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**Synthesis of gold/rare-earth-vanadate core/shell nanorods for integrating plasmon and fluorescence**

Jia-Hong Wang, Hao Huang, Da-Quan Zhang, Ming Chen, Ya-Fang Zhang, Xue-Feng Yu, Li Zhou, and Qu-Quan Wang

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**Integrating plasmon and fluorescence:** A general strategy was established for the growth of rare-earth-vanadate shells onto Au nanorod cores to form Au/GdVO₄:Eu core/shell heterostructures with efficient integration of plasmonic properties of Au nanorods and fluorescence properties of rare-earth ions.
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ABSTRACT
The nanoscale core/shell heterostructure is a particularly efficient motif to combine the promising properties of plasmonic materials and rare-earth compounds; however, there remain significant challenges in the synthetic control due to the large interfacial energy between these two intrinsically unmatched materials. Herein, we report a synthetic route to grow rare-earth vanadate shells onto gold nanorod (AuNR) cores. After modifying the AuNR surface with oleate through surfactant exchange, well-packaged rare-earth oxide (e.g., Gd2O3:Eu) shells are grown onto the AuNRs ascribed to the multiple roles of oleate. Furthermore, the composition of the shell have been altered from oxide to vanadate (GdVO4:Eu) using an anion exchange method. Attributing to the carefully designed strategy, the AuNR cores maintain the morphology during the synthesis process, thus the final Au/GdVO4:Eu core/shell NRs exhibit strong absorption bands and high photothermal efficiency. In addition, the Au/GdVO4:Eu NRs perform bright Eu3+ fluorescence with quantum yield as high as ~17%, and bright Sm3+ and Dy3+ fluorescence can also be obtained by changing the lanthanide doping in the oxide formation. With the attractive integration of the plasmonic and fluorescence properties, such core/shell heterostructures will find particular applications in wide areas from biomedicine to energy.

1. Introduction
Hybrid nanostructures based on plasmonic nanocrystals (such as Au) have become extremely promising candidates for developing nanotechnology and offer immense potential applications in biomedicine [1], sensor [2], catalysis [3,4], photovoltaics [5,6], and so on. Recently, great efforts in this area have been made to create core/shell heterostructures using Au nanocrystals as seeds and growing different materials on their surface [7-10].

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The use of pre-grown Au nanocrystals allows their shapes, sizes, and plasmonic properties to be rationally designed, and such core/shell heterostructures can maximize the interfacial area to combine the properties of both the core and shell materials [11-15]. However, the large interfacial energy induced by the lattice mismatch between Au and the shell materials is the main obstacle for nanoscale integration. One efficient route to solve this problem is the introduction of a compatible ligand/surfactant between Au and the shell materials (e.g., sulfides and oxides) to make interface tuning so that the lattice mismatch can be neglected [16,17]. Another route is to use the pre-grown Ag layer as a “bridge” to decrease the lattice mismatch, facilitating the subsequent growth of the sulfide and selenide shells [18,19]. Despite these significant progresses, challenges still remain in the shell synthesis for those dissimilar materials. It is particularly difficult to maintain the plasmonic properties of the Au cores and achieve good optical/electronic properties of the shell materials simultaneously.

Among these dissimilar materials, rare-earth compounds represent an important category [20-23]. The 4f intra-configurational transitions are independent of crystalline size/shape and are not susceptible to the environment, making it unnecessary to strictly control the monodispersity size to attain spectral purity. Furthermore, multicolor emissions can be achieved by simply employing different lanthanide ion (Ln³⁺) dopants for their abundant electron transitions, and such Ln³⁺ emitters are well distinguishable from other fluorophores because of their large stock shift, narrow fluorescence peak, long luminescent lifetime and excellent photostability [24,25]. The combination of rare-earth compounds with plasmonic nanocrystals has attracted increased research interest for enhancing upconversion luminescence [26], and developing the potential multitask applications integrated plasmon and fluorescence [27]. However, compared with those conventional methods [28-31], the synthesis of rare-earth compound shells onto Au nanocrystals is much more technical and specific because the crystal structures of these two materials are entirely different, and violent reaction conditions are generally required for the crystal growth of rare-earth compounds. It is known that the rare-earth compounds, such as vanadates and fluorides, often nucleate rapidly and grow to be angular particles with special crystalline orientation [32,33], which lead to that the direct formation of a spread-out shell appears unfavorable. Furthermore, high temperature and high pH are often required for the growth of rare-earth compounds with bright Ln³⁺ fluorescence, which may lead to the deformation of the Au nanocrystals. Therefore, there is still no efficient method for the growth of rare-earth compounds onto Au nanocrystals to form core/shell heterostructures.

In this research, we present a general route to the growth of rare-earth compounds onto Au nanocrystals with the efficient combination of plasmonic and fluorescence properties. The growth of GdVO₃:Eu shells onto gold nanorods (AuNRs) is used as a typical representation to demonstrate such a growth procedure (Fig. 1). The AuNRs are one of the most promising plasmonic materials due to their unique and tunable longitudinal surface plasmon resonance (SPR) mode in a wide range from the visible to near-infrared (NIR) region [34]. The synthesis of AuNRs generally relies on a cationic surfactant cetyltrimethylammonium bromide (CTAB) as the “shape-inducing” agent [35], which results in a large interfacial energy, preventing the growth of the shells with dissimilar materials. Therefore, a surfactant exchange method was first used to modify the AuNR surface using oleate as a ligand to replace the CTAB. Moreover, as shown in the schematic illustration of oleate, it could be assumed that a bilayer of alternate oleate was formed on the surface of the AuNR after ligand exchange, so that the oleate could act as a bridge to link Au surface with Gd³⁺. Meanwhile, due to the electrostatic force and chemical chelating caused by the carboxylic acid group in oleate [36], Gd³⁺ and Eu³⁺ ions could be absorbed around the AuNRs, the oxide (Gd₂O₃:Eu) seeds were nucleated, and the complete oxide shell was ripened with the hydrolyzation of hexamethylene tetramine (HMT), resulting in the formation of Au/Gd₂O₃:Eu core/shell NRs. In addition, a Na₂VO₄ assisted hydrothermal route was employed to alter the composition of the shell from oxide (Gd₂O₃:Eu) to vanadate (GdVO₃:Eu) through an in situ anion exchange process. The products
during the synthesis process were characterized in detail. Furthermore, the plasmonic and fluorescence properties, and the relationship between extinction and fluorescence in the final products of Au/GdVO₄:Eu core/shell heterostructures were investigated.

2. Results and discussion

2.1 Surfactant exchange of AuNRs

Figure 2 shows the surface modify of the AuNRs in the surfactant exchange. At the start of the entire procedure, uniform AuNRs coated with CTAB (named CTAB-AuNRs) were obtained using a seed-mediated growth method [35]. To obtain the oleate-coated AuNRs (called oleate-AuNRs), the CTAB-AuNRs were incubated with sodium oleate (NaOL) at 85 °C in an oven. The success of the surfactant exchange from CTAB to oleate was demonstrated by the X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) results [37,38]. As observed in the survey XPS spectra (Fig. 2(b)), the peaks arising from Br in CTAB disappeared, while the peaks arising from Na in NaOL appeared. Moreover, in the magnified XPS spectra of C 1s (Fig. 2(c)), the peak at 288.2 eV assigned to carboxylate groups further suggests the presence of oleate. In the FTIR signals (Fig. 2(d)), in addition to the similarities at 2920 and 2852 cm⁻¹ (C-H stretching), the main differences between the oleate-AuNRs and CTAB-AuNRs are focused on the region arranged from 1400 to 1600 cm⁻¹. The spectrum of the oleate-AuNRs clearly shows the signals at 1448 and 1560 cm⁻¹, which were assignable to the symmetric and asymmetric stretching modes of the carboxylate group in oleate, respectively; while the signal at 1479 cm⁻¹ assignable to the asymmetric mode of the head [Ni(CH₃)$_3$] methyl group in CTAB appears in the spectrum of the CATB-AuNRs. These investigations indicate that the CTAB bond on the NR surface was almost completely displaced by oleate through the surfactant exchange. In addition, the absorption spectra (Fig. 2(e)) demonstrate that the surfactant exchange results in a slight blue shift of the SPR peaks, and the inset transmission electron microscope (TEM) image demonstrates the good dispersibility of the oleate-AuNRs.

2.2 Growth of rare-earth oxide shell on AuNRs

The oleate-AuNRs were subsequently subjected to oxide overgrowth by adding rare-earth nitrates Gd(NO₃)₃ (with 5% Eu(NO₃)₃ doped) as the ion source and HMT as the oxygen agent; then, the mixture was treated under a mild hydrothermal
reaction at 85 °C for 5 h. The scanning electron microscopy (SEM) and TEM images show the products of ellipsoid-like Au/Gd:Ox:Eu NRs with almost unetched AuNR cores and well-packaged Gd:Ox:Eu shells (Fig. 3(a) and 3(b)). In the high-resolution TEM (HRTEM) image (Fig. 3(c)), the Gd:Ox shell is polycrystalline and consists of small crystallite domains with random orientations. The lattice spacing was measured to be 0.312 nm (Fig. 3(d)), which is consistent with the (222) planes of the cubic Gd:Ox structure. The chemical states of Gd in Gd:Ox are confirmed by XPS (Fig. 3(e)), the peaks belonging to Gd 3d/2 and Gd 3d/2 are centered at 1189.8 eV and 1221.7 eV, respectively. The line shape, peak positions and spin orbit splitting 32 eV are all in good agreement with previous published data of Gd:Ox nanoparticles [39]. In addition, the EDX spectrum in Fig. 3(f) indicates that the atom percentages of Au, Gd and Eu are 54.22%, 41.94% and 3.86%, respectively. The higher Eu doping ratio (approximately 8.4%) than that in the stock solution (5%) is most likely caused by the more active chemical activity of Eu3+ than Gd3+, which makes it easier for Eu3+ to chelate with the carboxyl group on oleate. Furthermore, the supplementary characterizations in Fig. S1 further confirm the successful large-scale synthesis of the Au/Gd:Ox:Eu core/shell NRs with almost no byproducts.

Based on the above observations, the formation process of the oxide shells could be suggested as below. When the rare-earth ions were mixed with the oleate-AuNRs, the rare-earth ions could be attracted by the carboxylic acid group in oleate due to the electrostatic force, and the strong chemical chelating between oleate and rare-earth ions led to the generation of instable rare-earth-oleate complex. These two factors urge the ion concentration to increase more around the AuNRs than in the free space. When the stock solution was heated up, HMT was hydrolyzed to release NH3, which further hydrolyzed OH− to combine with Gd3+ (Eu3+ doped), resulting in an intermediate product of Gd(OH)52− according to Eq. (1). Then, a decomposition reaction (Eq. (2)) occurred, causing the Gd:Ox:Eu shells to grow onto the AuNRs. The time dependent overall morphology and crystalline change of the oxide shells were characterized in Fig. S2, which confirms the shell formation.

\[
\text{Gd}^{3+} + 5 \text{OH}^- \rightarrow \text{Gd(OH)}_5^{2-} \quad (1)
\]

\[
\text{Gd(OH)}_5^{2-} \rightarrow \text{Gd}_2\text{O}_3 + 3 \text{H}_2\text{O} + 2\text{OH}^- \quad (2)
\]

To further identify the effects of oleate on the oxide shell formation, a set of control experiments were performed. When the Gd(NO3)3 and HMT were directly reacted with the CTAB-AuNRs, clean AuNRs and anomalous oxide particles were observed. A further experiment was performed by adding NaOL to the above reaction to make the surfactant exchange and oxide construction to carried simultaneously. The corresponding products were dispersible; however, numerous divisive domains instead of spread-out shells were generated (Fig. S3, in the ESM), which indicates that the self-nucleated nanocrystals were discontinuous because of the repulsive force of oleate on their surface. Moreover, the magnified XPS spectra of C 1s in Fig. S1(d) assigned to carboxylate groups further suggest the presence of oleate on the surface of the Au/Gd:Ox:Eu NRs, which means that the oleate also acts as a stabilizer for the products. These results demonstrate the multiple roles of oleate in the oxide shell.
formation: a) attracting rare-earth ions onto the Au surface, b) forming a metal-complex with the assistance of chemical chelating, and c) stabilizing the final products in the synthetic solutions. In addition, for the effect of oleate that enriched the rare-earth ions around the AuNRs to emerge, the reaction should proceed under an undisturbed and mild environment; stirring or excessive temperature would destroy the balance (Fig. S4 in the ESM). NaOH or other agents with strong hydrolyzation activity or high pH value will cause the rapid combination of Gd\(^{3+}\) and OH\(^-\) and will lead the oxide formation to be uncontrollable. If NaOH or NH\(_3\)-H\(_2\)O was used to replace HMT as the base source, the core-shell structures were absence and the products were lousy (Fig. S5 in the ESM).

For the growth of oxides on metal nanocrystal, the use of metal salts may generally cause aggregation of the seed particles [17], it is a great challenge to find one compatible ligand/surfactant for stabilizing the products and tuning the interface between two dissimilar materials simultaneously. The addition of multiple additives is a suggested efficient method; however, this addition often makes the synthesis complicated and difficult to control. In our strategy, due to the multiple roles of oleate, the synthesis is easily achieved and is thus suitable for large-scale production. Understanding the multi-roles of oleate will also aid in the rational design and growth of desired oxide shells to form different metal/oxide core/shell heterostructures. As a simple example, other lanthanide oxides Nd\(_2\)O\(_3\) and Yb\(_2\)O\(_3\) shells have been synthesized using same method (Fig. S6 in the ESM).

2.3 Anion exchange to transform oxide shell into vanadate

An in situ anion exchange approach was then used to alter the composition of the shell. Typically, using a hydrothermal treatment at 120 °C with Na\(_3\)VO\(_4\) as the vanadic acidification agent, the Gd\(_2\)O\(_3\):Eu shells were transformed into GdVO\(_4\):Eu shells, which was confirmed by the XRD analysis (Fig. 4(a)). As expected, the diffraction peaks are well assigned to the JCPDS card No. 17-0260 (Au) in red lines and the JCPDS card No. 86-0996 (GdVO\(_4\)) in blue lines, indicating that the obtained shell is GdVO\(_4\). The supplementary characterizations in Fig. S7 also confirm the successful large-scale synthesis of the Au/GdVO\(_4\):Eu core/shell NRs with few byproducts. The EDX spectrum (Fig. 4(b)) reveals that the Gd(Eu)/V atomic ratio is approximately 0.95, which is similar to the standard molar ratio in GdVO\(_4\):Eu. This result confirms the successful element changes in the anion exchange. Furthermore, it can be observed that the Eu dopant ratio is 6.7%, which only changes slightly during this process. The SEM and TEM images show the complete core/shell structure of the GdVO\(_4\):Eu NRs, and the vanadate shells appear to be a pile of closely arranged rod-like crystals with the same direction (Fig. 4(c) and 4(d)). The detailed structure was further characterized by HRTEM (Fig. 4(e)-(h)), the lattice fringes with a spacing of 0.36 nm agree well with the lattice spacing of the (200) plane of GdVO\(_4\) (Fig. 4(f) and 4(h)). It can be observed that the vanadate prefers to grow and array regularly, and the array orientation against the AuNRs is completely random. Due to the crystal domains in Gd\(_2\)O\(_3\) exhibit random orientations, it can be supposed that the growth orientation of GdVO\(_4\) is most likely dependent on the starting lattice arrangement in the anion exchange, which guides the subsequent growth orientation.

![Figure 4](image_url) Characterizations of Au/GdVO\(_4\):Eu NRs: a) XRD pattern, b) EDX spectrum, c) SEM image and d) TEM image of Au/GdVO\(_4\):Eu NRs, e) and g) HRTEM images of two typical Au/GdVO\(_4\):Eu NRs with different array orientations, f) and h) HRTEM images corresponding to the regions marked by the white square in e) and g), respectively.
The reaction mechanism of GdVO\textsubscript{4}:Eu shells are explained below. In the initial condition at a high temperature and high pressure, the Gd\textsubscript{2}O\textsubscript{3} was converted into Gd\textsuperscript{3+} ions according to Eq. (3). Then, the Gd\textsuperscript{3+} reacted with VO\textsubscript{4}\textsuperscript{3−} and developed a GdVO\textsubscript{4} layer at the solid-liquid interface (Eq. (4)).

\[
\text{Gd}_2\text{O}_3 + 6 H^+ + 3 H_2O + 2 \text{Gd}^{3+} \rightarrow 2 \text{GdVO}_4 
\]

(3)

\[
\text{Gd}^{3+} + \text{VO}_4^{3−} \rightarrow \text{GdVO}_4
\]

(4)

In most anion exchange cases, the preformatted vanadate layer may lead to the fast diffusion of Gd\textsuperscript{3+} and prevent the inward diffusion of VO\textsubscript{4}\textsuperscript{3−}. This process causes the vanadate products to be hollow or mesoporous [40,41]. Unlike these samples performed in previous literatures, because the as-grown Gd2O3:Eu shell is dense and the pH value for the ion exchange is nearly neutral (the pH value is 7.4 for the hydrolytic reaction taken by Na\textsubscript{3}VO\textsubscript{4}), the inward diffusion rate of VO\textsubscript{4}\textsuperscript{3−} anions is similar to the outward diffusion rate of Gd\textsuperscript{3+}; therefore, few hollow products are observed. The time dependent morphology and crystalline changes of the shells from oxide to vanadate characterized in Fig. S8 also have confirmed the success of anion exchange.

It is known that rare-earth vanadates are a promising class of rare-earth compounds with wonderful characteristics, such as bright fluorescence and chemical and thermal stability [42, 43]. However, the classical crystallization kinetics process often results in rapid nucleation and growth, which causes the direct shell formation to be unfavorable. Here, the \textit{in situ} anion-exchange approach with minimal crystal structure reorganization can be a more efficient method to obtain vanadate shells with few byproducts of free vanadate nanoparticles. Furthermore, considering the wide applicability of the anion exchange strategy, our study also suggests an efficient method to overcome the large interfacial energy between the metal and other rare-earth compounds \textit{e.g.}, fluorides and phosphates. It should be noted that the choice of temperature was for the sake of effective transformation in anion exchange. When the reaction temperature was lower than 120 °C, only few vanadates were generated.

2.4 Plasmonic properties of Au/GdVO\textsubscript{4}:Eu NRs

The plasmonic properties of the Au/GdVO\textsubscript{4}:Eu NRs were investigated. As shown in Fig. 5(a), an additional UV absorption band attributed to VO\textsubscript{4}\textsuperscript{3−} is appeared at 280 nm, which suggests that the rare-earth compound shell have been transformed from oxide to vanadate. Compared with the original CTAB-AuNRs, the longitudinal SPR band of the Au/GdVO\textsubscript{4}:Eu NRs red-shifted from 800 nm to 824 nm, and the full width at half maximum (FWHM) broaden slightly (~10 nm). These observations demonstrate that the Au/GdVO\textsubscript{4}:Eu NRs have well maintain the crystalline and extinction properties of the original AuNRs. In fact, it is a difficult to achieve similar results in the synthesis of hetero-nanostructures based on the AuNRs. In the previous cases for the growth of sulfides on the AuNRs, the S\textsuperscript{2−} ions usually cause gold crystal etching and surface defects formation [18]. On the other hand, in the latest available works to directly prepare rare-earth compounds onto the AuNRs, because of the high temperature annealing, the diffusion of the gold cores occurred and the SPR band became indistinct [44, 45]. In contrast, the growth procedure presented here can successfully avoid the crystalline damage risk of the AuNRs, and the little changed extinction makes the sample design to be easy control.

Moreover, the strong absorption band of the Au/GdVO\textsubscript{4}:Eu NRs in the NIR allow it to be used for photothermal conversion. An temperature elevation experiments (Fig. 5(b)) conducted in the aqueous solution under 810 nm light irradiation was employed to study its photothermal conversion ability. Using a reported method [46], the photothermal efficiency of the Au/GdVO\textsubscript{4}:Eu NRs was measured to be approximately 22%, which is slightly lower than that of the original CTAB-AuNRs (23%) due to the deviation of their longitudinal SPR peak against the wavelength of the incidence light. Since the photothermal conversion is seriously rely on the absorption across section and morphology of plasmonic nanocrystals, the effective photothermal conversion is a positive evidence to prove that the Au/GdVO\textsubscript{4}:Eu NRs maintain the excellent plasmonic properties of the AuNRs.

2.5 Fluorescence properties of Au/GdVO\textsubscript{4}:Eu NRs

As shown in Fig. 5(c), bright red fluorescence can be observed in the aqueous solution of the
Au/GdVO₄:Eu NRs under UV light irradiation. The excitation spectrum (black line) with a maximum at ~300 nm (monitoring at 617 nm) is assigned to the energy transfer from the oxygen ligand (O²⁻) to central vanadium ion (V⁵⁺) inside VO₃⁻. The emission lines located at approximately 594, 617, 648, and 697 nm are ascribed to the electric dipole transition of Eu³⁺ from the 5D₃ level to a sublevel of 7F_j (J = 1, 2, 3, 4), respectively, whereas the weak peak at 538 nm is attributed to the transition of 5D₁→7F₁. Using Rhodamine B as the contrast sample, the quantum yield of the Au/GdVO₄:Eu NRs in aqueous solution was measured to be as high as 17%. Furthermore, bright Sm³⁺ and Dy³⁺ fluorescence can also be obtained simply by changing the lanthanide doping in the oxide shell formation (Fig. 5(d)).

Since plasmonic materials are known as fluorescence quenchers, a key question is whether the combined fluorophores would still preserve good fluorescence, which means the heterostructure is whether be appropriate for practical fluorescence-based applications. This topic was further studied by a series of Au/GdVO₄:Eu NRs synthesized at different temperatures of 120, 140, 160 and 180 °C (Fig. 6). It can be observed that the Au/GdVO₄:Eu NRs synthesized at 120 °C show both the maintained SPR band and brightest Eu³⁺ fluorescence. When the reaction temperature was taken over 120 °C, the AuNR cores were shortened (Fig. 6(a)-(d)), the longitudinal SPR band was blue shifted (Fig. 6(e)), and the corresponding Eu³⁺ fluorescence intensity was decreased (Fig. 6(f)). Typically, when the reaction was taken under 180 °C, the AuNRs collapsed to quasi-phase, and the longitudinal SPR band was displaced by a shoulder at 670 nm. In an overview of the four samples, the absorption intensity at 617 nm increased linearly while the fluorescence intensity of Eu³⁺ decreased linearly (Fig. 6(g)). It is supposed that there is particular contact between these two factors.

Generally, the entire excitation and emission process of Eu³⁺ fluorescence can be described as follows: the VO₃⁻ groups first transition to the excited states under UV light excitation; the energy then transfers to Eu³⁺ ions through the vanadate sublattice; and the excited Eu³⁺ ions finally produce emissions in the de-excitation [47]. In this whole process, no charge transfer occurs, and all of the energy transfer occurs in the sublattice or during internal electron transitions. Hence, even if the vanadates are close to the AuNR cores, the quenching effect induced by the charge transfer could almost be avoided. However, the samples extinction at the wavelength (617 nm) of the Eu³⁺ emission would block the fluorescence transmittance; meanwhile, as well as the fluorescence quenching induced by charge transfer occurred rarely, the negative correlation coefficient for fluorescence intensity against absorption intensity is about 0.5, that as the absorption increased to four times, the fluorescence intensity decreased to half (Fig. 6(g)). For the case of the Au/GdVO₄:Eu NRs synthesized at 120 °C, the wavelength of the Eu³⁺ emission is exactly located in the valley region between the transverse and longitudinal SPR bands; thus, the self-absorption or scattering can also be minimized. The above finding suggests that the Au/GdVO₄:Eu core/shell NRs provide an efficient heterostructure to preserve the bright fluorescence that escapes from the quenching, and may find some particular applications in bioimaging and photovoltaic areas.

### 3. Conclusions

In conclusion, we have developed a general strategy for the growth of rare-earth-vanadate shells onto AuNR cores to form core/shell heterostructures. In the oxide (Gd₂O₃:Eu) shell formation, the oleate
coated through surfactant exchange played critical roles in (a) attracting rare-earth ions onto the Au surface; (b) forming a metal-complex with the assistance of chemical chelating; and (c) stabilizing the final products in the synthetic solutions. Then, the in situ anion exchange approach successfully altered the shell composition from oxide to vanadate (GdVO₄:Eu). During the entire reaction, the size, shape, and plasmonic properties of the AuNR cores were well maintained, and the final products of the Au/GdVO₄:Eu NRs exhibit bright Eu³⁺ fluorescence. In the synthetic methodology area, with an understanding of the multiple roles of oleate, the proposed surfactant exchange method can be applied to help rational synthesis of various metal/oxide core/shell nanostructures. Furthermore, due to the wide applicability of anion exchange, our synthesis strategy might be extended to the growth of other rare-earth compound shells such as fluorides and phosphates.

The Au/GdVO₄:Eu NRs accomplished in this work have combined the plasmonic properties of the AuNRs and fluorescence properties of rare-earth ions. Owing to the well maintained morphology of the AuNRs, strong NIR absorption and effective photothermal effects have been performed, and other functions related to the AuNRs such as two-photon luminescence, dark-field imaging and photoacoustic imaging could also be expected. Meanwhile, bright fluorescence from doped rare-earth ions (such as Eu³⁺, Dy³⁺ and Dy³⁺) with high quantum yield has been achieved, and the GdVO₄ host is also a good agent for magnetic resonance imaging. All these characters can be integrated in one Au/GdVO₄:Eu particle, which make it particularly suitable for multi-modal bio-imaging and therapy. In addition, the AuNRs are also promising material for photovoltaics that can enhance the solar light collection and scattering, using rare-earth vanadate as isolation layer and taking advantage of its multi-color fluorescence, this core/shell heterostructures would also be favourable for the solar cell. Above all, with the attractive combination of plasmonic and fluorescence properties, such core/shell heterostructures may find particular applications in wide areas from biomedicine to energy.

4. Methods

4.1 Materials

Chloroauric acid (HAuCl₄·4H₂O, 99.99%), hydrochloric acid (HCl, 36–38%), hexamethylene tetramine (HMT, 99.99%), sodium oleate (NaOL), and trisodium tetraoxovanadate dodecahydrate (Na₃VO₄·12H₂O, 99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Hexadecyltrimethylammonium bromide (CTAB, 97.0%), sodium borohydride (NaBH₄, 96%), silver nitrate (AgNO₃, 99.8%), and L-ascorbic acid (AA, 99.7%) were obtained from Sigma Aldrich (America). Gadolinium(III) nitrate hexahydrate (Gd(NO₃)₃·6H₂O, 99.99%), europium(III) nitrate hexahydrate (Eu(NO₃)₃·6H₂O, 99.99%), samarium(III) nitrate hexahydrate (Sm(NO₃)₃·6H₂O, 99.99%), dysprosium(III) nitrate hexahydrate (Dy(NO₃)₃·6H₂O,

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Figure 6 a-d) TEM images, e) absorption spectra, and f) fluorescence emission spectra of Au/GdVO₄:Eu NRs synthesized at different reaction temperatures. g) Slope comparison between the fluorescence intensity at 617 nm and the absorption intensity at 617 nm.
99.99%) and other lanthanide nitrates were purchased from Aladdin Industrial Inc. (Shanghai, China). All of the chemicals were used as received without purification. Ultrapure water with a resistivity of approximately 18.25 MΩ·cm was used as the solvent in all the experiments.

4.2 Synthesis of gold nanorods

The gold nanorods (AuNRs) were synthesized in aqueous solution using a seed-mediated growth method [48]. The 3-4 nm gold seed particles were prepared by mixing 4.5 mL of DI water, 0.5 mL of 5 mM HAuCl₄ and 5 mL of 0.2 M CTAB. The solution was stirred vigorously followed by the immediate addition of 600 µL of freshly prepared ice-cold 10 mM of NaBH₄. After vigorous stirring for 2 min, the seed solution was left at room temperature for further use. In the AuNR synthesis, 18 mL of 5 mM HAuCl₄ and 225 µL of 0.1 M AgNO₃ were added to 90 mL of 0.2 M CTAB, and then 225 µL of 1.2 M HCl and 11.1 mL of 10 mM ascorbic acid were added and gently swirled as the color changed from dark orange to colorless. After the color had changed, 150 µL of the CTAB-stabilized gold seed solution were rapidly injected. The resulting solution was gently mixed for 10 s and left undisturbed overnight. Finally, the solution was centrifuged at 12,000 rpm for 15 min to stop the reaction. The supernatant was removed, and the precipitate was resuspended in ultrapure water. The products are CTAB-coated AuNRs (CTAB-AuNRs) with aspect ratios up to 4.7. The concentration is estimated to be approximately 0.8 nM based on the extinction coefficient at the longitudinal SPR wavelength [49].

4.3 Surfactant exchange with oleate

A certain amount of NaOL was dissolved in 4 mL of warm water (~50 °C) to prepare 0.02 M of NaOL solution. The solution was cooled down to room temperature and then uniformly mixed with 6 mL of 1 nM CTAB-AuNRs. The mixture was sealed in an oven and incubated at 85 °C for 1 h. Finally, the solution was centrifuged at 10,000 rpm for 10 min followed by the removal of the supernatant. The products are oleate-coated AuNRs (oleate-AuNRs).

4.4 Synthesis of Au/Gd:O:Eu NRs

For the synthesis of Au/Gd:O:Eu NRs, 5 mL of oleate-AuNR solution was diluted with 14 mL of DI water, 0.5 mL of 0.1 M HMT aqueous solution and 0.5 mL of 0.01 M Gd(NO₃)₃ aqueous solution containing 5% Eu(NO₃)₃ were added in order followed by gentle shaking to achieve a well-dispersed solution. The solution was sealed in an oven carefully and incubated at 85 °C for 3 h. The solution was centrifuged at 8,000 rpm for 8 min followed by removal of the supernatant, and the precipitate was re-dispersed in 5 mL of water. The products are Au/Gd:O:Eu NRs.

4.5 Synthesis of Au/GdVO₃:Eu NRs

For the synthesis of Au/GdVO₃:Eu NRs, 5 mL of Au/Gd:O:Eu aqueous solution was mixed with 5 mL of DI water, 75 µL of 0.1 M NaAuO₃ aqueous solution was added with continuous stirring. The ratio of VO₃³⁻ against RE³⁺ (Gd³⁺ and Eu³⁺) was 1.5. Finally, the mixture was transferred to a Teflon bottle (20 mL in capacity) in a stainless steel autoclave, sealed and stored at 120 °C for 3 h. After the mixture was cooled to room temperature using a hydro-cooling process, the solution was centrifuged at 6,500 rpm for 8 min followed by removal of the supernatant. The products are Au/GdVO₃:Eu NRs.

4.6 Characterization

TEM images were taken using a JEOL 2010 (HT) transmission electron microscope at an accelerating voltage of 200 kV. HRTEM images were taken on a JEOL 2100F transmission electron microscope at an accelerating voltage of 200 kV. SEM was performed using an S-4800 high resolution field emission scanning electron microscopy at an accelerating voltage of 2.0 kV. EDX was performed on an EDAX equipped on a FEG SEM Sirion 200 operated at an accelerating voltage of 20.0 kV, and an EDAX equipped on JEOL 2100F transmission electron microscope at an accelerating voltage of 200 kV. XRD patterns were obtained on a Bruker D8 advance X-ray diffractometer using Cu-Kα radiation (λ = 0.15418 nm). XPS measurements were performed on a Thermo Fisher ESCALAB 250Xi instrument using monochromatic Al-Kα radiation (1486.68 eV). FTIR spectra were obtained using a Nicolet 5700 FTIR spectrometer equipped with a Continu µm-IR
microscope. Absorption spectra were acquired on a TU-1810 UV-Vis-NIR spectrophotometer (Purkinje General Instrument Co. Ltd. Beijing, China). Photoluminescence emission spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp as the excitation source.

4.7 Photothermal efficiency measurement

The photothermal efficiency was measured on a homemade setup as described in our previous work [50]. A 1 cm path length quartz cuvette containing 2 mL of the sample was covered with a foam cap. The cuvette was clamped on the top part above the sample surface, and the bottom of the cuvette was kept at approximately 0.5 cm above the magnetic stirrer. A fiber-coupled continuous semiconductor diode laser (810 nm, KS-810F-8000, Kai Site Electronic Technology Co., Ltd. Shaanxi, China) with a power density of 2.7 W/cm² and a beam diameter of approximately 0.5 cm illuminated the cuvette. A digital thermometer (TX3001, Xinte Digital Instrument Co. Ltd. Beijing, China) was used to monitor the temperature change. Its head was completely submerged in the solution and carefully prevented from direct illumination by the laser. Each sample in a cuvette was irradiated for 15 min under rigorous stirring, and the temperature was recorded every 30 s. All the samples were measured three times, and the average was used in the final analysis.

4.8 Fluorescence quantum yield measurement

The fluorescence quantum yield of the Au/GdVO₃:Eu NRs in aqueous solution was measured by comparing their integrated emission to the emission of a solution of Rhodamin B, which has the same optical density at the excitation wavelength (300 nm) [51].

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