Silver nanocluster films on ITO coated glass as novel substrates for the detection of molecules using Surface Enhanced Raman Scattering (SERS)

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Abstract. A novel surface enhanced Raman scattering (SERS) substrates were prepared by a nanocluster deposition system. Silver nanoclusters were deposited on the indium tin oxide (ITO) coated glass slides. These films were annealed at 300°C for two hours to obtain the required size distribution for the desirable optical properties. The surface morphology of the films was examined using filed emission scanning electron microscope (FESEM) and atomic force microscope (AFM). The surface plasmon resonance (SPR) of the pre annealed and the annealed Ag deposited ITO coated glass substrates were measured using UV-Vis spectrophotometer. The SERS studies were carried out on these substrates with Methylene Blue (MB) as a test molecule with $10^{-4}$ to $10^{-8}$ M concentrations using 514.5 nm and 632.81 nm laser excitation wavelengths. The results show that Ag nanoclusters of average particle size of ~150 nm act as very good SERS substrates for the detection $10^{-6}$ M of MB. Both the electromagnetic (EM) and chemical enhancement could be contributed to the SERS signal enhancement of MB molecule.

1. Introduction
Surface Enhanced Raman Scattering (SERS) is a spectroscopic tool for the detection of molecules adsorbed on the metal nanoparticles. SERS is a known powerful technique which can be used in analytical, biological, explosives detections [1] and medical diagnostics. SERS technique is the only one which can combine single molecule detection and chemical fingerprint [5]. Two effects are responsible for these enhancements one is Electromagnetic (EM) enhancement which is due to the excitation of localized surface plasmon resonance (LSPR) at the metal nanoparticle structures. And second one is chemical enhancement (CHEM) which is a contribution between the probed molecule and the substrate. The LSPR is depends on the size and shape of the nanoparticles, for which optimization is required. In our previous report we optimize the nanocluster size [2]. In this present study we use Methylene Blue (MB) as probed molecule. Optical absorption by UV- Vis spectrometer and surface characterization was carried using and Field Emission Scanning Electron Microscope (FESEM) and Atomic Force Microscope (AFM).

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2. Experimental

2.1 Preparation and characterization of Ag nanocluster films/substrates

ITO coated glass were used to prepare substrates for Ag cluster deposition. The surface contamination was removed by the sonication. Subsequently dried all these substrates using nitrogen gas before putting in the vacuum chamber. Silver nanoclusters (Ag NC’s) were deposited on these ITO coated substrates at a base pressure of 2 x10^{-6} Torr using cluster deposition system (NANODEP 60 from Oxford Applied Research, UK). Magnetron power was maintained at ~ 70 W. The Ag nanoclusters were formed while they traversed towards the substrates. A detailed description of cluster deposition is found elsewhere [3]. We annealed these substrates at 300 °C/ 2 hrs under Ar environment to grow nanocluster sizes. Optical absorption of these substrates at room temperature were carried using UV-Vis spectrophotometer in the range from 300-800 nm. Surface morphology of Ag NC’s on ITO coated glass (Ag NC/ITO glass) was carried using field emission scanning electron microscope (FESEM).

2.2. Surface Enhanced Raman Scattering studies

SERS spectra of MB adsorbed on Ag NC/ITO glass was recorded using micro-Raman spectrometer(LabRam HR) using laser excitation wavelengths of 514.5 and 632.8 nm at room temperature. The wide range of concentrations of MB was prepared from 10^{-4} to 10^{-8} M. For each test we took 10 micro moles of MB and dropped on the annealed Ag NC/ITO glass substrates and dried within the edges of the substrate at room temperature.

3. Results and discussions

Surface roughness of ITO coated glass is around 10 nm which was shown in figure 1B. Surface morphology of Ag NC/ITO glass were carried out by FESEM and FESEM image of annealed Ag NC/ITO glass substrate was shown in figure 1A. We calculate the average nanocluster sizes of Ag NC/ITO glass substrate which turn out ~ 150 nm. Surface plasmon resonance (SPR) of Ag NC/ITO glass substrates was turn out to be at ~ 590 as shown in figure 2. In this figure there are two maximum absorption peaks, one at ~ 360 nm is due to smaller size nanoclusters i.e. < 100 nm and second one at ~ 590 nm is due to bigger size nanoclusters i.e. > 100 nm. The laser excitation (633 nm) was chosen in such a way that the excitation wavelength of falls within the SPR absorption band of the nanoclusters and is also in resonance with the MB (~ 590 nm) absorption.

In this present study SERS measurements carried out with the laser excitation line of 514 and 633 nm. From our measurements we observe that the SERS spectrum from laser excitation wavelength of 633nm is better than the 514 nm. It is may be due to the SPR of Ag NC/ITO glass is close to the laser excitation wavelength (633 nm) and also the absorption band of MB is close to the laser excitation wavelength and SPR of Ag NC/ITO glass. Fig.4 shows SERS spectra of 10^{-4} M concentration of MB adsorbed on the Ag NC/ITO glass substrate. Peaks appeared at ~ 445, ~ 479, ~ 601, ~ 673, 773, ~ 806, ~ 1036, ~ 1228, ~ 1392, ~ 1429 and ~ 1623 cm^{-1} are characteristic peaks of MB [4]. The spectral assignments of these peaks are found elsewhere [4]. In the present data we got very good reproducible SERS spectra which is shown in figure 4. SERS measurements were taken on different locations over the Ag nanoclusters on ITO coated glass substrates.

We got very good SERS signals of MB even at 10^{-8} molar concentration. We compare the intensities of characteristic peaks with varying concentrations. Peak intensities of 479, 1036, 1429 and 1623 cm^{-1} were estimated by applying the Lorentzian shape to the spectral line [2] and resulting intensities were shown in figure 5.

Figure 5 shows the comparison of the Raman lines of 479, 1036, 1429 and 1623 cm^{-1} at different molar concentrations (i.e. 10^{-4}, 10^{-6} and 10^{-8}) of MB. Intensities of Raman line from 10^{-4} to 10^{-8} molar concentrations are linearly varying with concentration. This gives us confidence in the
efficacy of our measurements.

Figure 1A. FESEM image of annealed Ag nanoclusters on ITO coated glass substrate

Figure 1B. AFM image of ITO coated glass substrate, surface roughness was around 10 nm
Figure 2 UV-Vis spectrum of annealed AgNC's on ITO coated on glass substrate

Figure 3 SERS spectra $10^{-4}$ M MB adsorbed Ag nanoclusters on coated on glass substrate with laser excitation wavelength of 632.8 nm.
Figure 4 Reproducible SERS spectra of $10^{-4}$ M MB

Figure 5 Comparison of Raman lines at 479, 1036, 1429 and 1623 cm$^{-1}$ of MB at different molar concentrations ($10^{-4}$, $10^{-6}$ and $10^{-8}$ molar concentration) with laser excitation wavelength of 632.8 nm.

4. Conclusions

Novel SERS substrates were prepared using plasma inert gas phase condensation technique based cluster deposition system. AgNC on ITO coated glass substrates prepared using this technique were found to be good SERS-active substrates for detection of molecules. Very low concentrations of MB were detected in the present study. This technique can be used for trace analysis in analytical chemistry. Limit of detection of MB was 10 nM concentration.

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