscopy (TEM).

Keywords: Green synthesis, Ag:TiO₂nanocomposite, X-ray diffraction, Field emission scanning electron microscopy, TEM.

1 Introduction

A number of physical, chemical and biological synthesis methods have been used for the preparation of noble metal nanoparticles. Usually, physical methods employ high temperature, pressure and energy while most of the chemical methods use toxic and hazardous chemicals. The above drawbacks can be overcome by synthesis of metal nanoparticles through biological method. In biological method, nanoparticles are produced using either microorganism or plant materials. Biological synthesis of nanoparticles using microorganism (bacteria, fungi, actinomycetes and algae) is relatively expensive and time consuming rather than plant extract[1,2]. As a result, plant extract is used for the synthesis of metal nanoparticles because of cost effective and eco friendly nature. In recent years green synthesis of metal nanoparticles has assumed great importance owing to their wider applications in the areas of electronics, medicine and agriculture [3,4].

Plant extracts containing biomolecules, such as flavonoids, phenols, tannis, terpenoids, alkaloids, lipids, proteins, aldehydes, ketones, alcohols, carboxylic acids and so on may act as both reducing and capping agent in the green synthesis of noble metal nanoparticles. The functional groups present in the plant extracts react with metal ions and restrict the size of resulting particles into nano range. Furthermore, they serve as capping agent over the synthesised metal nanoparticles, hence providing stability as well as biocompatibility [2]. However concentrations of plant extract and substrate (metal ion), pH, temperature and exposure time affect the size, shape and stability of the nanoparticles [5, 6]. In the present work, we report the green synthesis of silver nanoparticles using the extract of black pepper as a reducing and capping agent. This method is simple, efficient, economic and environmentally benign. The green synthesized silver nanoparticles were mixed with the TiO₂nanoparticles for the Dye Sensitized Solar Cell (DSSC) applications. Because titania has some drawbacks which are (i) TiO₂ exhibits photocatalytic activity in the UV region only due to large band gap (anatase3.2 eV). (ii) TiO₂ shows fast recombination of electron-hole pair where the electrons in the conduction band can easily recombine with the valance band holes [7]. These limitations are overcome by incorporation of plasmonic silver nanoparticles into TiO₂ which reduces the recombination of electrons and improves the visible light harvesting and hence improve the efficiency of DSSC compared to bare TiO₂.

2 Experimental

2.1 Materials

Black Pepper and AgNO₃ were used as the preliminary materials for green synthesis of Ag nanoparticles. Black Pepper was collected from local grocery shop and AgNO₃ was purchased from Merck, India. Type 1 water (Milli– Q, 18.2 MΩ cm at 25°C) was used as solvent in the experiment. The Degussa P25 TiO₂ powder with the following features, such as crystallite size = 25 nm, BET
surface area = 48 m$^2$/g, anatase : rutile = 80:20, purchased from Evonik Degussa India Pvt. Ltd, Mumbai, India), polyethylene glycol (molecular weight = 600, Thomas Baker) and ethanol (China) were used for slurry preparation.

### 2.2 Preparation method of leaf extract

Black pepper were collected and washed with tap water twice then washed with Type 1 water. The cleaned pepper was shade dried for 2 days at room temperature. The dried pepper was ground into fine powder using kitchen blender. The fine powder of pepper weighing 5 g was boiled for 10 minutes using 100 mL of Type 1 water at 60°C. After cooling, the mixture was centrifuged (10,000 rpm, 5 minutes) and filtered using Whatman filter paper to obtain pepper extract. Initial pH of the pepper extract was found to be 6.53. The pH value of the pepper extract was attuned to 10 using 1 M NaOH solution. The resultant pepper extract was used for further synthesis process.

### 2.3 Synthesis of silver nanoparticles

The pepper extract was added drop by drop in 100 mL of 1 mM silver nitrate solution (pH = 5.23) under stirring till the pH value of the solution reached 10. The pale AgNO$_3$ solution changed from light yellow into dark brown by the addition of pepper extract. The colour change is the pointer of the formation of silver nanoparticles [8]. The silver nanoparticles were collected by centrifuging at 10,000 rpm for 15 minutes. The Ag nanoparticles were purified by washing with Type 1 water and ethanol by centrifuging at 10,000 rpm for 15 minutes. The last residue of the silver nanoparticles was dried in an oven at 60°C for 24 hours for further characterization studies.

### 2.4 Synthesis of AgNPs mixed TiO$_2$ nanocomposite

Degussa P25 titanium dioxide (1.8 g) was added gradually into mixer of Zirconia ball, ethanol and 1.8 mL of PEG. The stuffing were thoroughly mixed and stirred for half an hour then the purified colloidal silver nanoparticles was added to the well-dispersed TiO$_2$ slurry. The final mixture was kept into the pot-mill for a month. The similar procedure was followed for pure TiO$_2$ slurry apart from mixing of AgNPs. The resulting pure TiO$_2$ and Ag:TiO$_2$ nanocomposite slurry were used for preparing photoanodes of DSSCs.

### 3 Results and Discussion

The X-ray diffractogram of green synthesized AgNPs powder is shown in Fig. 1(a). Five Bragg peaks are observed at the angles of 2θ = 20.38.06°, 44.29°, 64.60°, 77.47° and 81.66° which correspond to the (111), (200), (220), (311) and (222) planes respectively, which may be indexed to the face centred cubic (fcc) crystal structure of silver (JCPDS card no 004-0783). The well resolved and strong XRD pattern clearly showed that the AgNPs formed by the reduction of Ag$^+$ ions using pepper extract are crystalline in nature [8]. Fig. 1(b) shows that XRD pattern of Ag:TiO$_2$ is composed of mixed anatase and rutile phases, which are in good agreement with the reference patterns of JCPDS card no. 21-1272 and 04-0551 respectively. The diffraction peaks observed at the angles of 2θ = 20.6°, 25.4°, 38.0°, 48.1°, 54.1°, 55.2°, 70.4° and 75.2° correspond to the anatase phase of TiO$_2$ and are assigned to the (101), (004), (200), (105), (211), (220) and (215) sets of crystallographic planes, respectively. The peaks at the 2θ values of 27.5°, 62.9° and 69.1° agreed well with rutile phase of the TiO$_2$ and are assigned to the (110), (002) and (301) sets of crystallographic planes respectively. In Fig. 1(b), the crystallographic peaks of silver are not clearly visible due to the low concentration of Ag. The nonappearance of any additional peaks in XRD patterns reveals the purity of the samples [9].

![Figure 1 XRD patterns of (a) synthesized AgNPs and (b) Ag:TiO$_2$ nanocomposite film](image-url)
of the presence of protein in the pepper extract which may bind over the silver nanoparticles through free amino groups or carboxylate groups and responsible for the stability of the nanoparticles [10]. The band 459 cm$^{-1}$ confirmed TiO$_2$ present in the silver nanoparticles.

Figure 2: FTIR spectra of (a) synthesized AgNPs and (b) Ag:TiO$_2$ nanocomposite

![FTIR spectra](image)

<table>
<thead>
<tr>
<th>Synthesized AgNP powder</th>
<th>Ag:TiO$_2$ nanocomposite powder</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>Wavenumber (cm$^{-1}$)</td>
<td></td>
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<tr>
<td>3357</td>
<td>3424</td>
<td>- OH stretching vibration of hydroxyl group [11]</td>
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<tr>
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<td>2935</td>
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<tr>
<td>1636</td>
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<td>-C=O stretching of amides (carbonyl and carboxylic stretching bands of peptide linkage of the protein) [13]</td>
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<tr>
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<td>C-N stretching vibration of aromatic amine [14]</td>
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<td>1080</td>
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</tr>
<tr>
<td>574</td>
<td>567</td>
<td>OH bending of the phenolic groups [16]</td>
</tr>
<tr>
<td>---</td>
<td>459</td>
<td>Ti-O stretching vibration [17]</td>
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</tbody>
</table>

Table 1. FTIR spectroscopic data of synthesized AgNPs and Ag:TiO$_2$ nanocomposite

Figure 3: UV-vis-NIR absorbance spectrum of (a) synthesized AgNPs, (b) pure TiO$_2$ film and (c) Ag:TiO$_2$ nanocomposite

![UV-vis-NIR absorbance spectrum](image)
The optical absorbance spectra of the green synthesized Ag nanoparticles, pure TiO$_2$ film and Ag:TiO$_2$ nanocomposite are shown in Figs. 3(a-c). The basic absorption wavelength of silver nanoparticles generally occurs in the range of 400 – 500 nm [18]. As seen in Fig. 3(a), the sharp absorbance peak at 413 nm corresponds to the surface plasmon resonance (SPR) of silver nanoparticles [19, 20]. The pure TiO$_2$ film does not absorb the light in the visible region due to its wide band gap as shown in Fig. 3(b) [21]. The absorption spectrum of Ag:TiO$_2$ nanocomposite film shown in Fig. 3(c) which show a broad absorption in the visible region centred at 438 nm, which is mainly due to the SPR of AgNPs. As compared to the silver colloid, the absorption band for Ag:TiO$_2$ film is red-shifted and broadened owing to the high refractive index (n = 2.52) of anatase TiO$_2$ [22].

The morphology of the synthesized samples were observed using FESEM. The FESEM image for green synthesized AgNPs is shown in Fig. 4(a), which appears to be spherical shape with an even size and average particle size is 35 nm. Fig. 4(b) shows the FESEM image for Ag:TiO$_2$ nanocomposite powder. The bright particles observed in this micrograph are expressive the presence of silver nanoparticles which are uniformly spread in the TiO$_2$ matrix [23, 24]. From this figure it is also observed that no important change in the morphology of the TiO$_2$ is noticed upon the mixing of AgNPs.

The results of Back Scattered Electron (BSE) image and elemental mapping of the Ag:TiO$_2$ nanocomposite are shown in Fig. 5(a). Accelerating voltages of 15 kV was applied for BSE image analysis. The lighter and heavier atoms in the BSE images show up as grey and white regions related to the TiO$_2$ and AgNPs respectively. This analysis confirms that the AgNPs are evenly distributed in the TiO$_2$ matrix. Elemental mapping also confirms the even distribution of AgNPs throughout the TiO$_2$ matrix. The EDX results for Ag:TiO$_2$ powder, shown in Fig. 5(b), confirms the presence of Ti, O and Ag and elemental composition analysis as inserted in the EDX image.
Figure 5: (a) Back scattered electron imaging and elemental mapping and (b) EDX spectrum of AgNPs mixed TiO$_2$ NPs composite.
TEM images were used to determine the particle size distribution of synthesized nanoparticles. The TEM image of synthesized Ag:TiO$_2$ nanocomposites slurry is pictured in Fig. 6(a) which clearly indicates that the Ag:TiO$_2$ nanocomposites are predominantly spherical shapes. The dark spots in Fig. 6(a) reveal the presence of AgNPs on the surface of TiO$_2$.

The typical size distribution of histogram is shown in Figure 6(b) the average particle size was found to be 26.28 ± 1.28 nm. The lattice resolved HRTEM image of the Ag:TiO$_2$ shown in Fig. 6(c), here the d-spacing values for the lattice fringes of 0.35 nm and 0.24 nm, which corresponds to the (101) and (004) planes of anatase TiO$_2$, respectively. Fig. 6(d) depicts the selected area electron diffraction (SAED) pattern of the nanocrystalline Ag:TiO$_2$ composite. The characteristic bright concentric ring patterns clearly reveal the diffraction from the (200), (101) and (101) planes of Ag, rutile and anatase TiO$_2$, respectively.
4 Conclusions

Silver nanoparticles were synthesized via simple, economic, efficient and eco-friendly green synthesis route using the aqueous extract of *pipernigum*. The pepper extract has served as a reducing and capping agent. The as synthesized AgNPs colloid was mixed with titanium dioxide slurry to produce Ag:TiO$_2$ nanocomposite. The green synthesized silver nanoparticles and Ag:TiO$_2$ nanocomposites were characterized by XRD, FTIR, UV-vis-NIR spectroscopy, FESEM, BSE and TEM. This novel approach for the green synthesis of silver and Ag:TiO$_2$ nanocomposite holds many precious attractions and offers capable and economic route to production of DSSC.

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