Terbium/zinc luminescent hybrid siloxane-oxide materials bridged by novel ureasils linkages

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Abstract

Covalently bonded silicate/modified aromatic acid luminescent composites have been prepared from 3-(triethoxysilyl)-propyl isocyanate (TEPIC) grafted salicylic acid and central metal ions (Tb, Zn). The existence of covalent linkages between TEPIC and silica matrices were realized by after hydrolysis and polycondensation processes of ethoxysilyl groups. Luminescence spectra were utilized to characterize the photophysical properties of the obtained hybrid material and the above spectroscopic data reveal that the triplet energy of modified salicylic acid in this favorable hybrid system matches with the emissive energy level of Tb^{3+}. In addition, Zn containing hybrids exhibit a broad band around 420 nm which may be beneficial to fabricate blue emission materials.
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1. Introduction

The introduction of organic components in inorganic hosts represents a relatively simple and widely used process to obtain organic–inorganic hybrids which attracted plenty of attention because of their intricate microstructure and mixed properties such as luminescent materials in lighting and displays, optical amplifiers, and lasers [1,2]. Generally, inorganic matrices doped with emitting centers like lanthanide organic complexes have already been found to show superior emission intensities and organic components are regarded as efficient sensitizers for the luminescence of rare earth ions, in short, the antenna effect. Our research group at present is concentrated on the lanthanide ions (Eu, Tb, Sm, Dy) or transition metal (Zn, Ru, Ir) complexes with aromatic carboxylic acid, bipyridyl or their derivatives [3–8]. In addition, anchored lanthanide complexes with different ligands in a sol–gel derived matrix have been investigated in many latest studies [9–11]. Indeed, the mild synthetic methods given by sol–gel approach which is based on hydrolysis/polycondensation reactions of metal alkoxides include several unique features like low-temperature processing and shaping, higher product homogeneity and purity, and the possibility to prepare non-crystalline solids. Furthermore, the microstructure, the external shape or the degree of combination between the two phases can be controlled by changing the sol–gel reaction conditions [12]. In recent years, the exact control of the coupling between the hosts and the guest molecule would contribute to the design of hybrid materials especially for definite applications. For instance, conventional doping approach seems difficult to solve the problem of quenching effect of luminescent centers because the high energy vibration by the surrounding hydroxyl groups and only weak interactions (such as hydrogen bonding, van der waals force or weak static effect) exist between organic and inorganic parts [13]. In addition, inhomogeneous dispersion of two phases and leaching of the photoactive molecules frequently occur in this sort of hybrid materials for which

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the concentration of complex is also largely restricted. Therefore, another attracting possibility in regard to the complexation of the rare earth ions using ligands that are covalently fixed to the hybrid networks has emerged. Until now, a few researches in terms of the covalently bonded hybrids with increasing chemical stability have appeared and the as-derived molecular-based materials exhibit monophasic appearance even at a high concentration of rare earth complexes [14–23]. Some previous reports have been done on complexes of lanthanide–pyridine–dicarboxylic acid or their derivatives and the feasibility of dicarboxylic acid system has been firmly proved [18]. Zhang and co-workers [14,15] started to modify 1,10-phenanthroline and di-pyridine in order to prepare the determined molecular-level hybrid materials. Our research team recently put more emphasis on rare earth coordination behavior and have now developed modified ortho, meta-aminobenzoic acid as "molecular bridge" which cannot only develop chelating effects that can bind to rare earth ions but also anchor a silica matrix with an aminoalkoxysilane group [16,19,20]. The idea is to limit the degrees of freedom of the active molecule so as to reduce the contribution of librational movements to optical dephasing. Carlos et al. [24,25] lately pointed out that amino-functional hybrids lacking metal ions could be divided into two major parts (di-ureasils and di-urethanesils) and the Eu^{3+} coordination shell involves the carbonyl-type oxygen atoms of the urea bridges. For the sake of restricting the phase separation between organic molecules and the rigid inorganic network, and to increase the concentration of dopant, in this work, totally different from previous amino moiety researches, we attempt to modify active hydroxyl groups of salicylic acid (Sal) by TEPIC bearing tri-alkoxysilyl group as a functionalized organic ligand (Sal-Si), then we designed a

covalently bonded hybrid inorganic–organic system that incorporated terbium nitrate and zinc acetate to Sal-Si. The reaction processes for the hybridization formula Sal-Si may be described as follows: Step I involves the individual hydrolysis of Sal-Si and tetraethoxysilane (TEOS). Step II, however, is followed by the polycondensation reactions which produces the sol and by an conglomeration of the sol particles that prepares the resulting gel (see Fig. 1). Hence, condensation of the tri-alkoxysilyl chromophores in the presence of lanthanides salts leads to the formation of novel structured hybrid materials consisting of efficiently sequestered lanthanide species linked to powerful modified Sal-Si grafted to the inorganic hosts. After drying in air at 60 °C, the gel turns into solid transparent material known as xerogel. In this experiment, the glass like characteristics sample were grounded as powders and the first results on luminescence are promising that the molecular-based hybrids bearing the RE–O coordination bond and Si–O covalent bond can exhibit green luminescence of Tb^{3+} and blue emission of Zn-complexes.

2. Experimental

2.1. Chemicals and procedures

3-(Triethoxysilyl)-propyl isocyanate was provided by Lancaster Synthesis Ltd. The solvents used were purified by common methods. Other starting reagents were used as received. A typical procedure for the preparation of Sal-Si was as follows: 2 mmol salicylic acid was first dissolved in dehydrate tetrahydrofuran by stirring and 2 mmol 3-(triethoxysilyl)-propyl isocyanate was then added to the solution by drops. The whole mixture was refluxing at 65 °C under argon for 18 h. After isolation, a pale yellow
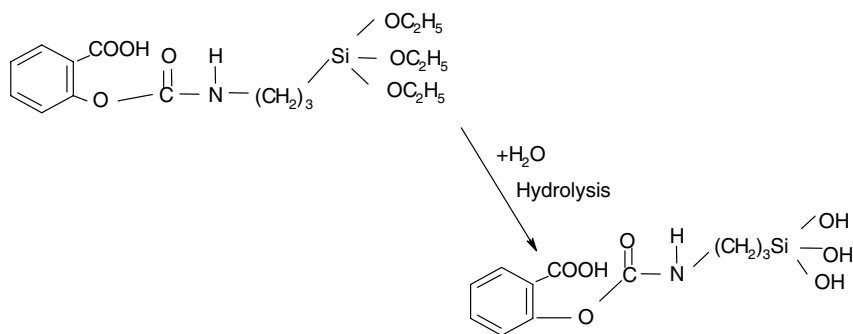
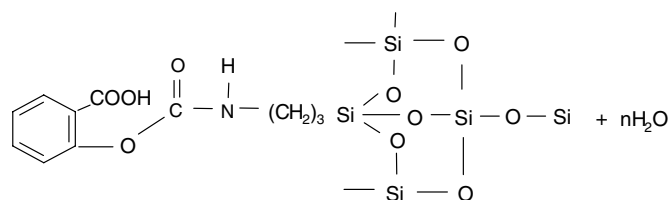Fig. 1. Scheme of hydrolysis and polycondensation processes between Sal-Si and TEOS.

oil Sal-Si was furnished. ^{1}H NMR (CDCl$_3$) C$_{17}$H$_{27}$O$_7$NSi: δ 14.35(1H,s), 8.40(1H,d), 7.87(1H,t), 6.79(1H,d), 6.26(1H, t), 4.16(1H,t), 3.65(2H,m), 3.45(1H,d), 3.28(2H,s), 1.77-(8H,m), 1.15(4H,d), 1.05(4H,s). ^{13}C NMR (CDCl$_3$): δ 165.9 (C$_7$), 164.5 (C$_1$), 146.1–141.4 (C$_2$–C$_6$), 128.6–126.9 (C$_3$–C$_5$), 120.6 (C$_4$), 116.6 (C$_8$), 66.5 (CH$_2$(OEt)), 40.3 (C$_9$), 30.1 (C$_{10}$), 23.3 (CH$_3$(OEt)), 7.9 (C$_{11}$). The sol–gel derived hybrid containing rare earth ions was prepared as follows: Sal-Si was dissolved in dimethylformamide (DMF) with stirring. A stoichiometric amount of RE(NO$_3$)$_3$ · 6H$_2$O (Tb(NO$_3$)$_3$ · 6H$_2$O and Zn(Ac)$_2$ · 2H$_2$O) was added to the solution. Then one drop of diluted hydrochloric acid was put into it to promote hydrolysis. The mole ratio of RE(NO$_3$)$_3$ · 6H$_2$O /Sal-Si/H$_2$O was 1:3:9. The mixture was agitated magnetically to achieve a single phase in a covered Teflon beaker, then it was aged at 60 °C until the onset of gelation which occurred within 3 days. The gels were collected as monolithic bulks and ground as powder materials for the photophysical studies (see Fig. 2).

3. Measurements

All measurements were completed under room temperature except that phosphorescence spectra (5×10^{-4} mol L^{-1} acetone solution) was measured under 77 K. ^{1}H NMR spectra was recorded in CDCl$_3$ on a bruker AVANCE-500 spectrometer with tetramethylsilane (TMS) as internal reference. Ultraviolet absorption spectra of these powder samples (5×10^{-4} mol L^{-1} acetone solution) were recorded with an Agilent 8453 spectrophotometer. Fluorescence excitation and emission spectrums were obtained on a Perkin–Elmer LS-55 spectrophotometer: excitation slit width = 10 nm, emission slit width = 5 nm. Scanning electronic microscope (SEM) was measured with JSM-6360LV.
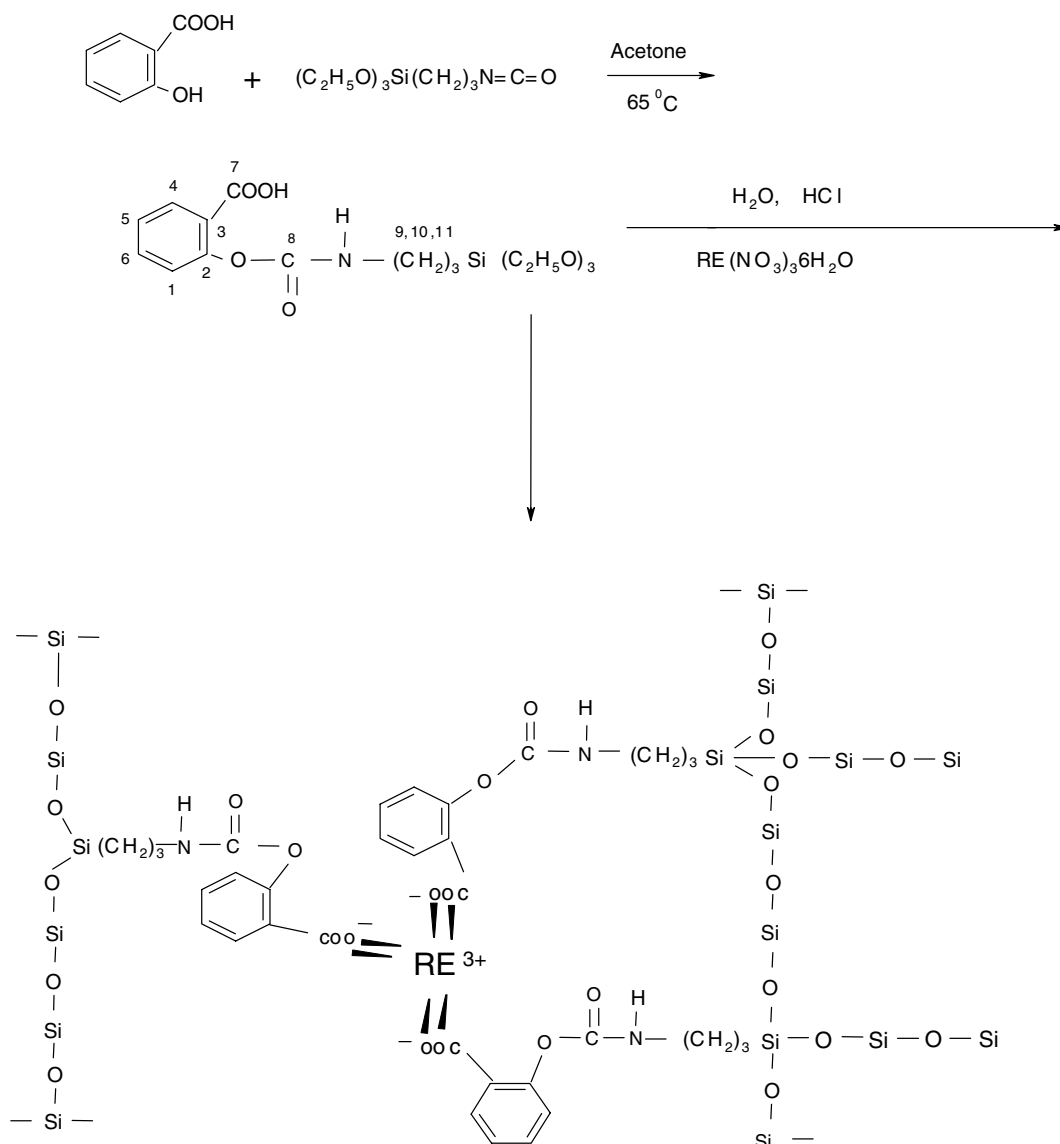

Fig. 2. Scheme of the synthesis process of Sal-Si and predicted structure of hybrid materials.

4. Results and discussion

Fig. 3 gives ultraviolet absorption spectra of (A) salicylic acid, (B) Sal-Si, (C) Sal-Si with excess Eu^{3+} ions. From the spectra, it is observed that a red shift (A → B) of the major π–π^* electronic transitions (from 331 to 335 nm) occur and it is estimated that during the grafting reaction of salicylic acid, the diverse ligand may promote the conjugating effect of double bonds and reduce the energy difference levels among electron transitions. In terms of B and C, the complexation between rare earth ions and Sal-Si increase the energy levels of the corresponding transitions and exhibits an obvious blue shift from 335 to 327 nm (B → C).

As for the phosphorescence spectra of (A) salicylic acid, (B) Sal-Si, (C) Sal-Si with excess Tb^{3+} ions (Fig. 4). Phosphorescence spectrum substantiates the character of the organic molecular ligands and a 18 nm blue shift was observed between A and B (from 434 to 416 nm). However, there is no difference between B and C because they belong to the same organic groups with the exception that C could transfer part of energy to terbium ions so as to reduce the relative intensities. From the phosphorescence emission, the maximum phosphorescence wavelengths of B located at 416 nm is due to the characteristic transitions of Sal-Si and the lowest triplet state energy can be determined to be 24038 cm^{-1}. According to Sato's result [26], the intramolecular energy migration efficiency from organic ligands to the central Ln^{3+} is the most important factor influencing the luminescence properties of rare earth complexes. The intramolecular energy transfer efficiency depends mainly on the two energy transfer processes [27]. One is from the lowest triplet state energy of organic to the resonant energy level by Dexter's resonant exchange interaction theory [28]:

$$k_{ET} = KP_{da} \exp(-R_{da}/L), \tag{1}$$

$$P_{da} = (2\pi Z^2/R) \int F_d(E)E_a(E)\,dE, \tag{2}$$

$$k_{ET} = KP_{da} \exp(-2R_{da}/L) = K \int F_d(E)E_a(E)\,dE. \tag{3}$$

The other is the reverse energy transition by the thermal deactivation mechanism [29,30]:

$$k(T) = A \exp(-\Delta E/RT), \tag{4}$$

where k_{ET} is the rate constant of the intermolecular energy transfer and P_{da} is the transition probability of the resonant exchange interaction. $2\pi Z^2/R$ is the constant relating to the specific mutual distance between the central Ln^{3+} ion and its coordinated atoms (O or N). $F_d(E)$ and $E_a(E)$ are the experimental luminescence spectrum of energy donor (ligands) and the experimental absorption spectrum of energy acceptor (Ln^{3+}) respectively, so both of them represent the overlap spectrum of Ln^{3+}. R_{da} is the intermolecular distance between donor atoms and acceptor atoms, and L is the van der waals radius. Both R_{da} and L may be considered to be constant in intramolecular transfer processes, so k_{ET} is proportional to the overlap of $F_d(E)$ and $E_a(E)$. With the decrease in the energy difference between the triplet state energy of conjugated carboxylic acid and Ln^{3+}, the overlap of $F_d(E)$ and $E_a(E)$ is increased. So from the above equation, it can be concluded that the more the overlap between the luminescence spectrum of organic ligands and the emissive energy of Ln^{3+}, the more the intramolecular energy rate constant k_{ET}. On the other hand, the activation energy ΔE in Eq. (4) is equal to the energy difference $\Delta E(Tr-Ln^{3+})$, while from the formula, the reverse energy transfer rate constant k(T) increased with decreasing $\Delta E(Tr-Ln^{3+})$ [31–33].
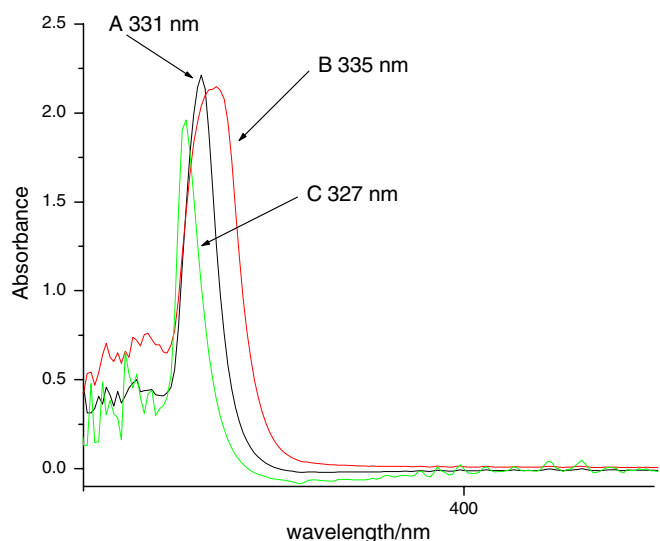

Fig. 3. Ultraviolet absorption spectra of (A) salicylic acid, (B) Sal-Si, (C) Sal-Si with excess Eu^{3+} ions.
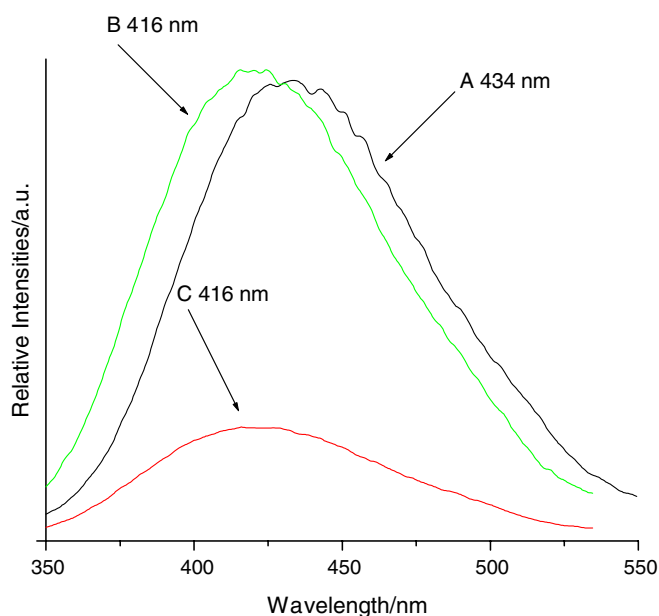

Fig. 4. Phosphorescence spectra of (A) salicylic acid, (B) Sal-Si, (C) Sal-Si with excess Tb^{3+} ions.

As discussed above, there should exist an optimal energy difference between the triplet position of Sal-Si and the emissive energy level Ln^{3+}, the larger and the smaller $\Delta E(Tr\text{-}Ln^{3+})$ will decrease the luminescence properties of rare earth complexes. In terms of lanthanide–aromatic acid complexes, the suitable value was proved to be around $4000 \pm 500 \text{ cm}^{-1}$ [26,27,29–35]. In consequence, modified organic monomer Sal-Si ($24\,038 \text{ cm}^{-1}$) will be more proper than original salicylic acid ($23\,041 \text{ cm}^{-1}$) in regard to the emissive energy level of center terbium ions ($20\,408 \text{ cm}^{-1}$, 490 nm, $^5D_4 \rightarrow {}^7F_6$ transition).

The excitation and emission spectra of the resulting hybrid materials are shown in Figs. 5 and 6. The excita-tion spectra was obtained by monitoring the emission of Tb^{3+} (Fig. 5) at 545 nm and dominated by a distin-guished band centered at 300 nm. As a result, the emis-sion lines of the hybrid material were assigned to the transitions from the $^5D_4 \rightarrow {}^7F_J$ ($J = 6, 5, 4, 3$) transitions at 490, 544, 587 and 620 nm for terbium and the most striking green luminescence was obtained. Fig. 6 provides blue emission (A) that gives a very broad band centered at 428 nm (bandwidth at half height about 80 nm) when excited under 282 nm and the emission spectra of salicylic acid doped with Zn^{2+} (B) directly. We could find that the mixture of Sal-Si organic ligand and metal ions display much weaker luminescence at room temperature than covalent bond composites. The quite enhanced lumines-cence efficiency of the Zn–Sal-Si complex centers is there-fore ascribe to the coordination between the Sal-Si ligands and Zn ions that firmly promotes the rigidity of the ligands and decreases the non-radiative energy loss of the ligand emission excited state. We still could not ex-clude other factors such as relatively rigid structure of sil-ica gel which prohibits the vibration of ligand of Tb^{3+} and limits non-radiative transitions. Consequently, we
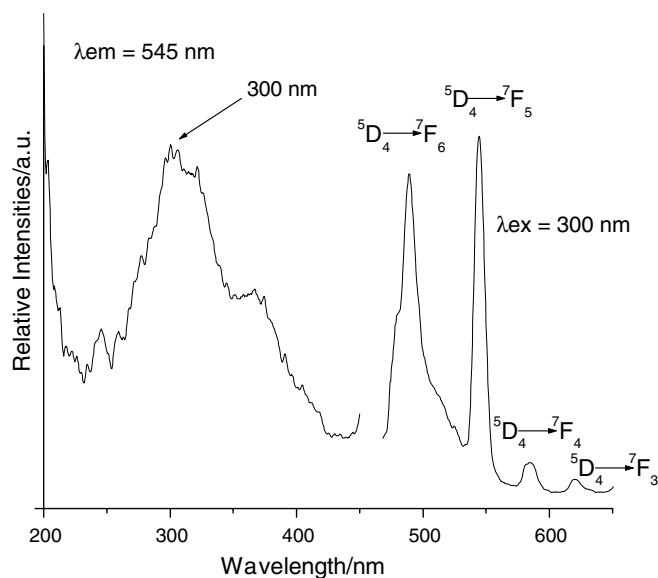

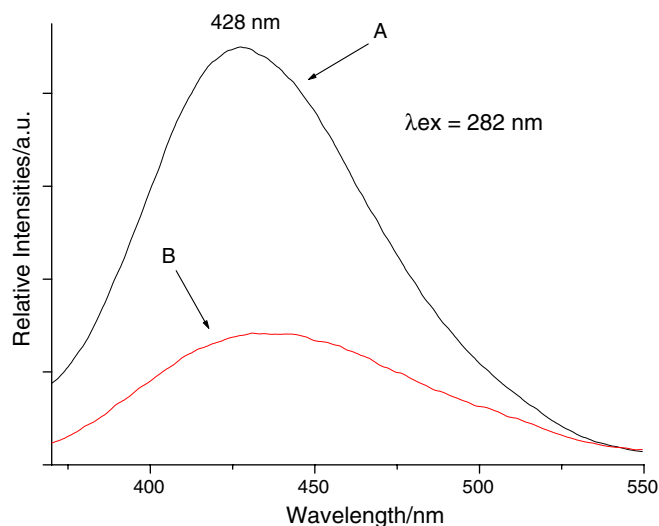Fig. 5. The excitation and emission spectra of the terbium resulting hybrid material.

Fig. 6. Emission spectra of Zn^{2+} containing molecular-based hybrids (A) and Zn^{2+} salt of salicylic acid (B).
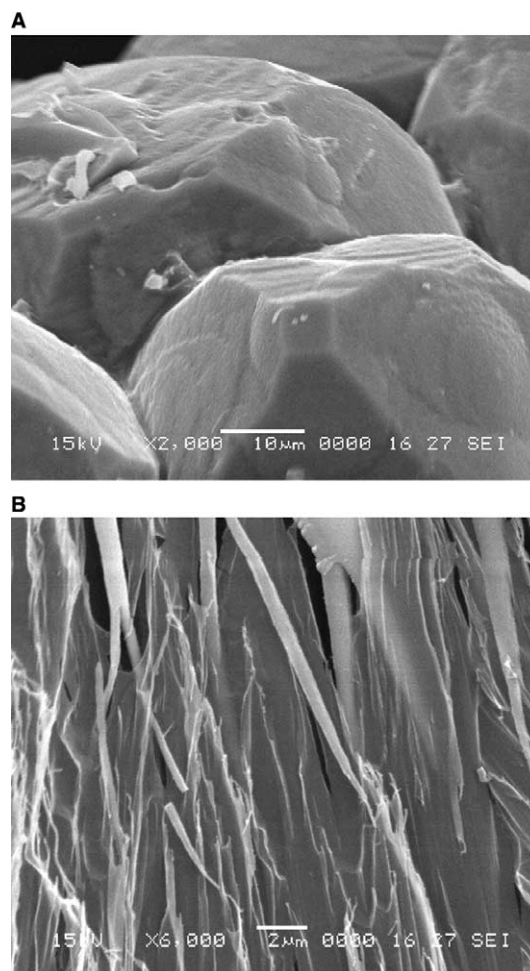

Fig. 7. SEM graphs of Zn resulting molecular-based hybrid material.

may expect that through this efficient way, leaching of the light-emitting molecules can be avoided; higher concentration of metal ions is reached and clustering of the emitting centers may be controlled.

The scanning electron micrographs for Zn (A) and Tb (B) containing hybrids are given in Fig. 7. It is worthy pointing out that from Fig. 7(A), we observed some attracting regular sub-micronmeter spheroids (approximately 50 μm) which were controlled by co-condensation reactions between Sal-Si and TEOS monomers. To our knowledge, it is less common to form the interesting smooth sphere particles under such low temperature (without calcinations and other templates) and we predicate that coupling agent TEPIC and crystal structure of Zn complexes will both be ascribed to promote the formation of the morphology. Beyond our expectation, many chains like structures within the hybrid's surface emerge in Fig. 7(B) which seems to be in good agreement with crystal structure of one-dimensional $[Tb(o\text{-}HOC_6H_4CO_2)_3 \cdot 4H_2O]_n$ coordination polymer [36]. It is estimated that the complex of $Tb(o\text{-}HOC_6H_4CO_2)_3 \cdot 4H_2O$ has the tendency of growing into infinite poly-chains from the microstructure view and it retains the coordinated positions in corresponding bulk materials.

5. Conclusions

To investigate the coordination behavior between diurethanesils and rare earth ions, we designed two novel molecular-based hybrid materials. Salicylic acid has been modified with 3-(triethoxysilyl)-propyl isocyanate (TEPIC) and acted as a crosslinking intermediate which plays double roles. On the one hand, it can coordinate to lanthanide ions through carboxyl groups; on the other side of the coin, the hydrolysis and polycondensation reactions among triethoxysilyl of Sal-Si and TEOS are ascribed to the formation of Si–O–Si network structures for the same ethoxy group of them. Meantime, the strong red or green luminescent systems with novel and unique microstructures (spheres and chains) were achieved. In addition, the resulting hybrids could be shaped as monoliths or as transparent films with desired luminescence efficiency. Variations of the organic ligand structure contribute to diverse coordinating properties and to various absorption capabilities. Therefore, the energy absorption and transfer from ligands to central ions, or the emission efficiency, could be increased by this potential approach.

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