

## L.6.: pH Dependent Reversible Aggregation of Chitosan Stabilized Silver Nanoparticles

Chitosan (CS), a naturally abundant polysaccharide has been used as a stabilizer for preparation of silver nanomaterials which have shown promising antibacterial properties. However, since CS contains amino groups which have a pKa around 6.5, CS stabilized silver nanoparticles are likely to aggregate at physiological pH and this might affect its biological activity. We have therefore investigated the pH dependent aggregation behaviour of AgNPs stabilized by CS by absorption and hyper-Rayleigh scattering spectroscopy.

The average sizes of the as prepared CS stabilized AgNPs were observed to be around  $20 \pm 9$  nm and had a surface plasmon absorption band at 395 nm.

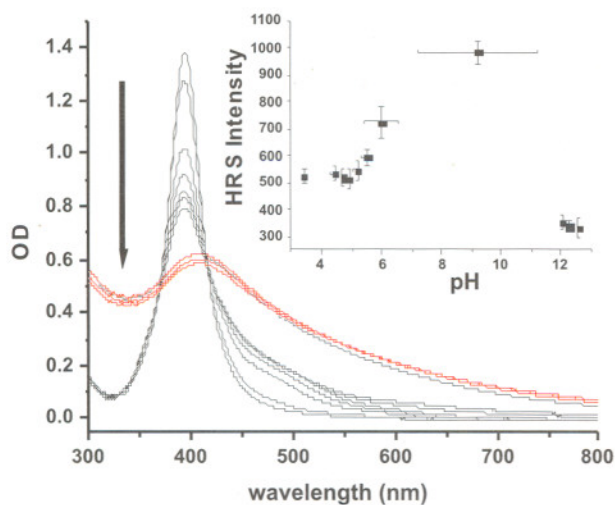


Fig.L.6.1: The pH dependence of the absorption spectra and HRS (inset) of CS-AgNPs. The arrow indicates increase in pH in steps as shown in the inset. Spectra shown in red are after pH 9.0.

In Fig. L.6.1 we show the absorption spectra of the polymer coated AgNPs as a function of the pH of the solution. The SPR intensity at 395 nm shows a gradual decrease with increasing pH till pH of  $\sim 9.0 \pm 2.0$ . This decrease is accompanied with a formation of a shoulder around 480 nm. Beyond a Ph of 9.0, a sudden drop in SPR intensity accompanied with broadening of the SPR band was observed. These changes in the absorbance spectra indicate an aggregation of AgNPs. The neutralization of the amino groups at higher pH is expected to affect the kinetic stability of a colloidal suspension (which is governed by the relative magnitudes of repulsive electric double layer and attractive

van der Waals potentials) and lead to aggregation. The aggregation of nanoparticles can also be monitored by HRS which has been shown to be more sensitive than Rayleigh scattering. The higher sensitivity of HRS arises due to the fact that compared to centrosymmetric nanoparticles second harmonic generation significantly increases for non-centrosymmetric aggregates. The changes in the HRS intensity of CS-AgNPs were also followed with increasing pH (inset in Fig.L.6.1). The HRS intensity increases with pH, maximises around  $\text{pH } 9.0 \pm 2.0$  and then drops down significantly. To understand the decrease in the HRS intensity after  $\text{pH } 9.0 \pm 2.0$ , TEM images of the nanoparticles were recorded as a function of pH. Aggregates at  $\text{pH } 9.0 \pm 2.0$  are observed to be noncentrosymmetric whereas at pH 12, they are spherical or centrosymmetric which can account for the dramatic reduction in HRS intensity.

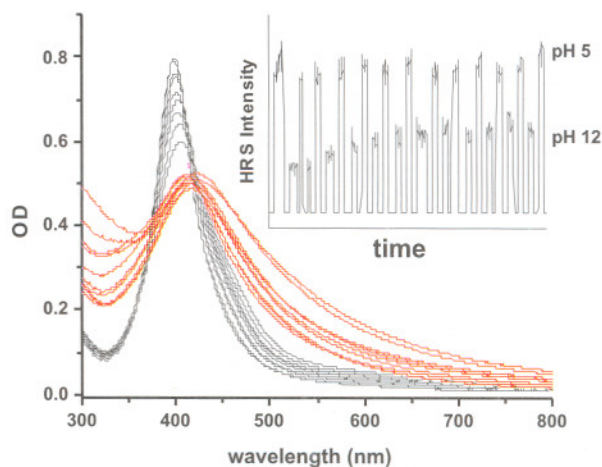


Fig.L.6.2: Changes in the absorption and HRS intensity (inset) of CS -AgNPs as the solution pH is cyclically changed from 5 to 12 Spectra shown in red are at pH 12.

The reversibility of the aggregation process of CS-AgNPs has been investigated by cyclically changing the pH of the solution. The effect of changing the pH cyclically from 5.0 to 12.0 on the absorption and HRS intensity of CS-AgNPs are described in Fig.L.6.2 for 10 pH cycles. The SPR absorption of the polymer coated AgNPs at low (5.0) pH and high (11.0) pH was similar over 10 cycles. Similarly, the HRS intensities (inset in Figure 2) were also observed to be alternating from a high value at low (5.0) pH to a low value over high (12.0) pH over more than 10 pH cycles. These results suggest that the pH dependent aggregation process in this polymer stabilized AgNPs are reversible, at least up to 10 pH cycles. (Chem. Phys. Lett. Vol. 511, pp 326-330, 2011).

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