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Development of Novel Deposition Method for Silver Nanostructures on Flexible and Nanopatterned Surfaces

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Abstract

Novel methods for the deposition of silver nanoparticles on variety of substrates have attracted attention for technological applications. Herein an in situ chemical deposition method has been established for the deposition of Silver nanoparticles (AgNP's) on different substrates. The substrates that were coated with AgNP's include flexible laboratory filter paper, nanopatterned aluminum substrate and soda glass. The approach yields uniform and well adhered coatings without agglomerations, within two minutes and such instant methods are rarely observed in literature. Presence of AgNP's has been confirmed by X-ray diffraction and SEM-EDS for the coatings. The average size of the particles coated on the substrates range from 50-100 nm. The coatings are best suited for biological and analytical applications such as wound healing, food packaging, Surface Enhanced Raman Spectroscopy, etc.

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*Keywords:*Thin films; Silver nanoparticles;Iin-situ deposition; plasmonic paper

1. Introduction

Silver nanostructures Silver nanostructures with large specific surface area, have attracted huge focus owing to their interesting optical, electrical and biological properties. These properties are governed by the shape and size of the nanoparticles which in turn are related to the method of synthesis. The coatings of these metal nanostructures are explored recently for variety of applications including Surface Enhanced Raman Spectroscopy (SERS) [Kuncicky et

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al (2006), Moskovits et al (2005)], color filters [Biswas et al (2004), Dirix et al (1999), Quinten et al (2001)], and all optical switching [Stegeman 1990], packaging materials in food and pharmaceutical industry[Lau et al (2000), Ekman et al (2009)] etc.

Recently Portable and cost effective diagnostic devices are being developed where paper is used as a substrate. [Martinez et al (2008), Ellerbee et al(2009)]. Further the advantages such as its abundance, inexpensive manufacturing, ease of recycling, biocompatibility and the biodegradability, make paper being used in consumer products [Samir et al (2005), Martinez et al (2010)]. Further the ability of paper to easily absorb liquids makes them being explored in biomedical diagnostic devices[Carrilho et al (2009)]. Plasmonic behavior of Silver nanoparticles coated on common laboratory paper has attracted paper being explored for Surface Enhanced Raman Spectroscopy. Paper is particularly suited for SERS studies as paper will not interfere with the Raman signal of analyte [Chang et al(2011)].

Anodized alumina templates are also being explored for different applications and are a popular choice for the nanomaterial synthesis owing to their ease of preparation, possible control over the pore properties such as pore-diameter, interpore distance and pore-density. These alumina templates can be used for patterning aluminum surfaces for SERS applications. The highly ordered, well patterned, hexagonally arranged honeycomb like nanostructures have suitable dimensions to make them good SERS substrates.

Various methods have been proposed to develop coatings of metal nanoparticles on various substrates. Gedanken et al (2011), have developed a sonochemical method for the deposition of silver nanoparticles on parchment paper. Their method requires a precise mixture of 25% aqueous ammonia and ethylene glycol. Ethylene glycol acts as reducing agent while the concentration of NH_3 controls the size of nanoparticles. Further the synthesis times are of the order of an hour. Chang et al (2011), have reported the gold nanorod coated paper for SERS applications where the paper was immersed in gold nanorod solution for two days. There is a need for developing a facile, rapid and economic deposition method which has to be versatile such that different types of substrates can be coated in a single batch. Solution based approaches are gaining popularity as they offer advantages over presently used deposition methods. The first being the ability to control the thickness, density of the coating. This is particularly important as the thickness can be easily controlled right from nanometer to micrometer range within a short span of time. Secondly solution methods can obtain conformal coverage which will resemble the shape of the substrate. Therefore obtaining a pattern similar to the surface of the substrate becomes possible which contrasts with blanket deposition methods such as dip coating methods.

Herein we report a two minute, solution chemical deposition method for the deposition of silver nanoparticles. The versatility of the process is shown by choosing three different materials as substrates. The substrates subjected to this rapid coating process are a laboratory filter paper, Glass substrate and a nanopatterned Aluminum substrate.

2. Experimental

The procedure for preparation of Anodic Alumina Template is explained in detail elsewhere [Choudhari et al (2012)]. The details about the pore properties were obtained by reported mathematical algorithm, based on the SEM images of the AAO membranes [Choudhari et al (2013)]. Nanopatterned Aluminum substrates were prepared from AAO membranes by an optimized chemical etching process similar to reported method[Choudhari et al (2012)]. The details about the experimental arrangement for the chemical deposition are reported elsewhere [Ranajit et al (2012)]. The ingredients of the reaction mixture for the deposition of AgNP's is are similar to the well-known Turkevich process. The dimensions of the substrates were at least 2.0 cm x 2.5 cm. The substrates were dropped in a round bottom flask containing the reaction mixture and allowed to boil for two minutes. The colorless solution gradually turns yellow and black, and the reaction was stopped at two minutes. The substrates were removed, washed repeatedly with water to remove the unreacted starting materials on the substrates and dried. The X-ray Diffraction patterns were collected on Rigaku Miniflex 600 using Cu-Kα radiation. Electron Microscope images were collected on Carl Zeiss Scanning Electron Microscope (SEM). EDS analysis was used to quantify the amount of Silver on the surface of substrate.

3. Results and discussion

The deposition method is based on the reduction of Ag^{+} ions at a temperature of 90-100 °C. The method takes less about two minutes for the deposition of Silver nanoparticles. It is interesting to note that the instrumentation used here is very simple and time taken for deposition is only two minutes. Further there is no need for special control of either the pH or alkaline conditions and multiple number of substrates can be coated simultaneously. The inset of Figure 1 shows the optical images of filter paper before and after AgNP deposition. The change of paper color takes place within a short time of two mintutes unlike other dip coating or self-assembly methods. While we intend to use the AgNP coated papers for analytical applications it is important to see that the coating is stable specially when contacted with solutions. Even vigorous rinsing with water did not noticeably change the colour of the substrates attesting to the fact that the nanoparticles are firmly adhering to the substrate and not loosely held. This observation suggests the stability and possible use of AgNP coated paper in solution medium. Further the growth of nanoparticles is believed to happen on the surface of the substrates used, which can be attributed to the different synthesis environment offered by the experimental arrangement. This rapid nature of deposition is advantageous and contrasts with self-assembly methods where the paper was immersed in a colloidal solution of nanoparticles for extended durations of several hours.

Use of papers for analytical applications can sometimes be limited due to the autofluorescence of paper which may interfere or mask the analyte signal in an optical analysis. Figure 1 shows the fluorescence spectra of filter paper using an excitation wavelength of 325 nm (He-Cd laser). The fluorescence spectra were collected by Ocean Optics spectrometer. The autofluorescence due to the cellulose shows a green emission centered around 500 nm. After coating the filter paper with AgNP's this autofluorescence is observed to be completely quenched (Figure 1), which makes use of paper advantageous for SERS applications. The quenching of paper fluorescence is believed to be due to non radiative energy transfer[Dulkeith et al (2002), Singamaneni et al (2007)].

The X-Ray diffraction patterns of the Silver nanoparticles coated on filter paper and on glass substrate are shown in figure 2 A and 2B respectively. Well defined diffraction peaks were observed in both cases attesting to the crystalline nature of the coating. All the diffraction peaks could be attributed to cubic Silver and was in accordance with the JCPDS card no: 87-0720.

The scanning electron microscope (SEM) images for the silver coated glass substrates and filter paper are shown in figure 3 a and 3b repspectively. The glass substrate is uniformly covered which can be compared with otherdeposition methods such as thermal evaporation, spray pyrolysis etc. It is clear from figure 3a that the average size of the particles on the surface of glass sample is of the order of 50-100 nm and the presence of sharp edges can beclearly seen.The SEM image of the AgNP coated filter paper (Figure 3b), shows the uniform distribution of Ag nanoparticles anchored on the paper and no large agglomerations could be seen. This is advantageous over thermal inkjet printing method[Pedro et al (2012)] where, once the Au NP-loaded paper was dried, small agglomerates ofnanoparticles irreversibly absorbed on the cellulose fibers could be clearly observed in the SEM image (at much

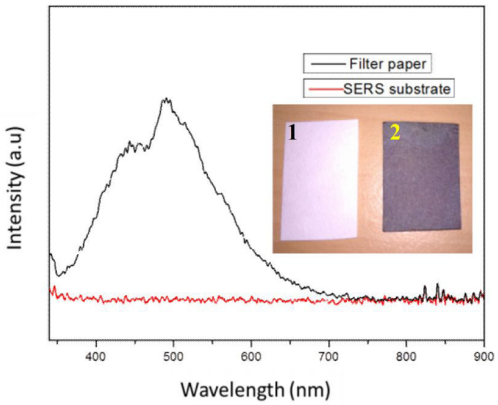

Fig 1. Fluorescence spectra (325nm excitation) showing the Quenching of autofluorescence of paper when coated withAg nanoparticles. Inset shows the optical images of filter paper (1) before coating and (2) after coating

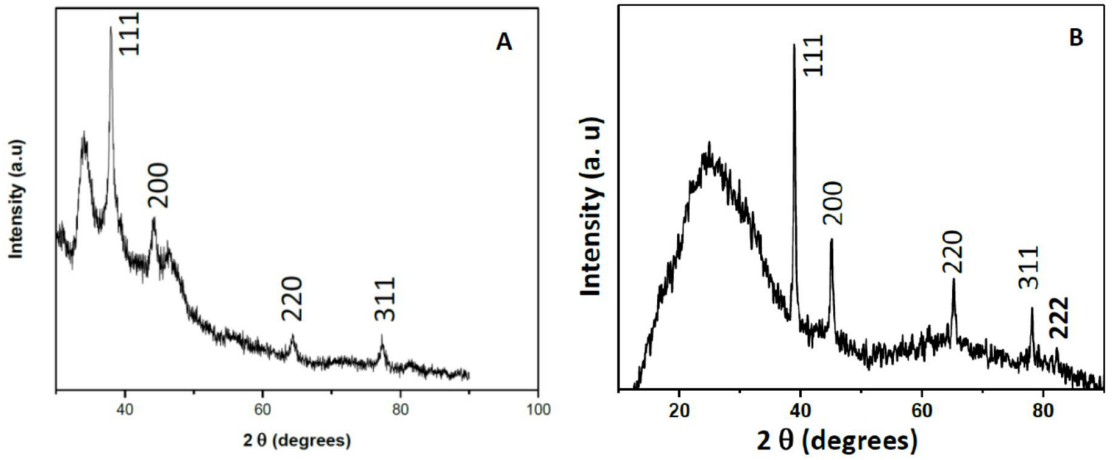

Fig 2. XRD pattern of AgNP coated (a) Plasmonic paper (b) glass substrate confirming the presence of Ag nanoparticles

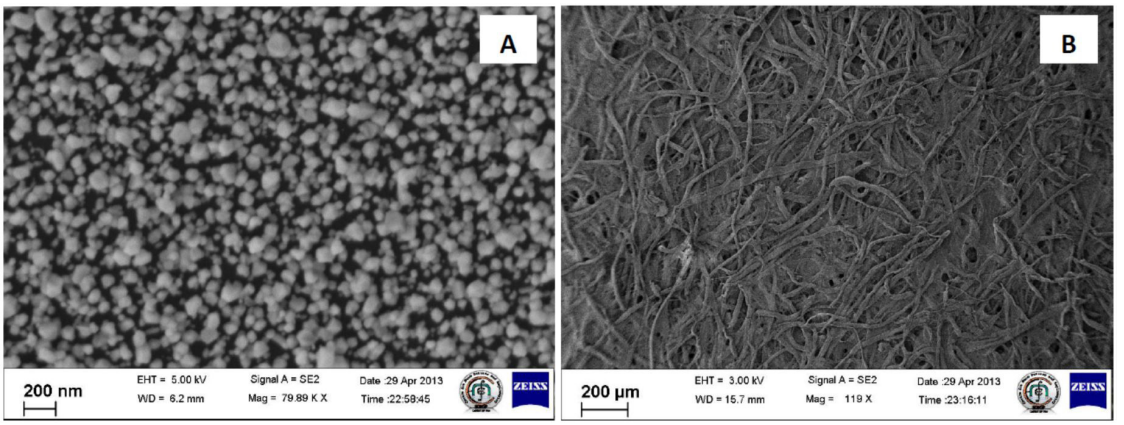

Figure 3. Scanning Electron Microscope (SEM) images for the Silver coated (a) glass substrates and (b) filter paper

lower magnification than that for our substrate). A high resolution SEM could not be obtained for AgNP coated filter paper, due to charging of the substrate. However as the glass sample was deposited in the same process we can assume the size of nanoparticles on the glass and paper are same. Presence of such small structures, the uniform surface coverage without any agglomeration, are beneficial particularly for SERS applications.

The same deposition method was also used to obtain coating of AgNP's on the surface of patterned metallic Aluminum substrate (MAS). Figure 4A and 4B shows the SEM images of the MAS without and with the AgNP coating respectively. Figure 4C shows the elemental mapping for Ag which clearly shows the uniform distribution of Ag nanoparticles throughout the substrate. Figure 4D shows the EDS quantification results for the MAS coated with Silver. Total amount of Silver nanoparticles present on the surface of MAS is close to 0.5%.

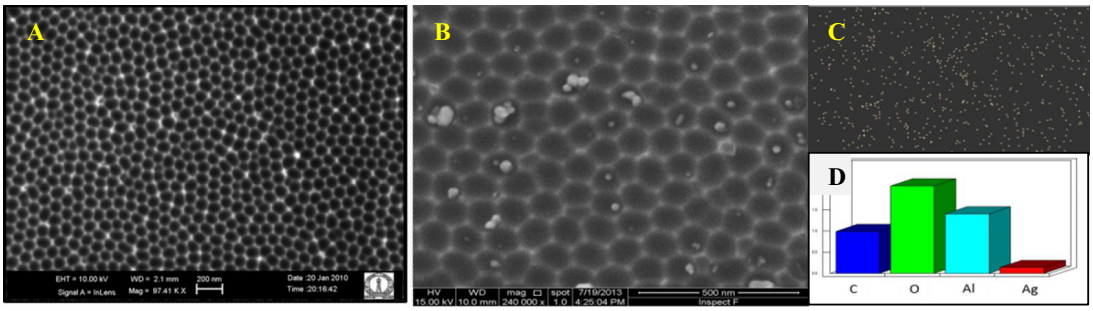

Figure 4. Scanning Electron Microscope (SEM) images of the (A) nanopatterned Metallic Aluminum substrate (MAS) (B) Silver coated nanopatterned MAS (C) elemental mapping confirming the uniform distribution of silver nanoparticles on MAS (D) EDS quantification results showing the presence of 0.5% Ag on the surface of Ag coated MAS

4. Conclusions

A rapid in-situ chemical deposition method for obtaining Silver nanoparticle (AgNP) coated substrates has been developed. Uniform and conformal coatings were obtained on all the substrates within two minutes, without agglomerations. The X-ray diffraction patterns and SEM-EDS confirm the formation presence of Ag nanoparticles on the substrates. The particles are firmly adhering to the substrates and the average particle size as seen by SEM image of Ag coated glass substrate is 50-100 nm. The versatility of the process is shown by coating three different types of substrates namely a filter paper, a glass substrate and a nanopatterned Aluminum substrate. The obtained coatings have properties suitable for different applications such as SERS, in food packaging, wound healing, biomedical devices etc.

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