

Ex-situ and *in-situ* post-photosynthesis of silver nanoparticles on polyamide fabric using daylight irradiation

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Silver nanoparticles (AgNPs) have been *ex-situ* post-synthesized in an aqueous solution and *in-situ* synthesized on polyamide fabric through a simple chemical reduction method by using silver nitrate (AgNO₃), stannous chloride (SnCl₂) and cetyltrimethylammonium bromide (CTAB) under daylight irradiation. SnCl₂ and CTAB act as reducing and stabilizing agents in the colloidal silver nanoparticles solution respectively. Post *in-situ* synthesis of Ag NPs have been carried out on polyamide fabric by spraying solution of AgNO₃, CTAB and SnCl₂ on the fabric and then irradiating under daylight for 2 h. Ag NPs solutions and Ag NPs loaded polyamide fabrics are characterized by UV-vis spectroscopy, dynamic light scattering (DLS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Appearing a strong plasmon resonance peak at 400 nm in UV-visible spectrum, XRD patterns and SEM images are found to clearly confirm the formation of silver nanoparticles. The UV-vis spectra also confirm no Ag NPs formation without daylight irradiation.

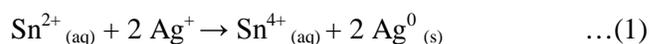
Keywords: *Ex-situ* post-photosynthesis, *In-situ* post photosynthesis, Polyamide fabric, Silver nanoparticles

1 Introduction

Silver nanoparticles (Ag NPs) are a new class of material with remarkable different physiochemical characteristics such as increased optical, electrical, electromagnetic and catalytic properties¹. Ag NPs are one of the most commonly used nanostructure material in consumer products due to their effective antimicrobial properties and low toxicity toward mammalian cells^{2,3}. Several methods have been employed for synthesizing Ag NPs however; the chemical reduction has been extensively investigated due to its simplicity and mild conditions^{3,4}. Photochemical reduction is one of the common techniques of chemical methods⁵⁻⁸. Application of ultraviolet (UV) light⁶, mercury metal halide lamp⁷ and xenon or sodium lamp⁸ for synthesizing Ag NPs has been studied by many researchers. This is usually composed of silver salts as a precursor, reducing agent, and stabilizer⁹. The mechanism of Ag NPs formation from solution has been elucidated, as metal colloids are formed from their ions in solutions through nucleation, followed by the growth step¹⁰⁻¹². Several reducing agents have been used including

sodium citrate¹³, ascorbic acid¹⁴, potassium bitartrate¹⁵, hydrazine¹⁶, and polyethylene glycol¹⁷. Ag NPs are not stable and rapidly undergo agglomeration due to the high reactivity. The stabilizing agents are used to separate the particles preventing agglomeration^{18,19}. Surfactants such as cetyltrimethylammonium bromide (CTAB), polymers such as poly vinyl pyrrolidone (PVP) and liposome²⁰, are usually used as stabilizer to control the size of NPs²¹⁻²³.

Stannous chloride (SnCl₂) is widely used as a reducing agent (in acidic condition), and in electrolytic baths for tin-plating such as silvering mirrors, where silver metal is deposited on the glass according to the following reaction²⁴:



SnCl₂ was also used as a mordant in wool dyeing due to its bright colour with some dyes to weighing silk, to analytical testing of Hg²⁺_(aq) and to identify gold compounds^{25,26}. To the best of our knowledge there is no published report on the post-photosynthesis of Ag NPs through reduction of silver nitrate with SnCl₂. Hence, this paper is focused on a simple daylight-assisted method for synthesis of Ag

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NPs in an aqueous solution and on the fabric surface by using Ag NPs precursor solution. A well-dispersed Ag NPs in aqueous solutions and polyamide fabrics surface have been characterized by UV-vis spectroscopy, dynamic light scattering (DLS), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2 Materials and Methods

2.1 Materials

Silver nitrate (AgNO_3 extra pure, >99.8%) as a precursor for preparation of Ag NPs, stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) as a reducing agent, and CTAB (cetyltrimethylammonium bromide) as a cationic surfactant to stabilize colloidal Ag NPs from Merck (Darmstadt, Germany) were used without further purification. Also, the scoured polyamide 6 (PA) knitted fabric with 90 g/m^2 weight was purchased from Tehran local market.

2.2 Methods

2.2.1 *Ex-situ* Post-photosynthesis of Ag NPs Solution

Ag NPs were prepared through a simple and environment-friendly daylight-assisted method in an aqueous solution. For preparing Ag NPs precursor solution, CTAB was added to an aqueous solution of AgNO_3 (1 mM as a constant concentration) along with rapid stirring and then a freshly prepared SnCl_2 solution was added dropwise to the solution under vigorous stirring (3500 rpm) for 10 min at room temperature in dark condition. The precursor solution was then exposed to the daylight for different durations (the average daylight intensity was 58.5 w/m^2), then Ag^+ was reduced and Ag NPs were synthesized. In this method, $[\text{CTAB}]/[\text{AgNO}_3]$ was an effective factor in Ag NPs synthesis. Also, diverse ratio of $[\text{SnCl}_2]/[\text{AgNO}_3]$ (Table 1), was considered to prepare Ag NPs with different particle size.

Table 1—Material ratio in various solutions
[AgNO_3]=1mM

Solution No.	[CTAB]/[AgNO_3]	[SnCl_2]/[AgNO_3]
1	0	0.25
2	1	0.25
3	2	0.08
4	2	0.12
5	2	0.16
6	2	0.25
7	3	0.25

2.2.2 *In-situ* Post-photosynthesis of Ag NPs on Polyamide Fabrics

Post-photosynthesis of Ag NPs was carried out by spraying the Ag NPs precursor solution on polyamide fabric at room temperature and then irradiating sample under daylight for 2 h. The colour appearance changed from white to yellow by formation of NPs on the fabric surface.

2.3 Test Methods

NPs were characterized with dynamic light scattering, using Zetasizer Nano HPPSv420 (Malvern Instruments, Ltd., Malvern, UK) at 25°C and the hydrodynamic diameter (z-average), mode values of the particle size and poly dispersity index (PDI) of the particle were determined. Z-average diameter is the intensity-weighted mean diameter derived from the cumulants analysis, and PDI is a dimensionless measure of the broadness of the size distribution calculated from the cumulants analysis²⁷. The diameter was correlated to the effective particle movement within a liquid, which was the particle diameter along with electrical double layer²⁷. The hydrodynamic diameter was described using the Stokes-Einstein equation²⁷. The ultraviolet (UV) absorbance spectra of different samples were prepared at room temperature with spectrophotometer (Optizen, Mecasys, Deajeon, Korea, 2120 UV) at 2 nm resolution. The spectrum wavelengths were obtained from 200 nm to 600 nm using a glass cuvette 1 cm optical path. Surface morphology of the samples was observed by using SEM with 30 keV at different magnifications using Hitachi S4160. An X-ray diffractometer type 3003pts, Seifert, Germany ($\lambda=1.54060 \text{ \AA}$ at 40 kV and 30 mA) with $\text{Cu } \alpha$ irradiation was used to confirm the formation of silver crystal on fabric surface.

3 Results and Discussion

3.1 UV-visible Spectroscopy

The UV-extinction spectra characteristics, such as the red or blue shifting, maximum absorption intensity, and full width at half maximum (FWHM) of absorption peaks are proved to be quite sensitive to the shape, size, size distribution, stabilizer, and refractive index of solution²⁸.

3.2 Formation of Ag NPs under Daylight Irradiation

The colour of $\text{AgNO}_3/\text{CTAB}$ solution remains unchanged in presence of SnCl_2 under dark condition, and then no considerable changes are observed in the

absorbance spectra of the solution. It is confirmed that no Ag NPs are synthesized under this condition. However, the clear solution gradually turns to yellow then reddish yellow with exposure to the daylight. A Plasmon band appears at 400-500 nm on the absorbance spectra indicating formation of metallic silver in the solution. Interestingly, no colour change is observed in the dark, and no silver Plasmon band is detected in this solution (Fig. 1).

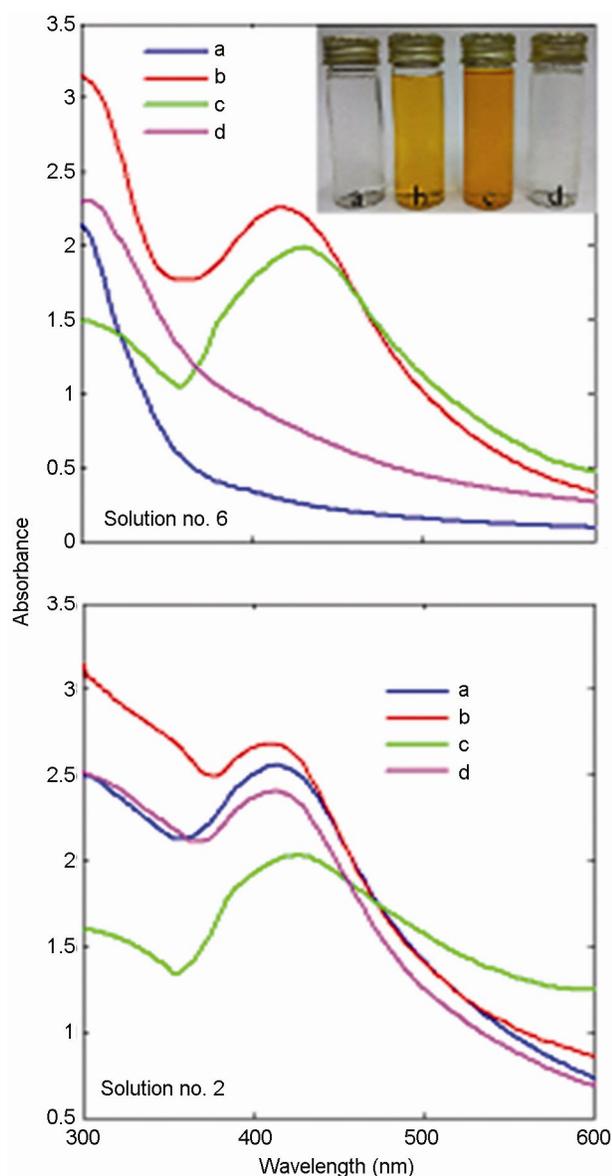


Fig. 1—UV-vis absorbance spectra of solution No.6 ($[\text{AgNO}_3]=1$ mM, $[\text{CTAB}]/[\text{AgNO}_3]=2$ and $[\text{SnCl}_2]/[\text{AgNO}_3]=0.25$) and solution No.2 ($[\text{AgNO}_3]=1$ mM, $[\text{CTAB}]/[\text{AgNO}_3]=1$ and $[\text{SnCl}_2]/[\text{AgNO}_3]=0.25$) irradiated via daylight during different times or in the dark condition [(a) freshly prepared, (b) irradiated via daylight for 2 h, (c) irradiated via daylight for 24 h, and (d) in dark for 24 h]

$[\text{CTAB}]/[\text{AgNO}_3]$ ratio lower than 2 leads to formation of Ag NPs instantly due to the presence of Ag^+ in the solution and direct reduction of Ag^+ with SnCl_2 . However, the ratio of higher than 2 leads to coverage of nearly all Ag^+ ions with CTAB and formation of Ag^+/CTAB and AgBr preventing reduction of Ag^+ with SnCl_2 . While, the daylight irradiation leads to reduction of Ag^+ with SnCl_2 and synthesis of Ag NPs, the rapid formation of metallic silver is confirmed with UV-vis spectroscopy (Fig. 2). This sensitive response to the daylight implies potential applications in the photographic and micro patterning fields. The ratios of 2 and 3 prevent synthesis of Ag NPs even with high concentration of reducing agent (SnCl_2). It is known that cationic surfactant (CTAB), slowly form Ag^+/CTAB , AgBr/CTAB , and AgBr structures through their quaternary ammonium groups²⁹⁻³¹. In fact the reduction of Ag^+ ions in the solution can only proceed under daylight irradiation according to reactions 2 to 5. A possible mechanism of Ag NPs formation in this system was proposed in Scheme 1. First, Ag^+ ions incorporated in CTAB micelles formed Ag^+/CTAB , AgBr , and AgBr/CTAB structures^{29,30}. Through daylight irradiation, AgBr salt leads to formation of Ag^+ , Br^- . The electron from Br^- reacts with Ag^+ and subsequently Ag^0 is synthesized^{31,32}.

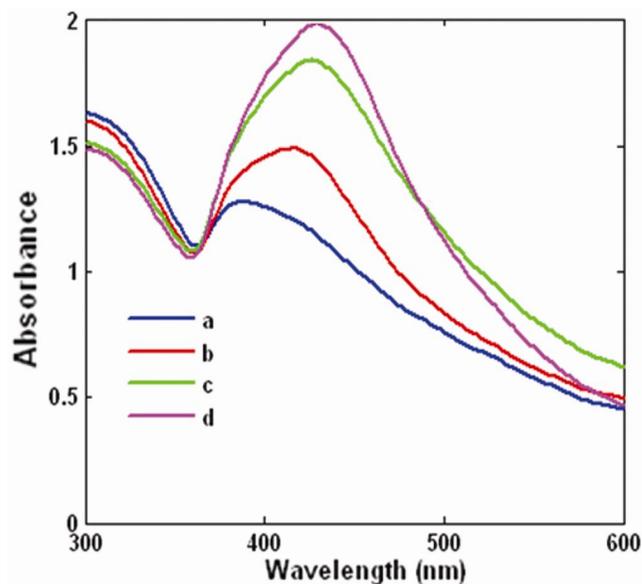
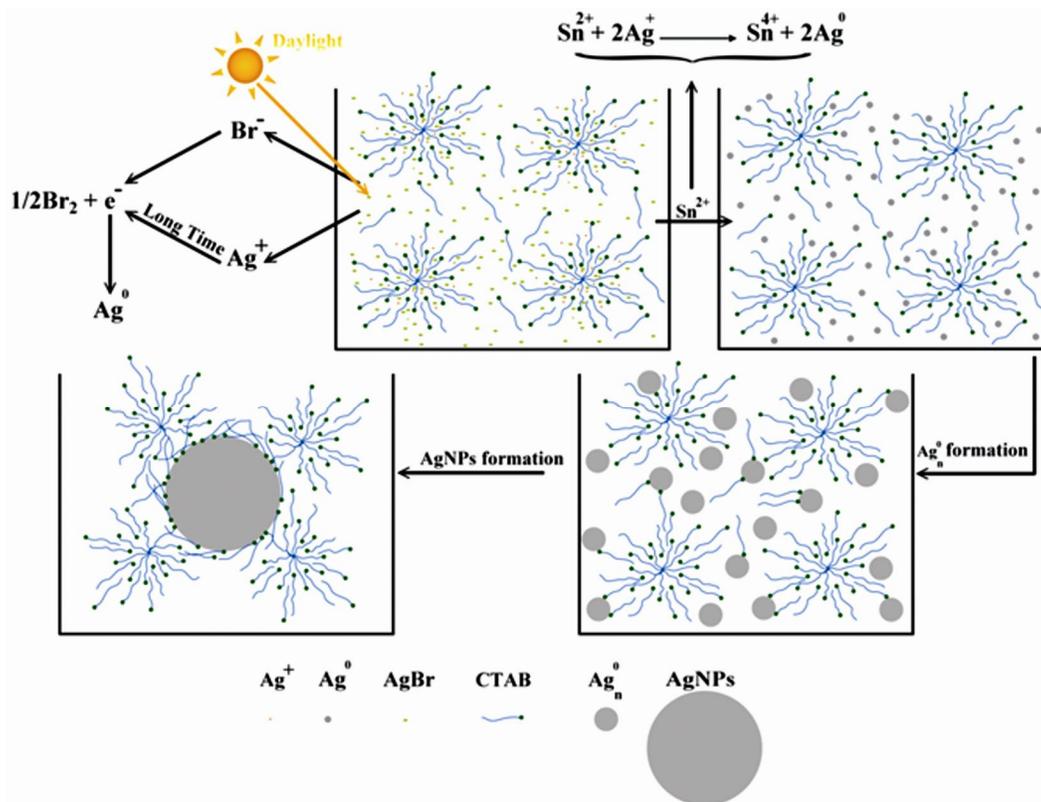
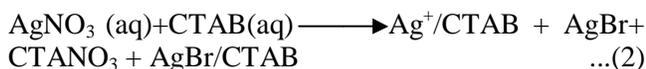


Fig. 2—UV-vis absorbance spectra of various solutions with constant ratio of $[\text{CTAB}]/[\text{AgNO}_3]=2$, irradiated under daylight for 24 h [(a) solution No. 3, (b) solution No. 4, (c) solution No. 5, and (d) solution No. 6]

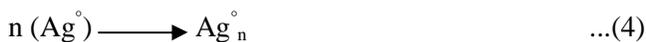
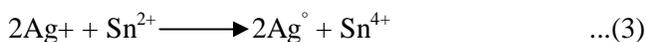


Scheme 1—A possible mechanism of Ag NPs formation

A long duration is needed for this phenomenon to happen, however presence of SnCl_2 greatly enhances the synthesis of Ag° , and nucleation is initiated. Thus, a considerable change is indicated in the UV-vis spectra of the solution, as shown in Fig. 1. This is very similar to the formation of the metal silver during the conventional photographic process, whereas silver halide is used as a semiconductor to capture incident light²⁹. Silver cluster is then formed through the agglomeration of silver atoms and Ag° ions. The reduction of Ag° ions and their following agglomeration is presented in following equations:



After irradiation:



CTAB chain stabilized Ag° ion through complexation, inhibits agglomeration of silver clusters and prevents the uncontrolled growth of silver NPs³⁰. Thus, CTAB plays multiple roles in the formation of silver NPs, as indicated below:

- (i) Induces reduction of Ag° ions through formation of $\text{Ag}^\circ / \text{CTAB}$ and AgBr
- (ii) Controls growth of AgNPs through complex formation with silver cluster
- (iii) Prevents agglomeration of Ag NPs through steric hindrance.

3.3 Effect of SnCl_2 Concentration

The UV-vis absorbance of Ag NPs solution with different concentrations of SnCl_2 is presented in Fig. 2. It is known that the red shift is due to the synthesis of larger Ag NPs. Also, according to the results, both SnCl_2 and CTAB influence the synthesis of Ag NPs.

3.4 Effect of Irradiation Time

The photosynthesis of Ag NPs is monitored with UV-VIS absorbance as a function of irradiation time (Fig. 1). An absorbance peak at around 400 nm is observed after 2 h exposure to the daylight. The prolonged irradiation time leads to gradually high absorbance peak with longer wavelength, confirming more Ag NPs synthesis with bigger size. Also, more silver nitrate is reduced and more nano silver is agglomerated with the longer exposure time. Further, the rate of Ag NPs synthesis is function of CTAB concentration.

3.5 Dynamic Light Scattering of Ag NPs

The hydrodynamic diameter (z-average) and poly dispersity index (PDI) of Ag NPs are demonstrated in Fig. 3. The hydrodynamic diameter of NPs reduces with the increase in CTAB, and the smallest Ag NPs, synthesized in the colloidal solution with $[\text{CTAB}]/[\text{AgNO}_3]=1$. It seems that, the increase in CTAB changes the shape of the surfactant aggregation around the NPs and increases the hydrodynamic diameter, as indicated through DLS results. In addition, CTAB concentration is also effective on the PDI of silver NPs as the lowest concentration of CTAB indicates the smallest poly dispersity index. The lowest poly dispersity index leads to narrow size distribution of nano silver particles, and higher CTAB content leads to higher poly dispersity index. Thus, Ag NPs with wide range of size are formed with high CTAB concentration.

3.6 X-ray Diffraction Patterns

The XRD patterns of the post-photosynthesized polyamide fabrics are presented in Fig. 4 indicating similar patterns as reported by others³³. Figure 4 (a) indicates the untreated polyamide fabric and Fig. 4 (b) shows the treated polyamide fabric with Ag NPs precursor solution under daylight irradiation for 2 h. All the prominent peaks at 2θ values 38° , 44.44° , 64.54° , 77.38° and 81.6° represent (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) Bragg's reflections of fcc structure of silver. The particles size is also calculated using Scherrer's equation, indicating an average particle size of 16 nm^{34} .

3.7 SEM Study

Prior to SEM, Ag NPs precursor solution was sprayed on surface of Al sheet and polyamide

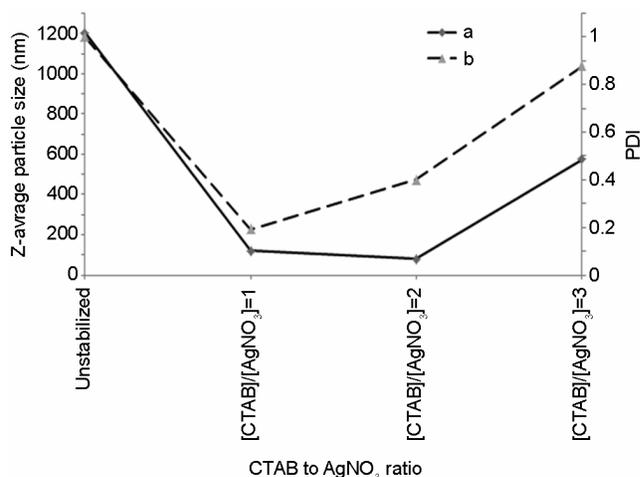


Fig. 3—Effect of various concentration of CTAB on (a) z-average of NPs and (b) PDI of silver NPs

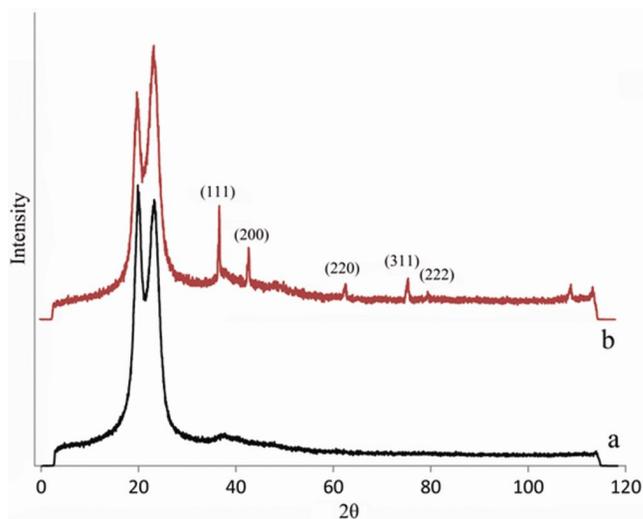


Fig. 4—XRD pattern of various fabrics (a) raw and (b) sprayed with Ag NPs precursor solution irradiated under daylight for 2 h (using solution No. 6)

fabric and then irradiated under daylight for 2 h followed by coating with a thin layer of evaporated gold. Figure 5 shows SEM images of solution No. 6 at room temperature in dark condition irradiated under daylight for 2 h. Figures 5 (a) and (b) show the raw and loaded polyamide fabric with Ag NPs respectively. Also, Fig. 5 (c) and (d) indicate the loaded Al sheet with Ag NPs. The SEM images show that the Al sheet and polyamide fabric surface are covered by NPs. The diameter of Ag NPs is lower than 100 nm as obtained from SEM images.

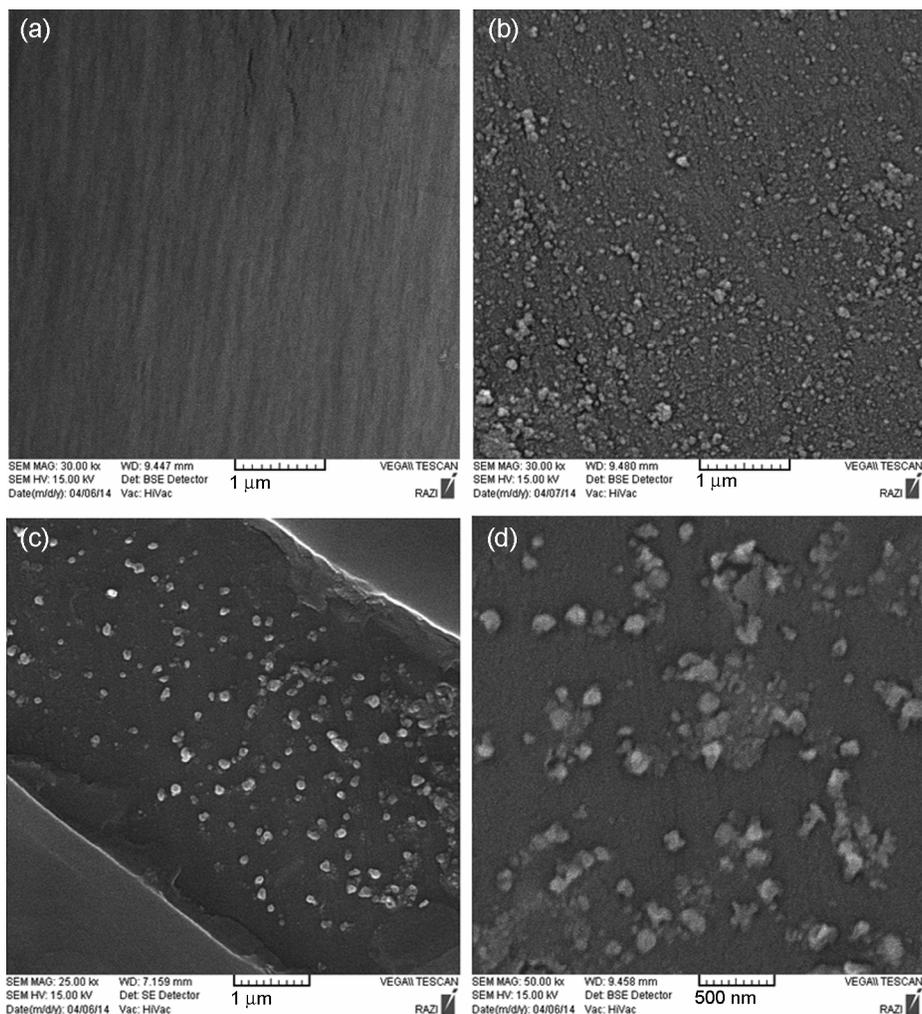


Fig. 5—SEM images of various substrates (a) raw polyamide fabric ($X=30,000$), (b) sprayed polyamide fabric ($X=30,000$), (c) sprayed Al sheet ($X=25,000$) and (d) sprayed Al sheet ($X=50,000$). Spraying was done with Ag NPs precursor solution No. 6 irradiated under daylight for 2 h

4 Conclusion

A novel method is developed for *ex-situ* and *in-situ* post-photosynthesis of silver nanoparticles through chemical reduction of silver nitrate with stannous chloride under daylight irradiation with CTAB as stabiliser. The effectiveness of daylight clearly indicates that no silver particles are synthesized without daylight irradiation. A possible mechanism is proposed to explain the formation of Ag NPs. Also, the influence of CTAB in photosynthesizing Ag NPs, stabilizing colloidal silver NPs and poly dispersity index is indicated. The formation of Ag NPs is proved with XRD spectrums and SEM micrographs. Overall, this research successfully discloses a new method of post *ex-situ* and *in-situ* photosynthesis of Ag NPs in aqueous solution and on the fabric surface at room

temperature through chemical reduction by stannous chloride under daylight irradiation. This method can be applied on different substrate for *in-situ* photosynthesis of silver nano particles wherever it is required. This also prolongs the shelf life of the solution in dark condition before application.

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