

White luminescent hybrid soft materials of lanthanide (Eu^{3+} , Sm^{3+}) beta-diketonates and Ag/Ag₂S nanoparticles based with thiol-functionalized ionic liquid bridge



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ABSTRACT

Thiol-ionic liquid (SHIL) is prepared and used as bridge to prepare multi-component soft hybrids materials $\text{Ag}(\text{Ag}_2\text{S})\text{-SHIL-Ln}(\text{L})_4$ ($\text{Ln} = \text{Eu}, \text{Sm}, \text{L} = \text{TTA}$ (thenoyltrifluoroacetylacetonate), TAA (trifluoroacetylacetonate), DBM (1,3-diphenyl-1,3-propanepione)) for its good solubility and functionality. Luminescence color of these soft hybrid materials can be adjusted through controlling different proportion of beta-diketonates (TTA, TAA, DBM) and silver species (Ag, Ag₂S). Especially the white luminescence can be realized for the special composition of Ag/Ag₂S and lanthanide beta-diketonate. The result can be expected to prepare luminescent soft materials to obtain the multi-color and white luminescence.

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Ionic liquids, whose salt's melting point is below 100 °C, have attracted widespread attention due to its intriguing properties, such as good solubility, excellent chemical and thermal stability [1,2]. Preparation of functionalized ionic liquid has been more and more popular, the research of the functionalized ionic liquid made ionic liquids diversified, the presence of functional groups make ionic liquids' application more widely. Many functional groups, such as amino [3], nitrile [4], carboxyl [5], sulfhydryl [6] have been incorporated into the ionic liquids. Through ion exchange and the role of chemical bond, ionic liquid can be link up with other positively charged compounds.

Silver nano materials possess unique catalytic, antibacterial, luminescence property, and high conductivity properties. by using the reducing agent and surface active agent to control the measurements of the nanoparticle sizes and morphology so as to make its physical and chemical properties adjustable and controllable [7]. In this paper, PVP has been used to act as reductant and surfactant to synthesize Ag nanoparticles. On the basis of Ag nanoparticle, this paper also introduces semiconductor Ag₂S nanoparticle into the research to discuss the effect of silver series semiconductor nanoparticles on the photochemical properties of the materials. Their strong band-gap luminescence makes them have a lot of potential value for the application as luminescent material [8,9].

Lanthanide complexes have excellent luminescent properties. There is a large number of lanthanide compounds used in luminescent material. Lanthanide salt with β-diketone compounds resulting from the

coordination has many advantages such as narrow-width, intense emission bands, high quantum efficiency, high color purity and long lifetimes [10–13]. Lanthanide complexes combined with nanometer semiconductor materials can also show a good luminous performance. Because of the differences of band gap, light intensity, light color of semiconductor materials, the luminescence spectrum properties of lanthanide hybrid materials can be controlled by adjusting the proportion.

In this paper, Ag nanoparticles were prepared according to the procedure in [14,15]. Ag₂S nanoparticles were synthesized with the methods in Ref. [16]. The ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium bromide was synthesized combined with the procedure reported in the literature [17,18]. Yield: 90%. ¹H NMR δ (ppm in D-DMSO): 9.19 (s 1H), 7.71 (s 1H), 7.74 (s 1H), 4.32 (t 2H), 3.88 (s 3H), and 3.72 (t 2H). Thiol-ionic liquid (SHIL) was further synthesized with the strategies reported in Refs. [2,6,19]. Yield: 85%. ¹H NMR δ (ppm in D-DMSO): 9.22 (s 1H), 7.78 (s 1H), 7.75 (s 1H), 4.23 (t 2H), 3.83 (s 3H), and 3.70 (t 2H). The lanthanide complexes are synthesized according to a modified literature procedure [20]. Subsequently, the final soft hybrid materials were prepared, whose basic composition was given in Table S1 and typical scheme was shown in Fig. 1.

The selected FT-IR spectra of soft hybrid materials of lanthanide (Eu^{3+} , Sm^{3+}) beta-diketonates and Ag/Ag₂S nanoparticles are shown in Fig. 2. For thiol-ionic liquid compound SHIL, the obvious band appearing at 2400–3600 cm^{-1} is due to the cyclic structure of π–π conjugate, imidazole ring characteristic peak and other characteristic peaks like C–H stretching vibration (2900 cm^{-1}) and –SH (2570 cm^{-1}). Besides, C=O stretching vibration exists at 1850–1650 cm^{-1} and C–O stretching vibration exists at 1300–1050 cm^{-1} , etc. The FTIR

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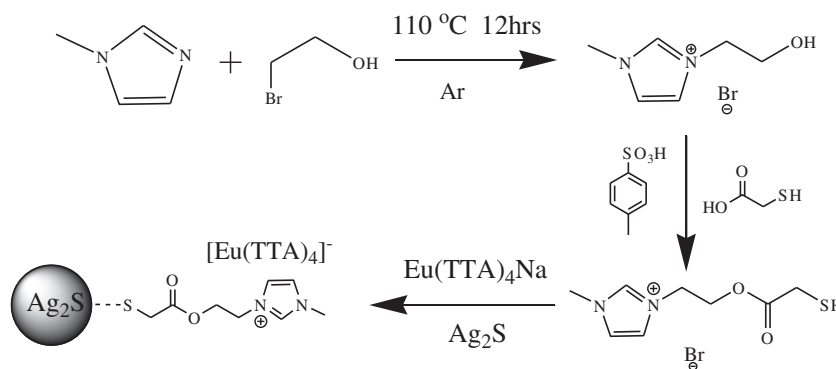


Fig. 1. The scheme for the synthesis of ionic liquid SHIL and typical soft hybrids $\text{Ag}_2\text{S-SHIL-Eu(TTA)}_4$.

spectra of the soft hybrids show apparent difference for the introduction of β -diketonate and $\text{Ag}/\text{Ag}_2\text{S}$, which indicates that the abundant $\text{C}=\text{O}$ groups of β -diketonates dissolved in SHIL produces the $\text{C}=\text{O}$ stretching vibration to some migration. The peaks of β -diketonate peak at $1600\text{--}1535\text{ cm}^{-1}$ ($\nu_{\text{C}=\text{O}}$) are stronger than that in FTIR spectra of SHIL. All these characteristic peaks show that the thiol-ionic liquid is linked with β -diketonate complexes. In addition, some peaks at $3500\text{--}3000$, $1300\text{--}1000\text{ cm}^{-1}$ may be the free hydroxyl absorption bands.

The room temperature X-ray diffraction (XRD) patterns of nanoparticles Ag and Ag_2S are shown in Fig. S1. All the samples are under wide-angle pattern, exhibiting that the obtained semiconductors are crystal from 10 to 70° . Diffraction peak positions of Ag sample are 38 , 44.4 , 64.4° . The positions are in agreement with the JCPDS card, and there is no Ag_2O peaks existing in the spectrum. Obviously, diffraction peak strength of Ag is low and peaks are quite wide, which illustrate that the size of this Ag material is small with about $10\text{--}50\text{ nm}$ [14,15]. Besides, the XRD pattern of Ag_2S reveals that the crystallinity of them is improved, which matches well with the monoclinic phase Ag_2S data (JCPDS Card No. 14-0072) [16,21].

The luminescence performance of multi-component lanthanide hybrid materials with thiol-functionalized ionic liquid bridge has been investigated at room temperature. This kind of luminescent hybrid material possesses tunable luminescent behavior. Fig. 3 presents the luminescent spectra and CIE diagram of $\text{Ag-SHIL-3Eu(TAA)}_4$ (A) and Ag-SHIL-Sm(DBM)_4 (B) soft hybrids. The excitation spectra of $\text{Ag-SHIL-3Eu(TAA)}_4$ (A) and Ag-SHIL-Sm(DBM)_4 (B) are obtained by monitoring the emission of Eu^{3+} ion at 614 nm and Sm^{3+} ion at

645 nm , respectively. There is a broad excitation band ranging from 300 to 400 nm in the excitation spectra of Ag-SHIL-Eu III , which is due to the $\pi\text{--}\pi^*$ transition of organic ligands and the Eu-O charge transfer transition state (CTS by interaction between the organic groups and the Eu^{3+} ion coordinated oxygen atoms) [22]. For Ag-SHIL-Sm(DBM)_4 hybrids, a strong relatively narrow absorption band ranges from 350 to 400 nm with maximum excitation at 390 nm , which originated from the $f\text{--}f$ transition of Sm^{3+} ion. Different from europium hybrids, the excitation bands to the organic ligand and charge transfer from ligand to Sm^{3+} is much weak. This suggests that the energy transfer from organic ligand to Sm^{3+} is not effective, resulting in the weak emission of Sm^{3+} in its emission spectrum. In their emission spectra, these two hybrid material have a characteristic emission of Eu^{3+} and Sm^{3+} . For the emission spectrum in Fig. 3(A), five main emission peaks (${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 0\text{--}4$) transitions) appear at 579 , 588 , 615 , 649 , and 700 nm of the hybrid materials. It can be observed that the emission intensity of 615 nm (electric dipole transition) is higher than that of 588 nm (magnetic dipole transition). For Fig. 3(B), three main emission peaks (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{j/2}$ ($j = 5, 7, 9$) transitions) appear at 560 , 602 , 645 nm , the red light emission of Sm^{3+} shows the strongest intensity near 645 nm (${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transition has the highest emission intensity). Both two soft materials have a broad blue emission peak ranging from 400 to 500 nm , that is caused by the luminescence of SHIL functionalized Ag nanoparticles. Not only white light, but also other color can be achieved through the different compositions of Ag components and lanthanide complexes from different reaction ratio. Ag-SHIL-Eu(TAA)_4 and $\text{Ag-SHIL-2Eu(TAA)}_4$ show the blue emission and yellow luminescence in Fig. S2 (A) and (B), respectively.

Fig. 4 shows the luminescent spectrum and CIE diagram of $\text{Ag}_2\text{S-SHIL-Eu(TTA)}_4$ soft material, whose luminescent color is in white region. The excitation spectra of $\text{Ag}_2\text{S-SHIL-Eu(TTA)}_4$ are obtained by monitoring the emission of Eu^{3+} ion at 614 nm . For the emission spectra in Fig. 4, there are five main emission peak ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 0\text{--}4$) transitions at 579 , 590 , 615 , 650 and 700 nm of the soft materials, which indicate that the energy transfer occurs between the TTA and Eu^{3+} ion. We can also observe that the emission intensity located at 615 nm (electric dipole transition) is the highest peak. Besides, the broad emission band ranging from 400 to 500 nm can be ascribed as the luminescence of SHIL functionalized Ag_2S component. For the soft hybrids of $\text{Ag}_2\text{S-SHIL-2Sm(DBM)}_4$ and $\text{Ag}_2\text{S-SHIL-5Sm(DBM)}_4$, their luminescence color is in blue region from the CIE diagrams (Fig. S3). This is owing to the band ranging from 400 to 500 nm that is extremely strong in spite of the emission of Sm^{3+} . Considering the limit of Sm complex immobilized in SHIL, the white luminescence cannot be obtained for these kinds of soft materials.

In summary, these hybrid soft materials of lanthanide β -diketonates and $\text{Ag}/\text{Ag}_2\text{S}$ nanoparticles are prepared with thiol-functionalized ionic liquid as bridge, which possesses controllable

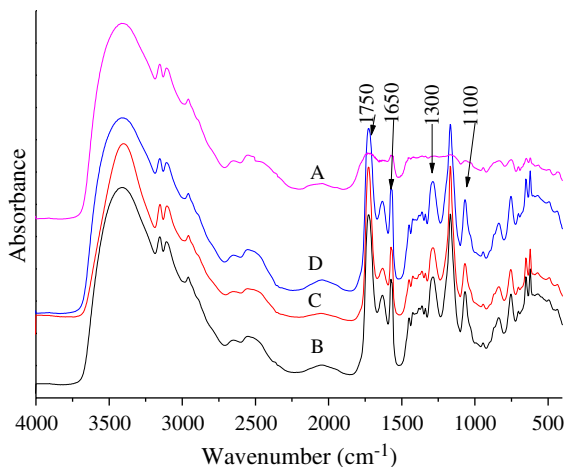


Fig. 2. Selected FT-IR spectra of liquid compound (A) SHIL and soft hybrid materials (B) $\text{Ag-SHIL-3Eu(TAA)}_4$, (C) Ag-SHIL-Sm(DBM)_4 , (D) $\text{Ag}_2\text{S-SHIL-Eu(TTA)}_4$.

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