Core/Shell/Shell Nanomaterials of NaYF₄: Yb, Er/Silica/Polystyrene with High Thermal Stability

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Abstract

Rare earth based nanomaterials with up conversion properties have attracted much attention because of their potential applications in device and solar energy conversion, as well as in new optical tags in biomedical research. Emission stability has been a concern in realizing these materials' application potential. Towards this goal, new core/shell/shell nanomaterials of NaYF₄: Yb, Er/silica/polystyrene is synthesized and characterized. Key steps include thermo decomposition method for production of rare earth nanocrystal core, followed with silica shell coated via hydrolysis in reverse micelle solution and, finally, polystyrene outer shell via atom transfer radical polymerization (ATRP). The structures of these nanomaterials are characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray powder diffraction (XRD). Corresponding upconversion spectra and thermal stability are acquired at each stage of the synthesis. Significant improvement in thermal stability upon coating with thin silica shell was found. The NaYF₄: Yb, Er/silica nanomaterials could be used as is, or functionalized using siloxane chemistry in conjunction with ATRP, as demonstrated in this work. This approach is of generic importance for production of useful rare earth-based nanomaterials, due to the mild reaction conditions used for the surface modification, and the versatility of ATRP to regulate structure and functionality towards designed applications.

Keywords

Core/shell, Core/shell/shell nanoparticles, Upconversion, Rare earth, Polystyrene, Atom transfer radical polymerization (ATRP), Thermal stability

Introduction

Recently, core/shell nanocomposite materials have attracted much interest because the core/shell design enables multi-modality imaging, and as well, incorporates designed chemical and biochemical functions [1-3]. Rare earth nanoparticles (RENs) with an upconversion property represent a desired class of phosphors in bio-imaging, security and solar applications due to the capability of absorbing red or infrared (IR) radiation and emitting visible photon [4,5]. The optical property reduces auto-fluorescence background, avoids photo-bleaching, and facilitates deeper penetration to a bio-specimen than conventional down-conversion phosphors [6-8]. Another potential application includes anti-counterfeiting because RENs could provide security marks invisible to human eyes, and thus be difficult to mimic [9-11]. In addition, RENs could improve solar energy harvesting efficiency by utilizing the IR region of the solar spectrum [12,13].

Advancing and realizing those applications requires that the

RENs should be compatible with their local environment and have high stability during an operation. Prior work has indicated that the stability of RENs' fluorescence property might be a concern under various temperatures [14-16]. Prior work indicated that the upconversion efficiency of hexagonal phased NaYF₄: Yb, Er would decay to 30% at 450 K, compared to the emission at room temperature, and that this decay is not reversible [16]. In addition, bare RENs are not bio-friendly, and should be modified by designed functionalities towards specific bio-applications [17-20]. Toward these needs, we designed core/shell/shell nanomaterials, shown in Scheme 1, aiming to improve stability via silica coating and make the materials environmental friendly via a polymer outer shell. Polymers are typically used as the coating to passivate RENs and to enable further functionalization. For example, RENs with oleic acid as the capping agent and methyl benzoate with poly(methyl methacrylate) as the binding agent have been used for new upconversion security ink for anti-counterfeiting fabrication [21]. Pre-made polymer chains, such as polyethylene glycol, polyacrylic acid and polyethyleneimine

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have been coated on fluoride based upconversion material by ligand exchange and layer-by-layer deposition approach [5,22]. New coating methods are necessary to increase flexibility and to enable control of thickness and functionality by design. However, most polymer-coating techniques are subject to the nature of the REN crystal surface, the capping agent of the crystal, or the polymer candidates for coating, limiting the versatile coupling of polymer with RENs. To date, surface initiated polymerization on noble metals such as gold [23,24], semiconductor quantum dots such as CdSe [25,26] and magnetic nanoparticles such as iron oxide [2,27] have been widely reported, which render the target substrate with a variety of functionalities carried by versatile polymers. However, direct surface grafting of polymer from RENs is challenging, given the fact that the most well-known class of RENs, the fluoride based material such as hexagonal phase $\text{NaY}_{0.78}\text{Yb}_{0.2}\text{Er}_{0.02}\text{F}_4$, shows relatively low reactivity for surface polymerization compared to the above substrates.

Here we report a simple method with mild reaction condition to form a polymer shell on REN core by silica coating and atom transfer radical polymerization (ATRP). First, thermo decomposition method was used to prepare the rare earth nanocrystal core, followed by silica inner shell coating via hydrolysis in reverse micelle solution, and finally a polystyrene outer shell via atom transfer radical polymerization (ATRP). The structures of these nanomaterials are characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray powder diffraction (XRD) while the corresponding up conversion spectra were measured. Materials were subjected to upconversion emission intensity to test their thermal stability. The results indicate clear improvement in stability in comparison to uncoated rare earth nanocrystal core. The mild reaction conditions used for the surface modification and the flexibility of ATRP to regulate structure and functionality are advantageous for research and development. This work paves the way to incorporate rare earth based nanocomposites to a wide range of applications such as display, solar cells, and biological tagging.

Materials and Methods

Materials

Rare earth oxides (Y_2O_3 , Yb_2O_3 , Er_2O_3), sodium trifluoroacetate, oleic acid (OA, 90%), oleylamine (OM, 70%), 1-octadecene (ODE, 90%), trifluoroacetic acid (99%), tetraethyl orthosilicate (TEOS), polyoxyethylene (5) nonylphenylether (IGEPAL CO-520), ammonia hydroxide solution (28-30%), 2-bromoisobutryl bromide, allyl alcohol, triethylamine, diethyl ether, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst), copper (II) bromide (CuBr_2), calcium hydride (CaH_2), magnesium sulfate (MgSO_4), tetrahydrofuran (THF, 99%) cyclohexane, absolute ethanol and hexane were purchased from Sigma-Aldrich and used without purification. Dimethylethyloxysilane was purchased from Fisher Scientific and used without purification. Copper (I) bromide (CuBr) was purchased from Sigma-Aldrich and purified until colorless through grinding it into a fine powder using a mortar and pestle, stirring in glacial acetic acid, consecutive washing with absolute ethanol and diethyl ether, and removal of the volatile materials. Styrene was also purchased from Sigma-Aldrich, dried over CaH_2

and vacuum-distilled. The ligand 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbipy) was purchased from Reilly Industries Inc. and purified with distillation. Water ($\geq 18.2 \text{ M}\Omega\text{-cm}$) was generated from a Milli-Q system (Q-GARD 2, Millipore, Billerica, MA). $\text{Y}(\text{CF}_3\text{COO})_3$, $\text{Yb}(\text{CF}_3\text{COO})_3$ and $\text{Er}(\text{CF}_3\text{COO})_3$ were prepared by dissolving the oxide in dilute trifluoroacetic acid solution and drying in an oven at 160°C overnight.

Synthesis protocols

Synthesis of rare earth doped nanoparticles: All the syntheses in this section were performed using standard oxygen-free conditions. The monodispersed oleic acid capped $\beta\text{-NaY}_{0.78}\text{F}_4\text{:Yb}_{0.2}\text{Er}_{0.02}$ nanoparticles were prepared by a 2-step thermo decomposition reaction [28]. The $\alpha\text{-NaY}_{0.78}\text{F}_4\text{:Yb}_{0.2}\text{Er}_{0.02}$ nanocrystals were synthesized in the first step. 2 mmol CF_3COONa , 1.56 mmol $\text{Y}(\text{CF}_3\text{COO})_3$, 0.4 mmol $\text{Yb}(\text{CF}_3\text{COO})_3$, and 0.04 mmol $\text{Er}(\text{CF}_3\text{COO})_3$ were added to a mixture of 20 mmol OA, 20 mmol OM, and 40 mmol ODE in a 100 mL, 3-necked flask followed by a 30 min vacuum to remove water and oxygen at 100°C . Then, the reaction mixture was heated to 290°C and reacted for 45 min under N_2 flow. The reaction was quenched by removing the heat followed by adding in excess absolute ethanol. The resultant turbid solution was then centrifuged to yield white precipitates. Such precipitate was then washed with ethanol 4x and dried in the vacuum oven at 70°C overnight to afford the $\alpha\text{-NaY}_{0.78}\text{F}_4\text{:Yb}_{0.2}\text{Er}_{0.02}$ nanocrystals. In step 2, $\beta\text{-NaY}_{0.78}\text{F}_4\text{:Yb}_{0.2}\text{Er}_{0.02}$ nanocrystals were prepared using the α -phase nanoparticles made in step 1. 1 mmol CF_3COONa and 1.3 mmol $\alpha\text{-NaY}_{0.78}\text{F}_4\text{:Yb}_{0.2}\text{Er}_{0.02}$ was added to a mixture of 20 mmol OA and 20 mmol ODE in a 50 mL, 3-necked flask followed by a 30 min vacuum to remove water and oxygen at 100°C . The reaction mixture was heated to 330°C and reacted for 15 min under N_2 flow. The reaction was quenched by removing the heat followed by adding in excess absolute ethanol. The resultant turbid solution was then centrifuged to yield white precipitates. Such precipitate was then washed with ethanol 4x and dried in the vacuum oven at 70°C overnight.

Synthesis of REN/silica nanoparticles: In a typical reaction, 1 mL CO-520, 60 mL cyclohexane, and 40 mL containing 80 mg REN nanocrystal solution in cyclohexane were mixed and stirred for 10 min. 4 mL CO-520 and 0.8 mL ammonia (wt 30%) were then added and the container was sealed and sonicated for 20 min until a transparent emulsion was formed. TEOS (0.4 mL) was added into the solution, and the solution was stirred for 2 days at a speed of 600 rpm. REN/Silica core/shell nanoparticles were washed by adding acetone to remove the excess amount of surfactant, and the nanoparticles were washed with ethanol/water (1:1 v/v) 2x.

Synthesis of surface initiator and REN/silica/polystyrene nanoparticles: In a typical reaction, a slightly excess amount of 2-bromoisobutryl bromide was added to the mixture of allyl alcohol and triethylamine in an ice bath. The mixture was brought to room temperature and then stirred for 18 h. The allyl 2-bromoisobutyrate was washed three times with 100 mL water, dried over MgSO_4 and distilled under reduced pressure. The distilled allyl 2-bromoisobutyrate was added with a few drops of Karstedt's hydrosilylation catalyst. A slightly excess amount of dimethylethyloxysilane was added drop wise and the reaction was heated at 80°C for 2-4 hours or until the

Figure 1: (A) A TEM image of the $\beta\text{-NaY}_{0.78}\text{F}_4\text{Yb}_{0.2}\text{Er}_{0.02}$ REN particles. Inset is the size distribution chart for the nanoparticles in the image. (B) A high-resolution TEM image of a typical single REN particle to reveal its crystallinity; (C) An XRD spectrum of as synthesized RENs in comparison to the standard $\beta\text{-NaYF}_4$ crystals (JCPDF # 28-1192); (D) A characteristic emission spectrum of REN particles under 980 nm laser excitation; (E) An EDX spectrum of REN.

vinyl photon disappeared in NMR spectrum to achieve the surface initiator BIDS. Then, REN/Silica particles were isolated from ethanol suspension by centrifugation and re-suspended in THF. The THF solution was heated at 85 °C. A slight excess amount (0.6 mmol, 1.2 mole equivalent) of BIDS was added and the mixture was heated at reflux for 12 h. The particles were isolated by centrifugation and washed 5 times to avoid any adsorbed initiator on surface. The particles were then suspended in hexane and solvent was removed by vacuum to obtain the initiator-modified REN/Silica nanoparticles.

The ATRP polymerization was performed using standard oxygen-free conditions. Initiator modified REN/silica particles from above, 0.6 mmol CuBr, 0.03 mmol CuBr₂, and 1.2 mmol dNbipy ligand were mixed into a Schlenk flask with a stirring bar. 60 mmol styrene was added by a syringe and the flask was deoxygenated (three freeze/vacuum/N₂ cycles). The mixture was stirred vigorously and sonicated to obtain a uniform suspension. The flask was heated to 110 °C and kept for 24 h. The polystyrene coated REN composite was isolated by precipitation with methanol, yielding a white powder [29,30].

Structural and spectroscopic characterization

The size and morphology of the nanomaterials were characterized by a transmission electron microscope (CM 12, Philips) at 120 kV acceleration voltages. Samples for transmission electron microscopy (TEM) were prepared by drying a drop of diluted particles solution on the copper grids coated with a thin carbon film. The samples were also characterized by a scanning electron microscope (Hitachi S-4100T) at 5kV acceleration voltages.

The element analysis of nanomaterials was characterized by energy dispersive X-ray spectroscopy (EDS) (INCA system, Oxford). Powder X-ray diffraction (XRD) patterns of the REN samples on zero-background substrates were recorded on an X-ray diffractometer (D/Max-2500, Rigaku). The spectroscopic properties of the nanomaterials were investigated using an inverted optical microscope (Olympus IX 50, Olympus America Inc., Melville, NY) equipped with an imaging dual grating monochromator and PMT detector (Acton

SP2150, Princeton Instruments). In addition to the lamps, we added 50 mW 980 nm diode laser (UH5-50G-980, World Star Tech) as the excitation source for RENs. Gel permeation chromatography (GPC) was measured in tetrahydrofuran (THF) at 30 °C and a flow rate of 1.00 mL/min. Three Polymer Standards Services columns (100 Å, 1000 Å, and linear) were connected in series to an isocratic pump, an autosampler, a column oven, and a refractive-index detector.

Results and Discussion

Key steps of our material synthesis to produce the designed REN/silica/polystyrene nanoparticles are shown in Scheme 1. First, rare earth upconversion nanocrystal cores were prepared by thermo decomposition method of rare earth trifluoroacetate salt [5,28]. Then, silica was coated on REN surface by reverse micelles method with Igepal CO520 surfactant [18]. The organosiloxane surface initiator 3-(2-bromoisobutryl)propyl Dimethylethoxysilane (BIDS) was synthesized and then coupled with the silica surface. Finally, the initiator-modified nanoparticles were used as macro-initiators for the ATRP polymerization of styrene on REN surfaces catalyzed by CuBr [29,31,32].

Synthesis and characterization of rare earth doped nanoparticles

The detailed synthesis protocols are summarized in the previous section 2.2.1. The afforded $\beta\text{-NaY}_{0.78}\text{F}_4\text{Yb}_{0.2}\text{Er}_{0.02}$ nanocrystals can dissolve in hexane, cyclohexane, and other nonpolar solvents. This observation is the quick verification that as synthesized $\beta\text{-NaY}_{0.78}\text{F}_4\text{Yb}_{0.2}\text{Er}_{0.02}$ nanocrystals were capped with the oleic acid capping ligand as shown in Scheme 1.

The size of REN cores was characterized using TEM. In the large area TEM micrograph as shown in Figure 1A, the individual REN particles can be clearly observed. Based on over 150 REN particles in this electron micrograph, the size distribution measured as 3%. The particle size for REN nanocrystals was found to be 20.6 ± 0.6 nm obtained by a detailed particle-size analysis of multiple TEM images and hundreds of particles. Figure 1B is a high-resolution TEM

Figure 2: (A) A TEM image of REN particles; (B) A zoom-in view from a high coverage region in (A); (C) A TEM image of REN/silica particles; (D) A zoom-in view of high coverage region in (C); (E) A TEM image of REN/silica/polystyrene particles; (F) A zoom-in view of high coverage region in (E).

image of one REN nanoparticle, in which the lattice fringes can be clearly distinguished. This indicates the high single crystallinity of our RENs. The single crystallinity of these RENs is further confirmed by XRD shown in Figure 1C. All the diffraction peaks in XRD pattern can be assigned by comparison with the standard single crystal of β - NaYF_4 (JCPDF # 28-1192). Our results are consistent with the prior knowledge that the two-step thermo decomposition method represents current state-of-the-art to produce RENs with the highest known uniformity, mono-dispersivity and single-crystallinity [28].

Figure 1D shows the emission spectrum of the RENs under 980 nm laser excitation. Two peaks are observed at 550 and 670 nm, which is consistent with the known upconversion characteristic [13,28]. The stoichiometry is determined via EDS shown in Figure 1E, where key elements are clearly present and pristine: Na (1.041 keV), Y (1.685 keV), F (0.677 keV) and Yb (1.948 keV). Quantitatively, $\text{F/Na/Y/Yb} = 4:1:0.8:0.2$, which is in good agreement of designed stoichiometry. Collectively, the RENs are readily produced with the hexagonal phase NaYF_4 (β - NaYF_4) nanocrystals doped with 20% Yb^{3+} and 2% Er^{3+} ions. This structure and stoichiometry represents optimal upconversion efficiency [33,34].

Synthesis and characterization of REN/Silica nanoparticles

The silica shell was coated on REN surface via TEOS hydrolysis in reverse micelle solutions as shown in Scheme 1. After introduction of the surfactant molecules and trace amount of water to the REN suspension, a thin water layer formed around the surfactant-bound REN. This water layer triggered the TEOS hydrolysis and subsequently resulted in the silica shell formation. The resulting core/shell nanoparticles can be dispersed in polar solvent such as water and ethanol, which was a quick in situ verification of successful coating of silica shell.

The addition of silica shell is evident by the presence of two TEM contrasts, dark core and grey shell, shown in Figure 2C. These two contrasts correspond to REN core and silica shell, respectively. The successful coating by silica is also supported by the increasing overall

size comparing TEM images before and after coating reactions, as shown in Figure 2A and Figure 2C, Figure 2C also reveals that the REN/silica nanoparticles are fairly uniform in size, with the diameter measuring 58.5 ± 1.8 nm. The silica shell thickness can be quantified from zoom-in TEM images before and after coating, as shown in Figure 2B and Figure 2D, respectively. The thickness of the silica shell is 19 ± 2 nm among hundreds of nanoparticles measured in TEM images. Our results are in good agreement with prior knowledge that TEOS hydrolysis based coating is a good generic protocol for enclosing nanoparticle surface with silica of designed thickness [18]. The spectra are identical qualitatively to that of RENs, and the upconversion intensity remains constant as well. The stability of the spectra will be discussed in later sections.

Synthesis and characterization of REN/silica/polystyrene nanoparticles

ATRP was utilized to add the outer polystyrene shell, as shown in Scheme 1. Organosiloxane based surface initiator, BIDS, was synthesized and attached to the silica coating driven by the strong conjugation between silica and organosiloxanes. The silanol group binds to the silica surface while the Br terminal sticks out and acts as the surface initiator for polymerization [27,29,31,35]. First, the surface initiator BIDS was synthesized and installed on the REN/silica surface. Polymerization can then only occur at the REN/silica surface through ATRP approach. Polymerization under a different monomer: initiator ratio at 100:1 and 300:1 was also conducted to study the influence of the chain length and molecular weight.

As reactions proceeded, we noticed dispersity of nanomaterials evolved accordingly. The RENs were well dispersed in non-polar solvent such as hexane or toluene. After the silica coating, the core-shell particles dispersed well in polar solvent, such as water or ethanol, forming a milky suspension. Upon the polystyrene grafting, the composite particles became well dispersed in polymer friendly solvents such as THF and toluene. These observations provide quick in situ indication that the surface modifications were successful and consistent with our designed functionalities.

Table 1: Molecular weight and polydispersity index of polystyrene coatings from the REN/SiO₂/polystyrene nanomaterials.

Monomer:initiator (mol:mol)	Mn ($\times 10^4$ g/mol)	Mw ($\times 10^4$ g/mol)	PDI
100:1	1.80	1.94	1.08
300:1	7.25	8.12	1.12

Figure 3: The emission spectra of RENs (green), REN/silica (grey), and REN/silica/polystyrene (brown) under 980 nm laser excitation.

Characterization of all nanomaterials followed similar protocols as used for the RENs. From images 2A-2C, the uniformity of resulting nanomaterials seems to be preserved. The final nanomaterials, REN/silica/polystyrene nanoparticles, measure 68.9 ± 2.2 nm in diameter, which means that the thickness of the polystyrene shell is 5 ± 2 nm. The fluorescence spectra are identical qualitatively and quantitatively to that of REN/silica nanomaterials. The stability of the spectra will be discussed in later sections.

One feature revealed in TEM images is the gap among nearest neighbor particles, which provides supportive evidence of surface coating. In the case of REN particles as shown in Figure 2B, the gap is 4.3 nm, which corresponds well with the closely packed RENs with the oleic acid coating (i.e. capping ligand). The gap among REN/silica particles is 9 nm, larger than that among RENs. This is consistent with the stronger repulsive interactions among nanoparticles due to the negative charges of silica and the surfactant of Igpal CO520 [36,37]. The gaps among nearest neighbor REN/silica/polystyrene particles are 6 nm, smaller than that among REN/silica nanoparticles. This is consistent with our ATRP procedures, during which the surfactants were removed, and the final exterior coating of uncharged polystyrene. Polystyrene are known to be relatively soft and more deformable in comparison to inner cores and middle silica shells [38]. The bright contrast surrounding the boundary of REN/silica/polystyrene nanoparticles is likely due to the charging effect of the polystyrene shells when imaged by TEM [39].

The grafted polystyrene was also characterized by GPC to obtain the molecular weight, as summarized in Table 1. The grafted polystyrene with 100:1 monomer/initiator ratio has a molecular weight of $M_n = 1.80 \times 10^4$ g/mol, $M_w = 1.94 \times 10^4$ g/mol and a polydispersity index (PDI) ($= M_w/M_n$) of 1.08, which is in good agreement with typical ATRP polymerization (PDI < 1.3), while PDI is typically larger than 2 for other conventional polymerization methods [30,40,41]. The narrow molecular weight distribution indicates the polymer coating process is relatively homogenous with similar polymer chain length. The polymer chain length, and the thickness of the polymer shell, can be readily tuned by varying the ratio between the monomer and surface initiator. Polymerization with 100:1 monomer/initiator ratio shows the thickness of polystyrene shell as 5 nm as indicated in Figure 2, which is in good agreement with ATRP carried out under similar

Figure 4: The thermal stability of RENs (black), REN/silica (red), and REN/silica/polystyrene (blue) using the ratio of 550 nm at test temperature and room temperature.

conditions [29]. Polymerization with 300:1 monomer/initiator ratio still keeps a very low PDI at 1.12, and increased the polymer chain length and molecular weight from 1.8 to 7.25×10^4 g/mol, which will lead the increased polystyrene shell thickness. However, the molecular weight of actual obtained polymers in both 100:1 and 300:1 ratio are larger than the theoretical values calculated from monomer/initiator ratio, which indicated that about 40%-60% of surface initiators are installed on particle surface.

Featured by controllable polymer thickness and better molecular weight, ATRP technique has been widely used to graft polymer from particle surface [2,29,31,42]. This technique not only enables us to tune the polymer shell thickness by control over the polymer chain length, but also potentially enables us to adapt the functional group into polymer chain for different of applications. The mild conditions of ATRP also help to preserve the structure and property integrity of the core materials.

Thermal stability of nanomaterials

The upconversion property of nanoparticles at each key steps were measured using our home built instrument with 980 nm laser source [13]. The upconversion emission intensity was plotted using the photon counts recorded by the detector under the same configurations, to allow quantitative comparison. The three particle solutions were prepared by dissolving REN, REN/silica and REN/silica/PS particles into hexane, ethanol and THF, respectively. The solution concentration of 2 mg/mL REN cores was used for all samples. A 25 μ L of solution was deposited onto 1 cm² surface of a clean cover slip and let dry. For each sample, the emission was measured by focusing the laser at various spots and then taking a statistical average to account for possible inhomogeneity and to ensure good accuracy. As shown in Figure 3, no significant decrease of photoluminescence of the RENs were detected upon silica and polymer coatings, indicating that the silica and polystyrene shells are transparent in the REN emission range. The coating reactions did not alter the structure of RENs, due to the mild reaction conditions used in our approaches.

The thermal stability of nanoparticles at each key step was also investigated by acquiring spectra as a function of temperature. The emission peak intensity at 550 nm was chosen to evaluate the thermal stability of our nanomaterials. The ratio of the 550 nm emission peak at test temperature and at room temperature was plotted vs test tem-

perature as shown in Figure 4. The RENs core without coatings showed the decay of emission clearly at high temperature (decreased to 0.77 at 300 °C) and REN/silica and REN/silica/polystyrene remained the same at test temperatures up to 300 °C. With the silica and polystyrene as the coating matrix, the upconversion properties of RENs are preserved. The possible mechanism for improved stability with surface coating might be due to the fact that the local environment of Ln^{3+} is better preserved due to inert coating than REN core alone. In other words, the movement or diffusion of the Ln^{3+} does not lead to significant changes in their local environment for the core/shell materials, which is analogous to improved stability among rare earth doped glass materials [43]. The addition of silica shells stabilized RENs and enabled a wide range of chemical modality such as siloxane function [44,45] and ATRP polymerization [29,31] as demonstrated by this work. The silica and polystyrene coating provided the superior spectroscopy stability and functionality, which could extend the rare earth based core particles into much wider applications.

Conclusions

In this work, we report a new core/shell/shell material with superior upconversion fluorescence stability by a simple method to protect the rare earth doped upconversion nanocrystals and enable further functionalization with surface chemistry. Silica shell is prepared using a mild room temperature hydrolysis reaction. The obtained 19 nm silica shell is sufficient to stabilize the rare earth doped upconversion nanoparticles against the high temperature and enable the further functionalization such as siloxane chemistry and atom transfer radical polymerizations. We have demonstrated the polystyrene shell with 5 nm thickness can be coated by the surface initiated ATRP approach. The grafted polystyrene chains have very narrow molecule weight distribution and the molecule weight as well as polymer shell thickness can be tuned with reaction parameters. The mild reaction conditions are essential to keep the structure and property integrity. The versatility of ATRP method enables the various functional group to be conjugated on rare earth based nanomaterial surface. Future works including incorporating designed functional groups into polymer shell, immobilization and patterning of the upconverting core-shell particles on functional surfaces and testing the composite material in biological and energy conversion applications in wide temperature range still need further investigation.

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