

# Optically Active Nanoparticle Coated Polystyrene Spheres

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## ABSTRACT

Nanoparticles (NPs) with either plasmonic or upconverting properties have been selectively coated onto the surfaces of polystyrene (PS) spheres, imparting their optical properties to the PS colloids. These NP coated PS spheres have many potential applications, such as in medicine as drug-delivery systems or diagnostic tools. To prepare the NP coated PS spheres, gold or core-shell NaYF<sub>4</sub>Tm<sub>0.5</sub>Yb<sub>30</sub>/NaYF<sub>4</sub> NPs were synthesized and separately combined with amino-functionalized PS spheres. The mechanism by which the NPs adhered to the PS spheres is attributed to interactions of the NP and a polyvinylpyrrolidone additive with the surfaces of the PS spheres. Two-photon fluorescence microscopy and SERS analysis demonstrate the potential applications of these NP coated PS spheres.

## INTRODUCTION

The unique optical properties of some nanoparticles (NPs) make them useful for an array of applications that include advances in medical, sensing and advanced computing technologies. Nanoparticle-based diagnostics, for example, have the potential to improve specificity and sensitivity for earlier and more accurate detection of pathogens and disease [1, 2]. Nanoparticles may also be used in medical treatment for photothermal therapy of cancer or as drug delivery agents [2, 3]. Other researchers are looking into the use of NPs for optical memory applications, for new sensors and to improve security technologies [4-6].

Upconverting (UC) NPs are of interest for their unique nonlinear optical properties [2, 4, 5, 9-11]. The UC NPs can perform photon upconversion, whereby the NPs absorb low energy radiation (i.e. near IR wavelengths) and emit high energy radiation (i.e. visible wavelengths). The potential of UC NPs in diagnostics has been shown in many studies [2, 5]. *In vivo* detection of UC NPs has been demonstrated in worms [10] and mice [11] with a good depth of detection owing to the low energy of the excitation wavelengths. Other researchers have used UC NPs for sensor applications [4] and nanoscale thermometry [9]. The applications of these nanomaterials will expand as research continues in this area.

Gold NPs are a relatively chemically inert platform whose chemical functionality is often determined by the molecular coatings on their surfaces [12]. Their surface chemistry can be easily modified to suit the needs of particular applications. In addition, their size, shape, and morphology can be fine-tuned to optimize their optical properties [13]. Gold NPs have an established track record as a stable and tunable platform for biological imaging, cancer therapeutics, and optical-based diagnostics [14]. One of the relatively unique applications for Au NPs is as surface enhanced Raman spectroscopy (SERS) substrates [15]. The tunable surface plasmon resonance (SPR) of the Au NPs is used in SERS to enhance the Raman spectral intensity of molecules bound or otherwise adhered to the surfaces of the Au.

This paper presents a simple method for the preparation of PS spheres decorated with either a uniform coating of UC or Au NPs. These materials are prepared by adhering polyvinylpyrrolidone (PVP) stabilized NaYF<sub>4</sub>Tm<sub>0.5</sub>Yb<sub>30</sub>/NaYF<sub>4</sub> NPs or Au NPs onto the surfaces of amino functionalized polystyrene (amino-PS) spheres. Previous literature reports the decoration of Au [17, 22] and UC NPs [16] onto larger spheres by a number of methods with varying degrees of uniformity and distribution of NPs across the surfaces of the larger sphere. Our method achieves a highly uniform coating of NPs on larger spheres by a two-step process. In this process, the NPs can be synthesized and fine-tuned prior to decoration onto the larger spheres, which is particularly useful for a range of applications as demonstrated herein. This method of coating the NPs onto larger spheres can overcome challenges for dispersing, purifying, and otherwise manipulating the NPs. The NPs can also be coated onto spheres of varying size. Control over the size of the larger spheres may be of use for *in vitro* or *in vivo* studies where uptake by cells is dependent on size of the particles [7] or for selective removal of these materials from a solution of interest. In addition, the incorporation of optically active NPs into photonic crystals is of interest for further tuning of their photonic properties [8].

## EXPERIMENTAL

The core-shell UC NPs of NaYF<sub>4</sub>Tm<sub>0.5</sub>Yb<sub>30</sub>/NaYF<sub>4</sub> were synthesized using a modification of a previously reported procedure [18]. The exact experimental procedure is detailed in our recent publication [19]. Chloroform, dichloromethane (DCM) and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Hexanes and diethyl ether from Caledon Inc. and anhydrous ethyl alcohol (EtOH) from Commercial Alcohols were also used. All chemicals were used as received, without any further purification. The UC NPs were transferred to the aqueous phase post-synthesis for coating onto the PS spheres following a procedure modified from a previous report [20]. A dispersion of oleate-coated NPs in chloroform (0.15 mL, 4wt%) was added to a 50 mL round bottom flask equipped with a stir bar, followed by 5 mL each of DCM and DMF. The reaction mixture was stirred and 150 mg of PVP (~ 10 kg mol<sup>-1</sup>, Sigma Aldrich) was added. Once the PVP had dissolved, the resulting mixture was refluxed for 12 hours. The reaction solution was then cooled to RT and the PVP-coated NPs precipitated by adding them to an excess of diethyl ether (90 mL) *via* Pasteur pipette. The NPs were isolated *via* centrifugation. The resulting pellet was washed with diethyl ether and isolated *via* centrifugation. The NPs were then dispersed in 5 mL of EtOH for further use.

Gold NPs were prepared by a modification of two previously reported syntheses [21]. Hydrogen tetrachloroaurate trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), 99.9%; tetrakis (hydroxymethyl) phosphonium chloride (THPC), 80% in H<sub>2</sub>O; PVP (~ 55 kg mol<sup>-1</sup>) and sodium hydroxide (NaOH), ≥ 97% were purchased from Sigma-Aldrich. A solution of 25 mM HAuCl<sub>4</sub> was prepared with deionized (DI) water (18.2 MΩ·cm) at least one day prior to use. PVP (1.22 g) was added to 45.5 mL DI water in a 100 mL round bottom flask equipped with a stir bar. Once dissolved, 2 mL of the 25 mM gold solution was added. After 5 minutes, 0.2 M NaOH (1.5 mL) and 84 mM THPC (1.0 mL), both prepared with DI water, were added to the round bottom flask and allowed to stir for 10 min. The mixture was then heated to 100°C and held for 3 hours. After cooling to RT, the Au NP dispersion was centrifuged for 30 minutes at 13500 RPM to remove less stable NPs from the solution. The resulting supernatant was used for further experiments.

The NP coatings were prepared by combining Au or UC NPs with amino-PS spheres (Polysciences, Inc. or Bangs Laboratories, Inc.). Before use, PS spheres were washed with EtOH and isolated *via* centrifugation. The pH of the reaction was adjusted by addition of 1% HCl,

prepared by dilution of concentrated HCl (Sigma Aldrich) with DI water. To prepare the UC NP coated spheres (UC-PS), 2 mL of the UC NP dispersion, 1% HCl (~50  $\mu$ l) and 1- $\mu$ m diameter PS spheres (50 mg dispersed in 0.5 mL DI H<sub>2</sub>O) were combined in a 20 mL glass vial equipped with a stir bar. The mixture was held for 3 hours at 55°C before cooling to RT and isolating the products *via* centrifugation. To purify the UC-PS from residual UC NPs, the isolated pellet was dispersed in EtOH and the UC-PS allowed to settle out of solution. After several hours, the UC NP containing supernatant was removed. Gold NP coated spheres (Au-PS) were similarly prepared with 180-nm diameter PS spheres. After 3 days held at 55°C, the solution was cooled to RT and the product isolated *via* centrifugation. The resulting pellet was washed several times with EtOH and water and isolated *via* centrifugation to remove residual Au NPs.

The as-prepared NPs and purified samples of NPs coated onto PS spheres were analyzed by transmission electron microscopy (TEM) on a FEI Tecnai G2 field emission scanning TEM. Purified UC-PS were drop cast from a dispersion in EtOH onto a glass slide, allowed to dry and sealed with a cover slip for imaging on a Leica SP5 laser scanning confocal two-photon microscope (FM) with a 980 nm laser-diode excitation source (150 W cm<sup>-2</sup>). An extinction spectrum of the Au NPs was obtained with a Varian Cary Win 300 Bio UV-Vis spectrophotometer. To perform Raman analysis, purified Au-PS were cast onto a piece of polished silicon wafer. The sample was then soaked for 2 days in a solution of ~ 1 mM 1,4 – benzenedithiol (1,4 – BDT) (Sigma-Aldrich, 99%) prepared in EtOH. Raman spectroscopy was performed with a Renishaw inVia Raman spectrometer coupled to a Leica DM2500 microscope. Spectra were obtained through a 50X objective lens (NA = 0.63) with excitation by either a 514 nm laser (output power ~ 15mW) or a 785 nm laser (200 mW).

## DISCUSSION

The coatings of UC and Au NPs uniformly cover the surfaces of the PS spheres (Figures 1 and 2). The NPs adhere to the surfaces of the PS spheres due to interactions between the NP, the PVP stabilizer, and the surfaces of the amino-PS spheres. The interactions of the PVP with the amino-PS are based on adsorption, and not on chemical reaction [22]. Attempts in our laboratory to coat the amino-PS spheres with NPs stabilized by groups other than PVP (i.e. sodium citrate) did not produce the same uniform coatings, suggesting that PVP plays an important role in the formation of uniform coatings by regulating the interactions between the NPs and the PS spheres. We suspect that differences in the time required for coating of UC NPs and Au NPs onto the amino-PS spheres results from differences in their interactions with the PVP stabilizing agent. Presumably, the Au NPs exhibit a stronger interaction with the PVP. This stronger interaction leads to a slower rate of assembly onto the PS spheres, since the PVP must be displaced to promote interactions between the amino-PS and the Au NPs. The density of NP loading on the surfaces of the PS spheres cannot be readily compared between the coatings of UC NPs and Au NPs due to differences in the density of amino-groups on the surfaces of the PS spheres and their nominal size. Further studies are required to elucidate the exact mechanism by which the NPs and PVP stabilizer interact with the amino-PS to induce uniform NP coating.

The core-shell UC NPs (Figure 1A) readily coat the surfaces of ~1- $\mu$ m diameter PS spheres with an exceptionally high density (Figure 1B). The UC-PS were successfully purified from residual UC NPs in solution, as evident from the TEM images. Analysis by FM of the UC-PS sample demonstrated imaging of discrete particles, with emission peaks from approximately  $\lambda = 400$  to 700 nm (Figure 1C). The lack of other emission sources in the background of the FM image further illustrates the lack of residual, unbound UC NPs after purification. This

demonstration also shows the potential utility of these materials for diagnostic applications, which include use as discrete UC-PS particles that are readily traced by microscopy techniques for *in vitro* or *in vivo* studies.

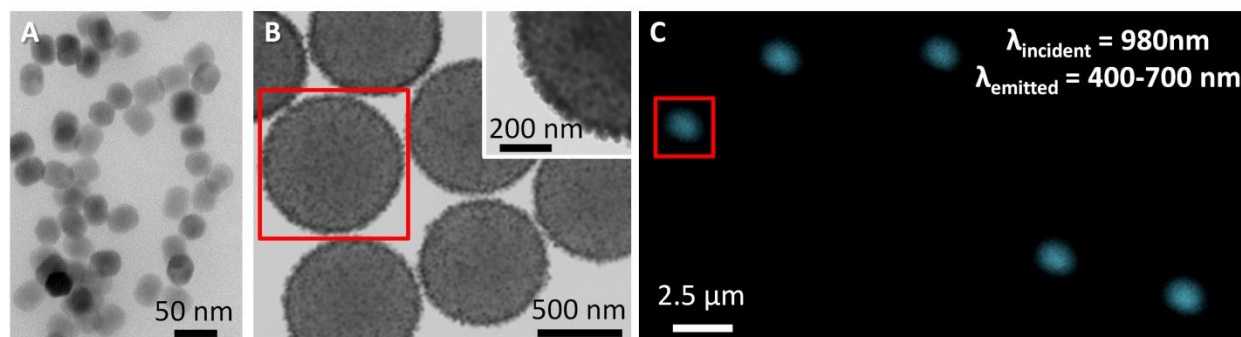


Figure 1. Transmission electron microscope (TEM) images of upconverting nanoparticles (UC NPs) ( $\text{NaYF}_4\text{Tm}_{0.5}\text{Yb}_{30}/\text{NaYF}_4$ ) before (A) and after (B) coating onto  $\sim 1\text{-}\mu\text{m}$  diameter polystyrene (PS) spheres. (C) Two-photon fluorescence microscope (FM) image of the UC NP coated PS spheres dispersed (UC-PS) onto a glass slide. The red box indicates that each particle seen in the FM image corresponds to a single UC-PS (based on size comparison).

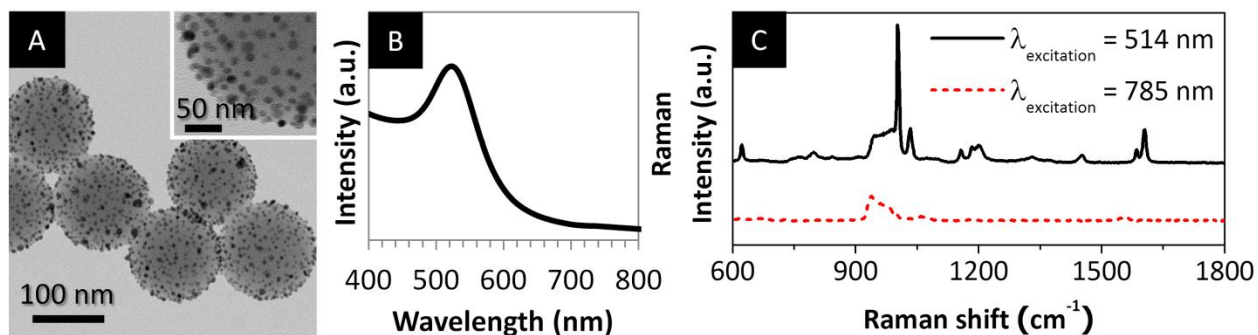


Figure 2. (A) Low and high (inset) magnification TEM images of Au NP coated  $\sim 180\text{-nm}$  diameter PS spheres (Au-PS). (B) Extinction spectrum of Au NPs dispersed in water. (C) SERS of 1,4-benzenedithiol on substrates of Au-PS drop cast on a piece of polished silicon wafer (offset for clarity). The Raman spectra were normalized by the background peak at  $\sim 940\text{ cm}^{-1}$ .

Gold NPs were coated onto the surface of  $\sim 180\text{-nm}$  diameter PS spheres and employed as a medium for SERS. Imaging by TEM reveals a uniform coating of Au NPs on the PS spheres and successful removal of residual unattached Au NPs. Wafer supported Au-PS were used for Raman spectroscopic analysis of 1,4 - BDT. As a control, a Raman spectrum was first collected with laser excitation at 785 nm (Figure 2C, dashed trace). This wavelength does not overlap with the SPR of the Au NPs (Figure 2B) and, therefore, does not induce a SERS effect. The observed peaks correspond to signal from silicon and PS [23]. Excitation by a 514 nm laser, which overlaps with the SPR of the Au NPs, results in SERS of the 1,4 - BDT (Figure 2C, solid trace). The observed peaks correspond with those reported in the literature for 1,4 - BDT [24]. The Raman enhancement of 1,4 - BDT on the Au-PS particles shows that these materials exhibit properties that make them suitable for other applications and further investigations in SERS.

## CONCLUSIONS

Core-shell UC NPs of  $\text{NaYF}_4\text{Tm}_{0.5}\text{Yb}_{30}/\text{NaYF}_4$  and Au NPs have been decorated as uniform coatings onto larger diameter PS spheres. These NP coated PS spheres are readily

purified from residual, unattached NPs after their preparation, as evident from TEM analysis of the purified products. The NP-based coatings formed as a result of interactions between the NPs, PVP stabilizers, and the surfaces of the amino-PS spheres. Differences were observed in the time required to coat the UC NPs and Au NPs onto the PS spheres. These variations likely result from differences in the relative strength of interactions between the PVP stabilizing agent and the corresponding NP. The potential utility of UC-PS as a diagnostic tool has been demonstrated by the use of FM, which could image discrete UC-PS particles of ~1- $\mu\text{m}$  diameter. The SPR properties of the Au-PS assemblies were used to demonstrate SERS of 1,4-BDT. The methods demonstrated herein provide a suitable route to creating uniform particles that retain the optical properties of NPs, but have the size and utility of particles >10x larger in diameter.

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