

## Full Length Article

## A soft chemistry-based route to enhanced photoluminescence of terbium ions and tin oxide nanocrystals codoped silica thin films

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## ABSTRACT

Tb<sup>3+</sup> ions and SnO<sub>2</sub> nanocrystals (NCs) codoped silica films are fabricated by a soft chemistry-based approach. Via precise adjustment of Sn amounts in precursors, the size and number density of SnO<sub>2</sub> NCs can be well controlled by a restrictive crystallization process. The characteristic emission intensity of Tb<sup>3+</sup> ions at 541 nm can be greatly enhanced by two orders of magnitude if sensitized by SnO<sub>2</sub> NCs with optimized size and number density. Photoluminescence excitation spectra of the films containing different Sn amounts indicate the non-radiative energy transfer process that takes place between Tb<sup>3+</sup> ions and surface of SnO<sub>2</sub> NCs. The photoluminescence intensity decay curves suggest two kinds of possible occurrence states of Tb<sup>3+</sup> ions in codoped samples. All these results suggest the SnO<sub>2</sub> NCs represent ideal sensitizers to effectively promote photoluminescence efficiency of Tb<sup>3+</sup> ions. Particularly, the soft chemistry-based method reported here is very flexible for the fabrication of rare earth ions doped amorphous thin films, permitting the precise control of size and number density of NCs as sensitizers. We anticipate this fabrication strategy greatly enriches the techniques for the preparation of thin films, providing great promise for the realization of on-chip integration of silica-based optical lasers and amplifiers.

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## 1. Introduction

Amorphous silica thin film doped with rare earth ions is considered as one of promising luminescent materials because of a broad diversity of potential applications for optical telecommunications, optical integration and biomedicine [1–3]. As a main member of rare earth ions, Tb<sup>3+</sup> ion has a stable emission band from the intra-4f shell transition, long-lived photoluminescence (PL) emission and host-dependent spectral line shape. Unfortunately, the small absorption cross sections ( $\sim 10^{-21}$  cm<sup>2</sup>) of Tb<sup>3+</sup> ions in silica matrix result in low emission quantum efficiency [4]. So far, it still remains a great challenge to obtain high-efficiency luminescence from Tb<sup>3+</sup> ions doped silica thin films. As one of effective strategies to improve the emission efficiency, codoping Si nanocrystals (NCs) with large absorption cross sections has been reported [5–8]. However, the narrow energy band gap of Si NCs as sensitizers of Tb<sup>3+</sup> ions may lead to back energy transfer process from Tb<sup>3+</sup> ions to

Si NCs, which severely hinders the improvement of non-radiative energy transfer efficiency. Recently, many metal oxide nanomaterials with wider band gaps, such as ZnO [9], In<sub>2</sub>O<sub>3</sub> [10], have been introduced to replace Si NCs as more robust and efficient sensitizers of Tb<sup>3+</sup> ions. The larger absorption cross sections allow the metal oxide nanomaterials to absorb more excitation energy while the wider band-gaps may effectively avoid back energy transfer effect. Nonetheless, the more efficient luminescence from Tb<sup>3+</sup> ions doped silica matrix still remains a challenging goal for their maximum utilization [11]. In particular, for optical telecommunication, the development of waveguide-type broadband optical lasers and amplifiers that can be integrated on an array of optoelectronic devices greatly lags behind, owing to limited techniques available that can be applied to the fabrication of rare earth ions-activated thin films [12]. At present, the main preparation of thin films commonly relies on the physical vapor deposition (PVD) technique including co-sputtering and pulse laser deposition (PLD) [13–16]. Such conventional methods inevitably consist of the preparation of targets and exploring various deposition parameters. For most reported metal oxide thin film sensitizers, the random distribution and spatial agglomeration of sensitizing agents inside films

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inevitably give rise to uncontrollable space distance and mismatching energy level between sensitizers and rare earth ions, which brings about undesirable multicarrier Auger recombination process and low sensitization efficiency [17]. In short, the controllable fabrication of NCs sensitizers for rare earth ions-activated thin films still remains a challenging subject of continuous research effort.

Here, rare earth  $Tb^{3+}$  ions and  $SnO_2$  NCs codoped silica thin films are fabricated by a soft chemistry-based method. In marked contrast with PVD or PLD technique, this soft chemistry method appears as a straightforward approach to prepare rare earth ions-activated silica thin films with flexibility to regulate the size and number density of NCs as sensitizers. Besides, the amounts of sensitizing agents can be readily controlled by adjusting the precursors used, which greatly overcomes the complex and expensive procedures inherent to the PVD or PLD method. In this work, tin oxide ( $SnO_2$ ) NCs are selected as sensitizers and codoped into silica thin films with  $Tb^{3+}$  ions via a sol-gel process.  $SnO_2$  NCs have the following three characteristics: (1)  $SnO_2$  is a semiconductor with a wide band gap of 3.6 eV at 300 K, [18] effectively reducing the probability of reverse energy transfer from  $Tb^{3+}$  ions to  $SnO_2$  NCs, comparing with the Si NCs with narrower energy band gap. (2) The preparation of  $SnO_2$  NCs is compatible with the formation of silica thin films by post annealing process. According to our previous reports [19–21], annealing treatment at 1000 °C not only removes the vast majority of hydroxyl groups, but also forms  $SnO_2$  NCs with high crystallinity and uniform size. (3)  $SnO_2$  NCs isolate surrounding  $Tb^{3+}$  ions to avoid them from reaching the defect states existed in the amorphous silica.

## 2. Material and methods

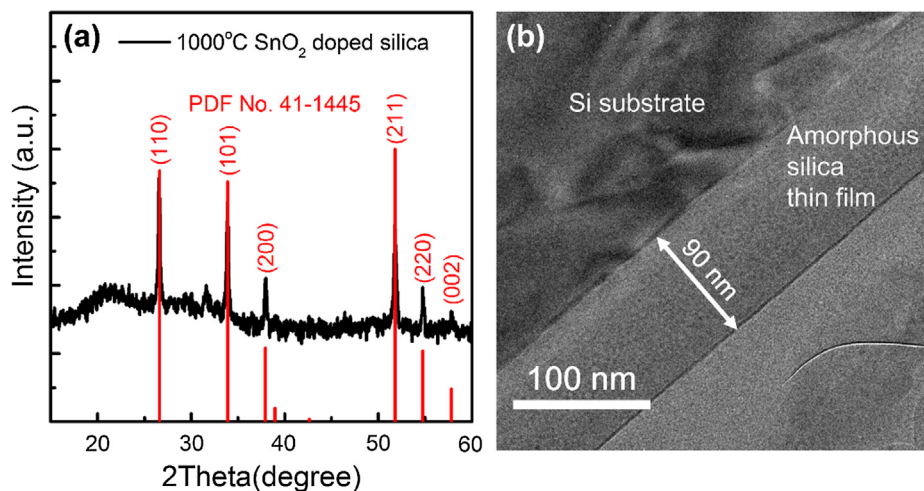
Silica sol precursor was formed by mixing tetraethyl orthosilicate (TEOS), deionized water and ethanol at a volume ratio of 4:2:4. Then dilute hydrochloric acid was dropped into the precursor to adjust the pH value close to 2.0. Subsequently, different amounts of tin chloride and terbium nitrate were dissolved into the precursor to obtain desired amounts. The precursor was stirred at 65 °C for 2 h and aged at room temperature for one day. All chemical products were used as received without further purification. After a series of hydrolysis and condensation reactions, the viscosity of the solution gradually increased as the sol became interconnected to form the gel (a rigid tetrahedral silica network).

Meanwhile,  $Sn^{4+}$  ions and rare earth  $Tb^{3+}$  ions monomers were distributed homogeneously in silica network, respectively. The final gel was spin-coated at a constant speed of 8000 rpm for 30 s onto clean Si substrates to form silica thin films followed by the post-annealing at 1000 °C. During the sol-gel transformation, the rapid evaporation of ethanol and deionized water caused the silica network to shrink under the process of post annealing. The rigid silica network would confine the growth and final dimensions of produced  $SnO_2$  NCs and also prevent them from agglomeration.

Microstructures of  $SnO_2$  NCs were confirmed by X-ray diffraction (XRD) and high resolution transmission electron microscopy (TEM). The cross-sectional samples for TEM observation were fabricated by mechanical grinding, polishing and dimpling, followed by Ar-ion milling. Steady-state photoluminescence (PL) and photoluminescence excitation (PLE) spectra were obtained by use of a Fluorolog-3 system equipped with a 325 nm He-Cd laser and a wavelength-tunable Xe lamp as excitation light sources. Time-resolved PL spectra were measured by FLS 980 fluorescence spectrophotometer based on the time-correlated single photon counting (TCSPC) technology. A Hamamatsu R928 PMT was used as the detector during measurements. All the spectra were measured at room temperature and corrected for the system response and sample thickness.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns for the samples containing 20% Sn (the molar ratio of Sn molecules to Si molecules, the same as follows) after annealing at 1000 °C. Several sharp diffraction peaks correspond to the tetragonal rutile crystalline phase of  $SnO_2$  crystals (JCPDS NO. 41-1445) while the broad band on the background is assigned to the amorphous silica matrix. Those sharp diffraction patterns indicate that the stable  $SnO_2$  NCs with a tetragonal rutile crystalline phase have been formed via 1000 °C annealing process. It is worth mentioning that there is no other phase of  $SnO_2$  crystal even after annealing at 1000 °C and the crystallization degree changes little with the increasing annealing temperature, which indicates that  $SnO_2$  NCs are very robust and can be effectively confined in amorphous silica matrix. Fig. 1(b) shows the cross-sectional TEM characterization of the amorphous silica thin film. It is found that the amorphous silica thin film with a smooth surface can be identified on the Si substrate. When the rotation rate



**Fig. 1.** (a) XRD patterns of the 20% Sn doped silica matrix after annealing at 1000 °C. The red line is the standard X-ray diffraction patterns of  $SnO_2$  crystals with tetragonal rutile crystalline phase (PDF No. 41-1445). (b) The cross-sectional TEM image of amorphous silica thin film structure fabricated by spin-coating technique. The thickness of the thin film is around 90 nm.

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