INTRODUCTION

To date, paper substrates have been shown to be efficient substrates for routine Surface Enhanced Raman Scattering (SERS) analysis in a number of reports (Luo and Fang, 2005, Berthod et al., 1988, Cabalín and Laserna, 1995, Ma and Fang, 2006, Niu and Fang, 2006, Wu and Fang, 2003). However, very few studies have controlled the distribution of nanoparticles within paper, and none has optimized paper as a nanoparticle substrate. Different adsorption and aggregation states of nanoparticles would produce different coupling of electromagnetic fields surrounding the nanoparticles. Therefore, it is necessary to understand and be able to manipulate the influence of the paper’s morphology or surface characteristics (such as through post-treatment) to control and quantify the adsorption state of nanoparticles, in order to achieve the desired magnitude of the SERS and SPR effects.

In this study, we have engineered the surface charge of paper substrates using water-soluble cationic polymers to control the adsorption state of gold nanoparticles (AuNPs) and retain the desired structure on the paper substrates to amplify their SERS signal. Cationic polymers (or polyelectrolytes) adsorb readily on the negatively charged surface of cellulose fibers and fillers, changing their surface forces. This adsorption is mainly electrostatically driven, and depends on the properties of polymer (molecular weight, charge density, branching) and the surface properties of the particles (surface area, surface charge, surface chemical composition and porosity). In this study, the concentration effects of AuNPs and cationic polymers on the adsorption and aggregation states of AuNPs on paper substrates are analysed to produce highly active SERS substrates.

MATERIALS

Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O), sodium citrate tribasic dihydrate (Na₃C₆H₅O₇·2H₂O) and 4-aminothiophenol (4-ATP) were purchased from Sigma-Aldrich and used as received. Cationic polyacrylamide (CPAM) of high molecular weights (13MDa) (F1 Snowflake Cationics) were purchased from AQUA+TECH, Switzerland. Whatman filter paper #1 was selected. Ultrapure water purified with a Millipore system (18 MΩ·cm) was used in all aqueous solutions and rinsing procedures.
**Instrumentation**

Scanning electron micrographs (SEM) were obtained using a JEOL 7001 FEG system operating at 5 kV and 180 pA. All Raman and SERS spectra were obtained in air using a Renishaw Invia Raman microscope equipped with 300 mW 633 nm laser.

**RESULTS AND DISCUSSION**

AuNPs of different concentrations (0.75 mM, 0.50 mM, 0.25 mM, 0.10 mM) were prepared by diluting the stock solution (1.00 mM). To promote more adsorption of AuNPs on the paper substrates, the untreated filter papers were dipped into the AuNPs solution for 24 hours. The distribution of AuNPs is denser and uniform on the paper substrate when higher concentrations of AuNPs were used (Fig. 1).

![Fig. 1: FESEM images of (a) 0.10 mM (b) 0.25 mM, (c) 0.50 mM and (d) 0.75 mM (e) 1.00 mM AuNPs on untreated filter papers.](image)

In order to assess the SERS potential of the AuNPs paper substrates, 4-aminothiophenol (4-ATP) was chosen as the probe molecule in the Raman analysis. As shown in Fig. 2, the SERS signal intensities of AuNPs-treated paper substrates increased with an increasing concentration of AuNPs. This is due to the higher coverage of nanoparticles over the paper surface which leads to increased contact points between the AuNPs as shown in their FESEM results, and thus a greater enhancement of the electromagnetic field.
To induce more adsorption and aggregation of AuNPs for amplifying their SERS signals, paper substrates were pre-treated with different concentrations of CPAM to engineer their surface charge. After dipping the paper substrates in the cationic polymers, they were rinsed with water and then dipped in 1mM of AuNPs solution for 24 hours.

As shown in Fig. 3, there is a significant increase in the adsorption and aggregation of AuNPs as the concentration of CPAM is increased. This could be due to their increasing zeta potentials with increased concentration. Hence, there is a greater electrostatic interaction between the paper surface and AuNPs. Besides that, a flat conformation of polymer is often favoured at lower concentration due to low density of chains on the surface (Sennerfors, 2006). Increasing the concentration leads to more surface access (increased extended tails and loops) (Sennerfors, 2006); thus more adsorption and aggregation of AuNPs is achieved.

Fig. 3: FESEM images of 1.00 mM AuNPs deposited on CPAM treated filter papers with polymer concentration of (a) 0.001% (b) 0.005%, and (c) 0.010%.
As observed in Fig. 4, the SERS intensity of 4-ATP on AuNPs paper substrates increases dramatically with the increase of the concentration of CPAM. The assembly of AuNPs are brought into closer vicinity by forming a random distribution of two- and three-dimensional clusters within the cellulose microstructure when the concentration of CPAM is increased. These lead to the increase of the number of junction sites between the AuNPs and thus much more intense SERS band are produced.

CONCLUSION

The AuNPs coated paper substrates had been demonstrated to be a SERS active substrate for probing 4-ATP. Increasing the concentration of AuNPs undoubtedly increased their surface coverage on the paper substrates and amplified their optical signals. The control of the adsorption and aggregation state of AuNPs on the paper substrates were achieved by engineering the surface charge of paper using cationic polymer (CPAM), with the higher aggregation was achieved by the use of higher concentration.

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