

Gold-nanoshells as surface plasmon resonance (SPR)

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ABSTRACT

Coreshell plasmonic nanoparticles (CS) are a class of nanoparticles that exhibit optical absorption in the near IR regime and have potential biomedical applications in imaging, therapy and sensing. We present our preliminary investigation on the applications of CS as a surface plasmon based sensor to study the functional properties of human blood. CS particles of size about 1 μm exhibit broad absorption between 650 nm to 1000 nm, the regime generally used to study blood saturation. We synthesized CS particles of size about 1 μm , coated with a thin shell. The core medium was polystyrene and the nano-shell layer was gold. The plasmon peak of CS varied with blood concentration. The study showed that 750 nm plasmonic peak of CS exhibits the wavelength shift of 4.11 ± 0.26 nm per hematocrit.

Keywords: Surface plasmon, nanoshell, coreshell, Mie scattering

1. INTRODUCTION

Surface plasmon (SP) represents a collective oscillation of free electrons of metal at its surface¹. An excitation of SP depends on the metal nanoparticle size, shape and dielectric properties of the adjacent medium. This is evident from the studies that the solid gold (Au) nano-spheres of size 60 nm exhibit maximum SP excitation in water dielectric medium whereas in air as surrounding dielectric medium, 90 nm sized Au nanospheres exhibits maximum SP excitation². The main applications of solid gold (Au) nano-spheres are limited within the visible regime. Its application cannot be extended to infrared regime as it exhibits peak absorption around 530 nm and it can be detuned about 30 nm by changing its size and shape and surrounding dielectric interface³. Nanoshell or core shell is another kind of plasmonic material that has potential applications in the biomedical field⁴. The nanoshell exhibits optical absorption in the infrared regime where human tissue possess less optical attenuation due to reduced infrared light scattering and absorption. The other advantage of using CS particles is that its plasmonic excitation can be detuned to wide range from near infrared to about 2000 nm of optical wavelength⁴. The present aim is to examine how CS particles can be used to study the functional parameters of blood.

2. MATERIALS AND METHODS

2.1 Materials

The materials used for the synthesis of the Au nanoshell were: 2-Aminoethanethiol hydrochloride (AET), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDAC) (Sigma-Aldrich), 2-(N-Morpholino)ethanesulfonic acid hydrate (MES) (Sigma-Aldrich), gold(III) chloride hydrate (chloroauric acid) (Sigma-Aldrich), sodium hydroxide (NaOH) (Sigma-Aldrich), tetrakis(hydroxymethyl)phosphonium chloride (THPC), potassium carbonate (Sigma-Aldrich), formaldehyde (HCHO) (Sigma-Aldrich), ammonium hydroxide (Sigma-Aldrich), Phosphate-buffered saline (PBS) and HPLC water.

2.2 Procurement of blood

Blood is collected by netCAD (Vancouver, Canada), the research division of Canadian Blood Services, under protocol 2013-001 which involves standard Canadian Blood Services collection and testing procedures of whole blood, and delivery overnight at 4C, with continuous monitoring during shipment to ensure no temperature deviations occur. This procedure has been approved by the research ethics boards of both Ryerson University and Canadian Blood Services

2.3 Blood sample preparation

Three concentrations of blood (with hematocrit levels 1.6%, 0.8%, and 0.4%) were prepared in PBS solution. The guidelines on handling the blood were followed in accordance to the recommendations of the International Society for Clinical Hemorheology and the European Society for Clinical Hemorheology and Microcirculation⁵. The blood was centrifuged in room temperature at 2000xg for 6 min to separate the plasma and the buffy coat. Isotonic phosphate buffered saline (PBS) was used to wash RBCs for two times. The centrifuged RBC was then used to prepare three blood samples with hematocrit levels (1.6%, 0.8%, and 0.4%) in PBS.

2.4 Synthesis of Au nanoshell

Au nanoshells or core-shell nanoparticles are synthesized as described in literature⁶. Polystyrene spheres (PS) of size 1 μm are used as the core medium. The surface of the PS spheres are activated with carboxylic acid ligand. Au nano-shells are obtained from carboxylated surfaced polystyrene spheres. To dress Au nanoparticles around the PS sphere, the carboxylic acid group of polystyrene spheres needs to be thiolated as it can readily form transition metal thiolate complexes with metal ions. Thiolation of polystyrene spheres is achieved using 2-Aminoethanethiol hydrochloride (AET) which could readily forms amide bond with carboxylic acid by replacing the hydroxyl group. After thiolation, it is dressed with Au nanoparticles to form an Au nanoshell. The growth of the nanoshell around PS core involved two step processes. First the PS is dressed with Au nanoparticles of smaller size followed by larger sized Au nanoparticles. Reduction of gold reagent such as hydrogen tetrachloroaurate(III) trihydrate in the presence of tetrakis(hydroxymethyl)phosphonium chloride (THPC) resulted in Au nanoparticles of size 1-2 nm. The usage of Au (THPC) nanoparticles resulted in sparse coverage of Au nanoparticles around the PS spheres. Further shell growth around PS spheres is achieved using potassium carbonate (K_2CO_3) reduced hydrogen tetrachloroaurate(III)trihydrate. The reduction tetrachloroaurate(III)trihydrate yielded Au nanoparticles of size 2 to 5 nm.

Carboxylate microspheres from Polyscience, Inc were used for the gold nanoshell preparation. The microspheres were available in aqueous suspension with concentration 2.5% (w/v). 0.3 ml of solution was used to prepare gold nanoshells. The prepared gold nanoshells were dispersed in 10 ml of HPLC water and preserved as stock solution for further studies.

Three samples (A, B and C) containing the mixture of CS and blood with hematocrit level 1.6%, 0.8%, and 0.4% were prepared for the present studies. 1 ml of each blood (hematocrit level 1.6%, 0.8%, and 0.4%) was mixed with 2 ml of stock solution of the prepared CS particles. All optical absorption spectra were acquired with a spectrophotometer (PerkinElmer) and electron microscopy was done with a Tecnai G2 transmission electron microscope (TEM).

3. RESULT AND DISCUSSION

Core shell particles with Au shell were imaged with transmission electron microscopy which confirmed the thin gold coating (Figure 1). Optical absorption studies show that the CS particles exhibited plasmonic peaks around 750 nm and 850nm respectively (Figure 2a). The optical properties of the CS are also investigated using Mie scattering theory.

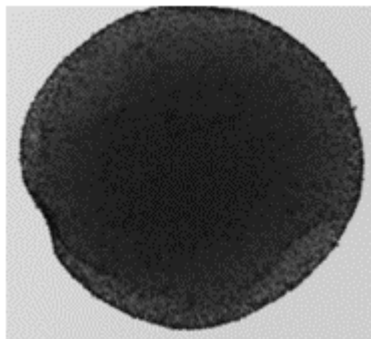


Figure 1. The TEM image of CS particles.

These studies show that CS particles exhibit multi plasmonic peaks which are absent in the synthesized CS particles.

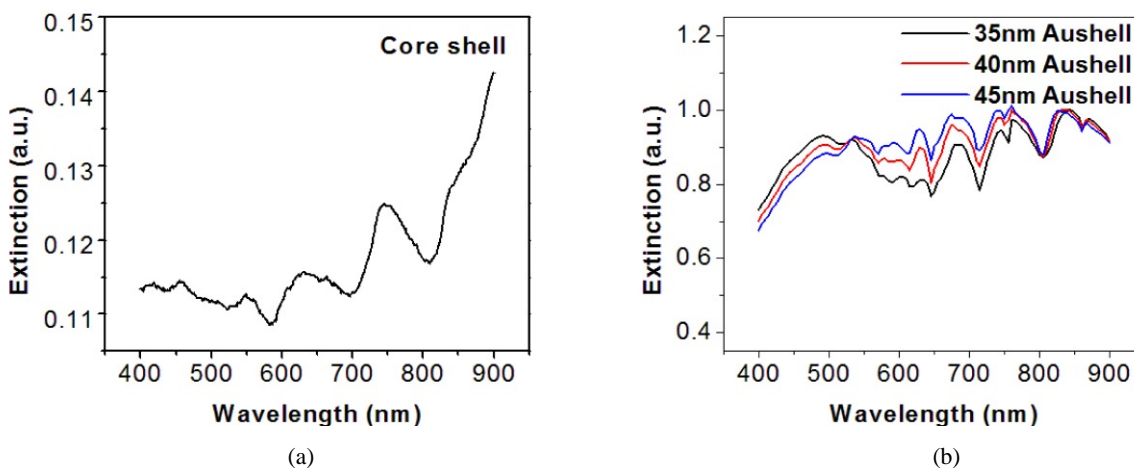


Figure 2. (a) Experimental measurements of the optical extinction coefficient of 1 μm core-shell particles and (b) Theoretical Mie scattering studies of 1 μm core-shell particles with Au shell thicknesses of 35, 40 and 45 nm.

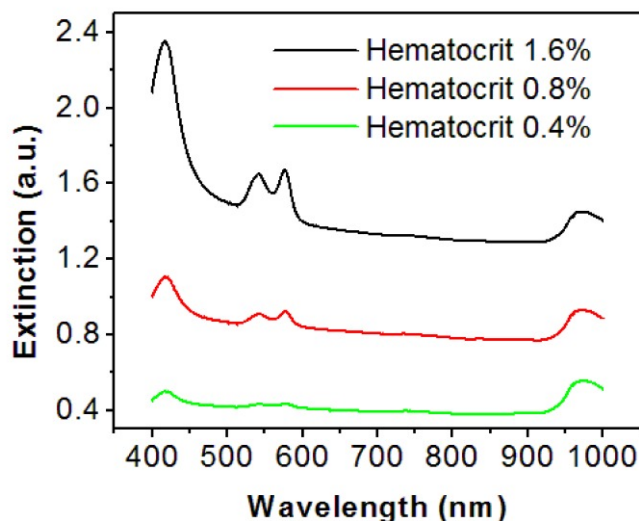


Figure 3. Optical absorption spectra of blood with hematocrit levels 1.6%, 0.8%, and 0.4%

This is because as the shell that is formed using finite sized Au nanoparticles as building blocks are distributed randomly on the core particle (resulting in amorphous distribution around PS). The sensing properties of CS particles are investigated by changing dielectric properties of the surrounding medium. One way of accomplishing this is by changing the blood haematocrit. Blood is used for the present studies as it exhibits significant absorption variation at 750 nm and 850 nm respectively, and this depends on the haemoglobin oxygenated or deoxygenated state. The oxyhemoglobin has significantly lower ($518 \text{ cm}^{-1}/\text{M}$) absorption at 750 nm than deoxyhemoglobin ($1495.24 \text{ cm}^{-1}/\text{M}$), while at 850 nm deoxyhemoglobin exhibits slightly higher absorption ($1058 \text{ cm}^{-1}/\text{M}$) than oxyhemoglobin ($691.32 \text{ cm}^{-1}/\text{M}$)⁷. Figure 3 shows optical absorption spectra of blood with hematocrit levels 1.6%, 0.8%, and 0.4%. The addition of blood with hematocrit level 1.6%, 0.8%, and 0.4% to CS (Sample A, B and C) showed a shift in plasmon peak with increase in blood concentration.

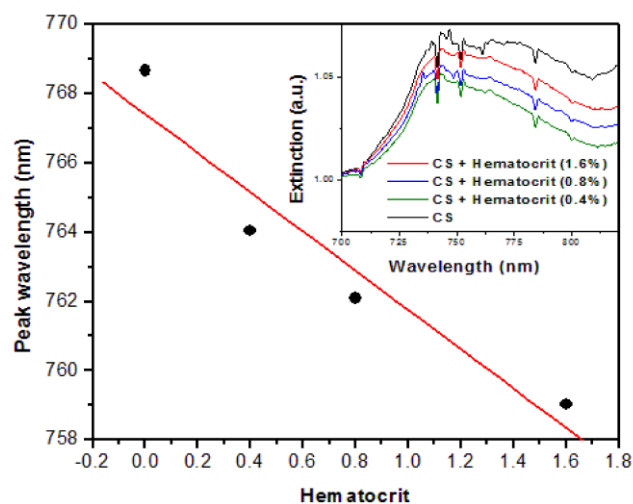


Figure 4. A plot of the 750 nm plasmon peak wavelength shift as function of blood hematocrit level. Inset: The optical extinction spectra of 750 nm plasmon peak of CS, sample A, B and C.

Figure 4 shows a plot of the blue end plasmon peak wavelength (750 nm) versus hematocrit level. The inset in figure 4 represents the optical extinction spectra of 750 nm plasmon peak of CS, sample A, B and C. The solid dots represent the experimental measurements and the solid red line represents the linear fit to these measurements. The plasmon peak showed a red shift with increasing hematocrit concentration. The 750 nm plasmonic peak wavelength shift was measured to be 4.11 ± 0.26 nm per percent dilution of hematocrit.

4. DISCUSSION AND CONCLUSION

The synthesized CS particles exhibit prominent peaks at 750 nm and 830 nm, the wavelength regime used to investigate oxygen saturation of blood for photoacoustic measurements in some commercial instruments. The study of the 750 nm plasmon peak of CS in blood shows a 4.11 ± 0.26 nm wavelength shift per percent dilution of hematocrit. These particles can be used as agents to study functional properties of blood by examination of the plasmon shifts using imaging technologies such as photoacoustic imaging. As CS offers better absorption than many other molecular species, CS can be employed novel class of contrast agent for photoacoustic based imaging – thus enabling in principle the plasmonic sensing of blood constituents in-situ. It can also find applications in scattering-based acoustic and optical imaging methodologies which offer a new approach to non-invasive point-of-care detection, diagnosis, and monitoring.

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