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Terbium and barium codoped mesoporous silica nanoparticles with enhanced optical properties

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A B S T R A C T

In this study, we showed for the first time that barium (Ba) codoping improves the luminescent properties of terbium (Tb)-doped SiO_2 nanoparticles (NPs). In particular, the quantum yield (QY) of SiO_2-Ba,Tb NPs was found to be ~10.7%, whereas the QY of bare SiO_2-Tb NPs was only ~4.3%. Several mechanisms for luminescence enhancement have been proposed. We strongly believe that this methodology can be used to create alternative silica-based NPs with improved optical characteristics.

1. Introduction

Lanthanide-based nanostructures (nanophosphors) have received a lot of attention as optically stable nanoprobes for bioimaging, sensing, security, and photovoltaic applications. Fabrication simplicity, high quantum yields, nonbleaching, large Stokes shifts, and chemical stability make them more popular than traditional fluorescent organic dyes and semiconductor quantum dots [1–3]. Although these lanthanide-based nanostructures demonstrated promising results, their widespread applicability for a variety of applications is still hampered by a number of factors. First, the use of efficient but scarce and costly lanthanide elements (yttrium, gadolinium, etc.) as host materials is not practical from an economic point of view. Second, a transparent SiO_2 coating is usually required for surface passivation purposes. Hence, the development of low-cost optical nanoprobes with excellent optical properties is still a crucial task.

To date, several research groups have attempted to use SiO_2 as a host material because of their well-established synthesis protocols, chemical stability, lowcost, and nontoxicity. For example, several strategies, such as water-in-oil [4,5], thermolysis [6], and adsorption [7–9] have been proposed for lanthanide-doped SiO_2 NPs. Among them, water-in-oil and thermolysis methods are less preferable because of poor control over morphology, inhomogeneous dopant distribution, synthesis complexity, and generation of chemical wastes. In the adsorption method, one can prepare the desired morphology and size of mesoporous SiO_2 nanostructures and later incorporate lanthanide cations into negatively charged silica pores. The main drawback of this method is that only a small amount of cations remain in SiO_2 NPs, which in turn results in luminescent materials with low quantum yields (QYs).

The codoping strategy can be considered one of the promising methods to resolve the issue of the low QY of metal-doped SiO_2 NPs prepared by adsorption methods. For example, various chemical elements, such as Zn [10], Bi [11], Li [12], Al [13], and Ba [14], are often reported as codopants to improve the optical properties of phosphor materials. In some cases, these elements can distort the local bonding around the activator, leading to a change in luminescence intensity. Hence, in the present study, we opted to employ adsorption-based codoping strategy to improve the optical properties of metal-doped SiO_2 NPs. Terbium was used as an optical activator, while barium was used as an earth-abundant codopant. According to a literature survey, metal codoped mesoporous SiO_2 NPs, especially Ba and Tb codoped SiO_2 have not yet been explored.

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2. Materials and methods

Mesoporous silica NPs were prepared according to recently reported protocol [9]. In brief, 10 mg of silica and X mg of $TbCl_3 \cdot 6H_2O$ (X = 1, 2, or 3 mg) were dissolved in 6 mL of deionized (DI) water followed by sonication for 3 min to obtain a colloidal solution. The as-prepared colloidal solution was stirred for 24 h (700 rpm) to achieve adsorption–desorption equilibrium. Metal-activated SiO_2 NPs were collected, dried, and calcinated at 600 °C for 1 h (ramping rate of 5 °C/min). To prepare Tb(III) and Ba(II) codoped silica NPs, 2 mg of $TbCl_3 \cdot 6H_2O$ and 30 mg of $Ba(NO_3)_2$ were dissolved in 6 mL of DI water followed by the addition of 10 mg of SiO_2 NPs. Further procedures were the same as described above for bare SiO_2-Tb NPs. Characterization details can be found in Supporting Information.

3. Results and discussion

First, SiO_2-Tb NPs with various $TbCl_3 \cdot 6H_2O$ salt concentrations (1–3 mg) were prepared to reveal the difference in activator adsorption. Figure S1 (Supporting Information) shows that all samples yielded an average concentration of ~ 3.1 ± 0.5 wt%, demonstrating a negligible difference in Tb adsorption. Consequently, 2 mg of $TbCl_3 \cdot 6H_2O$ was selected as the optimal loading concentration. Next, codoped SiO_2 NPs were prepared by introducing Ba(II) ions. Figures S2 and S3 (Supporting Information) show EDX elemental analysis for both SiO_2-Tb and SiO_2-Ba,Tb NPs. In both cases, main elements such as Si, O, and Tb were easily detected, suggesting the successful incorporation and even distribution of Tb(III) ions. In addition, the uniform incorporation of Ba was also confirmed by EDX elemental analysis for SiO_2-Ba,Tb NPs.

We observed no significant morphological and structural difference between SiO_2-Ba,Tb NPs and SiO_2-Tb NPs; thus, morphological and structural analysis data were presented for SiO_2-Ba,Tb NPs only. Fig. 1 shows that SiO_2-Ba,Tb NPs had a well-defined quasi-spherical shape with a mean size distribution in the range of ~70–80 nm. High-resolution TEM image (Fig. 1 inset) reveals that the synthesized NPs have a well-resolved porous structure even after high-temperature calcination. According to TEM analysis, no aggregates were formed inside the SiO_2 pores, indicating the uniform fixation of dopants to the pore walls. Elemental analysis revealed that Tb concentrations in both samples were nearly identical (~3.1 ± 0.3 wt%), while Ba(II) content in SiO_2-Ba,Tb NPs was found to be ~1.8 wt%.

The surface area and pore size distribution of SiO_2-Ba,Tb NPs were further studied using a nitrogen porosimeter. Fig. 2 shows the

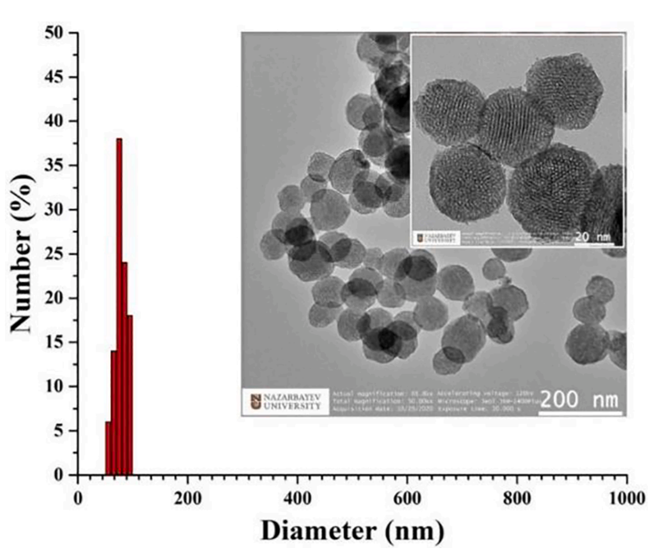

Fig. 1. Size distribution of SiO_2-Ba,Tb NPs. The inset shows low- and high-resolution TEM images of SiO_2-Ba,Tb NPs.

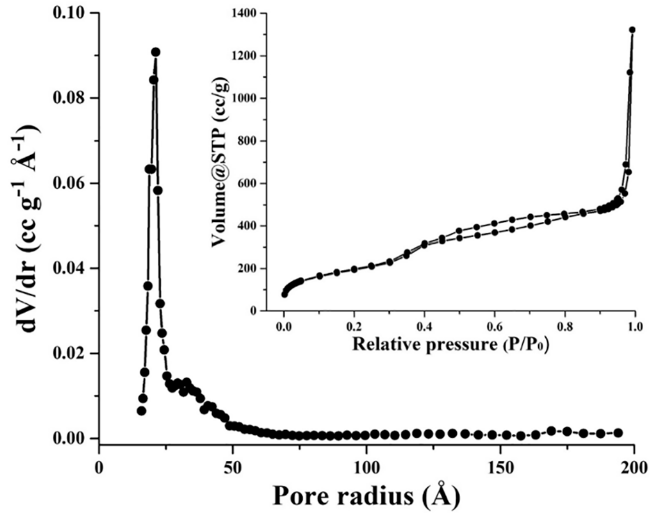

Fig. 2. BJH pore size distribution and BET nitrogen adsorption isotherms (inset) of SiO_2-Ba,Tb NPs.

Barrett–Joyner–Halenda (BJH) pore size distribution and Brunauer–Emmett–Teller (BET) surface area isotherms (inset). SiO_2-Ba,Tb NPs demonstrated a type IV adsorption–desorption isotherm with a calculated specific surface area of ~573.9 m^2/g and pore size of ~3–4 nm. For comparison, the specific surface area for undoped SiO_2 NPs was ~717.3 m^2/g (data not shown). The observation of the type IV isotherm suggests the formation of a mesoporous structure with a narrow pore size distribution [15]. A decrease in surface area can be attributed to the codopants incorporation into silica pores.

The formation of silica-based NPs was further confirmed by FT-IR spectroscopy. Fig. 3 represents the corresponding FT-IR transmittance spectra showing some well-defined bands. For example, the major band at 1068 cm^{-1} with a shoulder at approximately 1220 cm^{-1} belongs to the asymmetric stretching vibrations of siloxane groups (Si-O-Si) [9]. The peak at 807 cm^{-1} can be ascribed to the symmetric stretching vibrations of Si-O-Si [9]. It should be noted that no other bands were detected, suggesting the formation of pure silica structures after the thermal treatment process. The structural properties of the prepared SiO_2-Ba,Tb NPs were also assessed by XRD. The typical XRD pattern revealed a broad peak which corresponds to the amorphous structure of SiO_2 (Fig. 3, inset).

The optical properties of SiO_2-Ba,Tb and SiO_2-Tb NPs were further

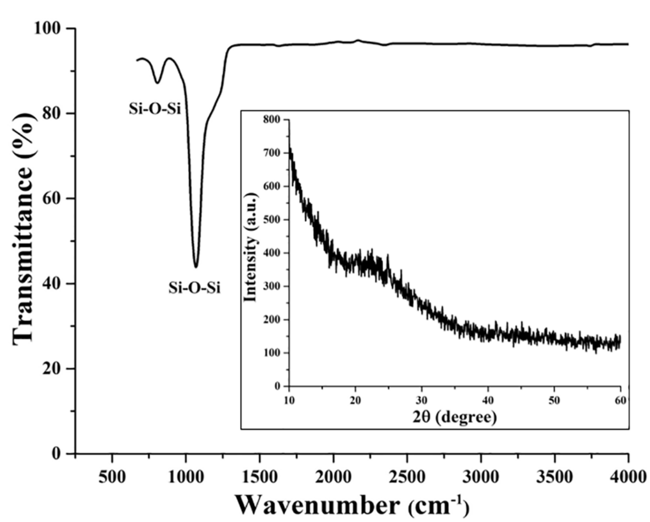

Fig. 3. FTIR analysis and XRD pattern (inset) of SiO_2-Ba,Tb NPs.

analyzed using photoluminescence (PL) spectroscopy. The QYs of these NPs were analyzed at different wavelengths in the range of 250–350 nm with a step of 5 nm. The QY scan revealed that the maximum QY values were 10.7% and 4.3% (λ_{exc} = 260 nm) for SiO_2-Ba,Tb NPs and SiO_2-Tb NPs, respectively. Hence, the optimal excitation wavelength was selected to be ~ 260 nm. Fig. 4 shows the room-temperature PL emission spectra of SiO_2-Tb and SiO_2-Ba,Tb NPs. PL analysis revealed four characteristic Tb emission peaks centered at 487 nm ($^5D_4$-$^7F_6$), 545 nm ($^5D_4$-$^7F_5$), 585 nm ($^5D_4$-$^7F_4$), and 624 nm ($^5D_4$-$^7F_3$) [16,17]. One can observe that the intensity of the $^5D_4$-$^7F_5$ transition at 545 nm prevails; hence, the green color is mostly perceived to the naked eye (Fig. 4, inset). We can speculate that the enhancement of QY in SiO_2-Ba,Tb NPs can be associated with the incorporation of Ba(II) ions. Among the possible options is that crystalline BaO with Tb (III) ions can be formed after the thermal treatment, which results in luminescence improvement similar to that of Al- and Tb-codoped SiO_2 glass [18]. Another mechanism involves better Tb(III) ion-ion separation by Ba(II) codopant, which inhibit the cross-relaxation processes [19,20]. Moreover, the luminescence enhancement can be also associated with charge transfer from Ba element, leading to the improved QY, as it shown with Ba-doped carbon dots [21]. The exact enhancement mechanism has yet to be determined and will require more sophisticated experiments in the near future. Nevertheless, a straightforward codoping strategy led to a significant luminescence enhancement of metal-doped silica NPs, which can be useful in the development of efficient silica-based optical materials.

4. Conclusion

In summary, mesoporous silica NPs codoped with Tb(III) and Ba(II) ions have been successfully synthesized using a facile adsorption method. We showed that Ba(II) codoping strategy significantly improves the quantum yield of SiO_2-Tb NPs by a factor of ~2.49. We believe that proposed method can be expanded for the fabrication of other lanthanide-doped SiO_2 NPs with enhanced optical properties.

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CRediT authorship contribution statement

Kamila Zhumanova: Investigation, Formal analysis, Validation, Writing – original draft. **Nursalim Akhmetzhanov:** Investigation, Formal analysis, Validation. **Moon Sung Kang:** Formal analysis, Validation. **Anara Molkenova:** Formal analysis, Validation, Supervision. **Iruthayapandi Selestin Raja:** Formal analysis, Validation. **Ki Su Kim:** Conceptualization, Methodology, Validation, Supervision. **Dong-Wook Han:** Conceptualization, Methodology, Validation, Supervision. **Timur Sh. Atabaev:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

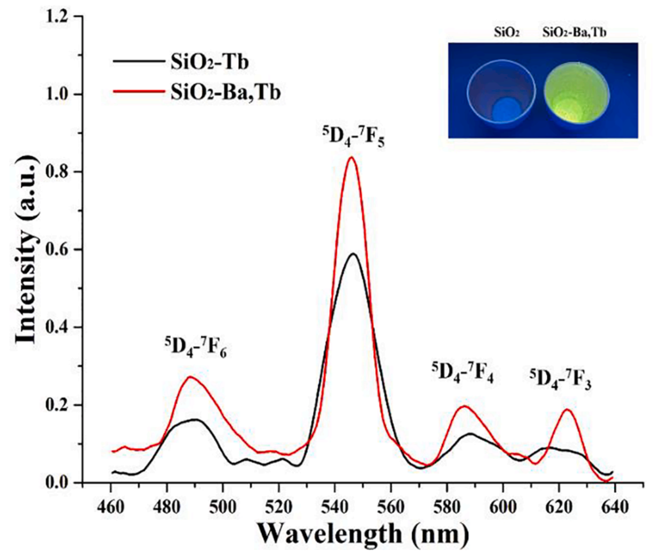

Fig. 4. PL emission spectra of SiO_2-Tb and SiO_2-Ba,Tb NPs. The inset is a digital image of bare SiO_2 (non-luminescent) and SiO_2-Ba,Tb (luminescent) NPs under UV excitation (λ_{exc} = 254 nm).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2022.132500.

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