Optical Characterization of Chemically Reduced Silver Nanoparticles for Dye Sensitized Solar Cells

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Noble metal nanoparticles (NPs) are found their potential applications due to their physical, chemical and biological properties as compared to the bulk materials. In this work, colloidal silver (Ag) NPs are prepared by chemical reduction method and various investigations are presented using UV-vis spectroscopy, fluorescence (FL) spectroscopy, dynamic light scattering (DLS) particle size analyzer, Fourier transform infrared (FTIR) spectroscopy and energy dispersive X-ray (EDX) spectrometer. The transmittance spectrum (UV) showed the presence of Ag NPs at the lower spectral region, and FL study revealed the emission peak of colloidal Ag NPs at wavelengths of 360 nm and 645 nm with the excitation wavelength of 320 nm. FTIR spectrum endorsed the various functional groups related to the elements present in the sample. The average diameter of the Ag NPs is 58 nm as estimated by DLS technique. EDX spectra confirmed the peaks of elements confirming the formation of Ag NPs. Further, Ag NPs are used in the dye-sensitized solar cell (DSSC) fabrication and result is explored.

Keywords: Nanoparticles, Silver, FTIR, EDX, DSSC.

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1. INTRODUCTION

Silver nanoparticles (Ag NPs) are one of the most attractive inorganic materials because of its applications in catalysts, antimicrobial, diagnostics, optical, electrochemical devices, solar cells etc. In general, the optical and electronic properties of metals depend on their structure, for example, nanoparticles, nanotubes, nanowires, nanocubes, nanosheets etc. Among these, synthesize of Ag nanoparticles can be done by using chemical reduction, laser ablation, microwave radiation assisted synthesis, thermal decomposition of silver compounds and bio-green synthesis routes. From these methods, the chemical reduction method is used to prepare colloidal Ag NPs with their stable and distinct shape by using reducing agents such as hydrazine, ammonium formate, dimethylformamide and sodium borohydride [1, 2]. Parveen et al. investigated the surface plasmon resonance effect of prepared Ag NPs and electrochemically deposited on the TiO_2 photoanode for dye-sensitized solar cell (DSSC). They reported the enhanced current density from 6.3 to 129 $\mu A/cm^2$. This enhancement was due to the light absorption and improved the charge carrier separation of the Ag NPs and TiO_2 respectively [3]. Lokman et al. studied the thickness effect of TiO_2 photoanode along with the integration of Ag NPs. They employed the chemical reduction method to synthesize Ag NPs. The conversion cell efficiency was 6.92 % which was attributed to the induced plasmonic effect by the Ag NPs [4]. Liu et al. synthesized TiO_2 nanotubes in presence of Ag nanoparticles using in-situ photodeposition process. Ag-TiO_2 nanotube composite was used as a photoanode in DSSCs and showed 7.2 % cell efficiency and 53.63 % fill factor [5]. Bonsak et al. fabricated Ag NPs by chemical reduction method for solar cell applications. The particle size was varied in accordance to the choice of reducing agents such as sodium borohydride and trisodium citrate dihydrate. After the synthesis, those particles were deposited on bulk silicon solar cells which showed 9 % enhanced quantum efficiency in infra-red spectrum [6]. Christy et al. prepared the synthesis of Ag NPs using chemical reduction method and studied their optical, structural and morphological properties for antimicrobial activity. The EDX spectrum showed the presence of silver whereas the formation of face-centered cubic (FCC) structure was confirmed by XRD pattern [7]. Berginc et al. prepared and studied colloidal Ag NPs solution by sol-gel method for DSSC applications. These silver nanoparticles were deposited on the porous TiO_2 layer using dip-coater and optical absorption measurements. The Ag NPs deposited on porous TiO_2 layers showed the enhanced performance of the DSSC. The improved performance was attributed to the induced plasmonic effect [8]. Saravanan et al. studied the power conversion efficiency of DSSCs using Ag NPs. The photovoltaic performance was found improved with the addition of 2 wt. % Ag NPs and enhanced cell efficiency from 2.83 to 3.62 % was noticed [9].

This paper presents the synthesis of Ag NPs via chemical reduction method for DSSC application. The source materials and synthesis procedural steps are presented in section 2. The results obtained after various characterization are discussed in section 3. Finally, section 4 concludes the paper.

2. EXPERIMENTAL APPROACH

The experimental procedural steps are shown in Fig. 1. At first, the silver nitrate (1.5 mg of $AgNO_3$) solution was prepared using 30 ml deionized water and named as solution 'A'. Next, the solution 'B' was pre-

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pared by using aqueous based sodium borohydride (2 mg of $NaBH_4$). All these solutions were kept in ice to prevent the agglomeration during the synthesis process. The formation of colloidal silver NPs was noticed after the addition of solution 'A' into solution 'B'. Here, the $NaBH_4$ acts as the highly reducing agent. After the synthesis process, the resultant solution appeared like dark green which was turned to change transparent (green) color after the centrifuging it. By centrifuging the solution at 10000 rpm silver NPs were collected.

Optical measurements of the prepared colloidal Ag NPs were carried out by using UV spectroscopy (Perkin Elmer-Lambda 35), fluorescence (FL) spectroscopy (Perkin Elmer-LS 45, USA), Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer-Spectrum Two, USA), dynamic light scattering (ZETA, UK), energy dispersive X-ray (EDX) spectroscopy (APEX, Germany).

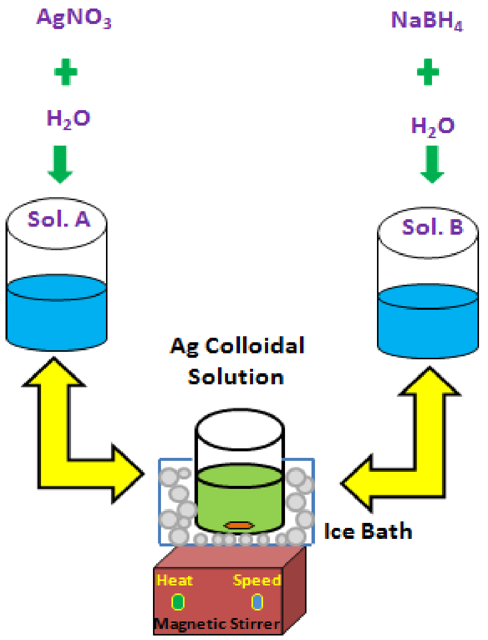

Fig. 1 – The experimental steps of the chemical reduction process of Ag NPs

3. RESULTS AND DISCUSSION

Fig. 2 illustrates transmittance spectrum of colloidal silver NPs in the wavelength range from 190 to 1100 nm. Transmittance spectrum shows the highest transmission at a wavelength of 350 nm which corresponds to the Ag NPs. In general, metal NPs (Ag, Au and Cu) possess high optical transmittance in shorter wavelength region [10, 11]. The FL emission spectrum of colloidal silver NPs is shown in Fig. 3. We can observe peaks at wavelength of 360, 421, 645 and 719 nm at the excitation wavelength of 320 nm. As the excitation wavelength (λ) increased, the electrons will be excited to the low energy level due to that these electrons will be emitted to the higher wavelengths (infrared). Particularly, the intense peak observed at a wavelength of 645 nm is associated with the excitation of electrons from the lower to higher energy level. In the shorter wavelength region, smaller emission peaks can be observed. In fluorescence emission peaks of Ag NPs at excitation wavelength below 420 nm, the lower spectrum emission peaks may not appear [12, 13].

The colloidal silver NPs were studied to analyze the functional group by FTIR in the range from 600 to 4000 cm^{-1} as shown in Fig. 4. The prepared NPs exhibit two major transmittance peaks at 1635 cm^{-1} and 3315 cm^{-1} which are related to the C=C and O-H functional groups respectively. Similarly, result has been

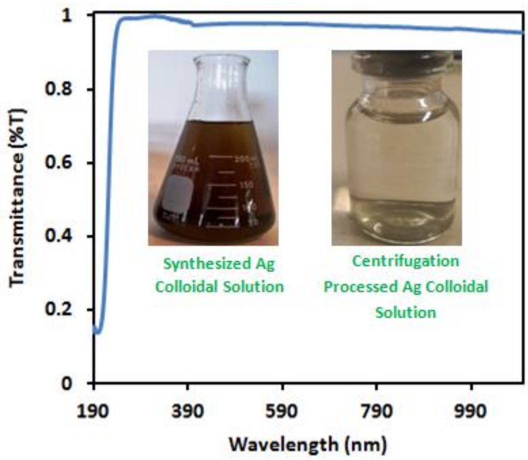

Fig. 2 – UV-visible transmittance spectrum of colloidal Ag NPs

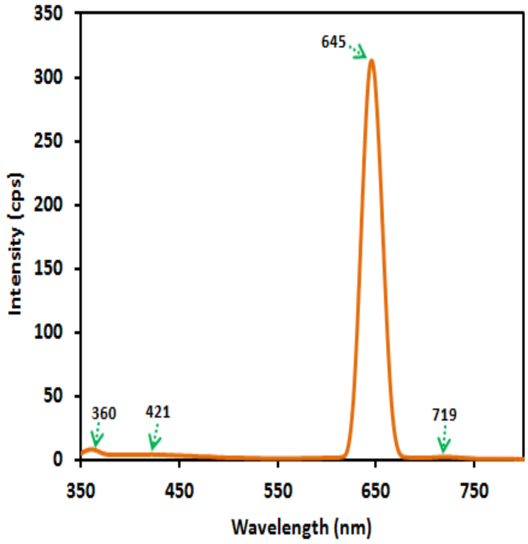

Fig. 3 – FL spectrum of colloidal Ag NPs

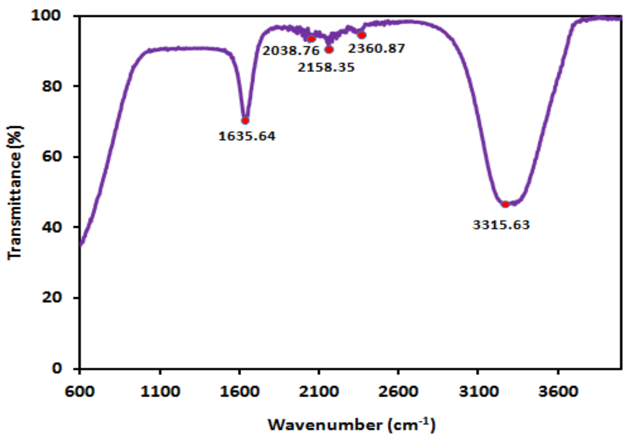

Fig. 4 – FTIR spectrum of synthesized Ag colloidal solution

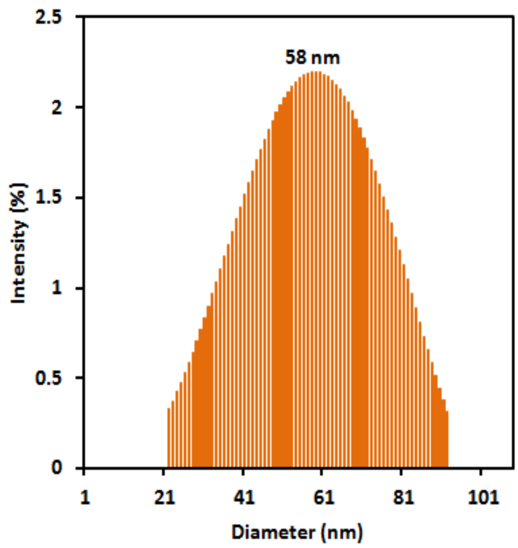

Fig. 5 – Silver NP size distribution

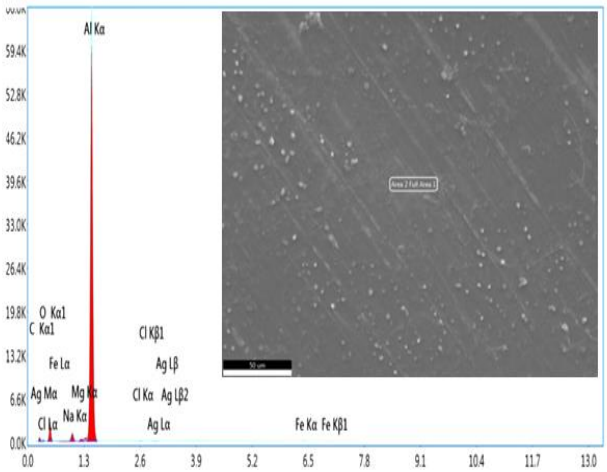

Fig. 6 – EDX image of Ag colloidal solution

reported by Senthil et al. (2017) [14]. The colloidal Ag NPs were examined using dynamic light scattering technique and the result is shown in Fig. 5. Before the measurements, the synthesized Ag colloidal solution was sonicated in order to disperse the Ag NPs. The mean particle diameter is found to be approximately 58 nm as appearance of a narrow size distribution from 20-95 nm.

EDX spectrometer was used to identify the elemental composition of synthesized material as shown in Fig. 6. The intense peak appeared at ~ 1.5 keV is due to the used aluminium substrate. The typical silver element peak was observed at ~ 0.35 keV and our result coincides with the reported ones [15, 16]. Further, the list of presented elements in the colloidal Ag solution and corresponding weight (%) are tabulated (Table 1), which was confirmed by the formation of Ag NPs.

Table 1 – Atomic percentage of present elements from EDX spectrum

Elements	C	O	Na	Mg	Al	Ag	Fe	Cl
Weight, %	9.7	9.6	2.0	0.9	76.7	0.09	0.5	0.2

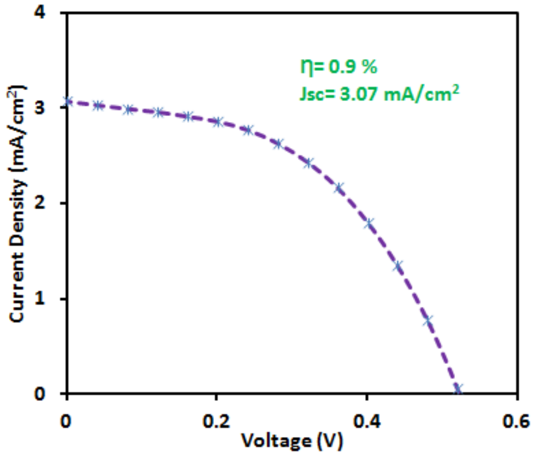

Fig. 7 – *J-V* curves of DSSCs fabricated with Ag NPs

To prepare the photoanode of DSSC, TiO_2 NPs were mixed with Ag NPs collected by the centrifuging the colloidal solution. After the prepared photoanode it was dipped in the Ruthenizer 535 (N719) dye for 18 h and later it was rinsed in ethanol to remove dye molecules from the surface. Finally, DSSC was assembled and characterized.

Fig. 7 shows the current density (J_{sc}) vs. voltage (V) characteristic of DSSC as much as 0.9 % cell efficiency along with 0.52 V open-circuit voltage, 0.49 fill factor and 3.07 mA/cm^2 current density.

4. CONCLUSIONS

By employing the chemical reduction method, colloidal Ag NPs were prepared and investigated for their optical properties. The FL study revealed Ag emission peaks while FTIR study endorsed the vibrational peaks related to the functional groups. The obtained particle diameter was around 58 nm as confirmed by the through dynamic light scattering investigation. EDX analysis showed the presence of Ag. Using the prepared Ag NPs, DSSC was fabricated and tested for its performance which yielded 0.9 % conversion efficiency with its current density and open-circuit voltage of 3.07 mA/cm^2 and 0.52 V respectively. Furthermore, the photovoltaic performance will be enhanced by optimizing various parameters in DSSC device.

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Оптична характеристика хімічно відновлених наночастинок срібла для сонячних елементів, чутливих до барвника

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Наночастинки (НЧ) благородних металів знайшли своє потенційне застосування завдяки своїм фізичним, хімічним та біологічним властивостям порівняно з сипучими матеріалами. У цій роботі НЧ колоїдного срібла (Ag) готують методом хімічного відновлення, а різні дослідження представлені за допомогою УФ-спектроскопії, флуоресцентної (FL) спектроскопії, аналізатора динамічного розсіювання світла (DLS), інфрачервоної спектроскопії з перетворенням Фур'є (FTIR) та енергетично-дисперсійного рентгенівського (EDX) спектрометру. Спектр пропускання (УФ) показав наявність НЧ Ag в нижній спектральній області, а дослідження FL виявило пік випромінювання колоїдних НЧ Ag на довжинах хвиль 360 нм і 645 нм при довжині хвилі збудження 320 нм. Спектр FTIR схвалив різні функціональні групи, пов'язані з елементами, присутніми у вибірці. Середній діаметр НЧ Ag становить 58 нм за розрахунком методом DLS. EDX-спектри підтвердили піки елементів, що підтверджують утворення НЧ Ag. Крім того, НЧ Ag використовуються при виробництві сонячних батарей, чутливих до барвника (DSSC).

Ключові слова: Наночастинки, Срібло, FTIR, EDX, DSSC.