



Novel multi-component photofunctional nano hybrids for ratio-dependent oxygen sensing

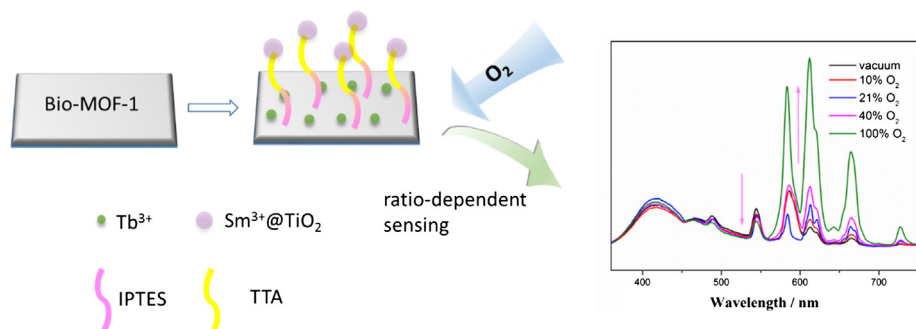


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GRAPHICAL ABSTRACT

A hybrid which is composed of $\text{Sm}^{3+}@TiO_2$ and $\text{Tb}^{3+}@Bio-MOF-1$ can be a good platform for ratio-dependent oxygen sensing.



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ABSTRACT

In this paper, an anionic metal-organic framework Bio-MOF-1 ($\text{Zn}_8(\text{ad})_4(\text{BPDC})_6\text{O} \cdot 2\text{Me}_2\text{NH}_2$) and a luminescent complex (Sm^{3+} doped TiO_2 , labeled as $\text{Sm}^{3+}@TiO_2$) have both been prepared as previous reports and their photophysical properties are investigated. Subsequently, Tb^{3+} is introduced to Bio-MOF-1 via cation exchange and the obtained $\text{Tb}^{3+}@Bio-MOF-1$ can exhibit characteristic emission bands of Tb^{3+} . Exposed to varying concentration of oxygen, the luminescent intensity of Tb^{3+} decreased as increasing oxygen content. However, the luminescent intensity of as-prepared $\text{Sm}^{3+}@TiO_2$ is enhancing with the increase of oxygen content. With the assistance of IPTES (3-Isocyanatopropyltriethoxysilane) and TTA (2-Thenoyltrifluoroacetone), $\text{Sm}^{3+}@TiO_2$ was assembled with $\text{Tb}^{3+}@Bio-MOF-1$ successfully. As we had expected, the hybrid shows a ratio-dependent oxygen sensing performance, which makes it a good candidate for sensing of oxygen.

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1. Introduction

Molecular oxygen (O_2) plays important roles in many fields, such as biological metabolism [1–3], food packing [4], and the stability of ecosystem [5,6]. Based on this, the determination of oxy-

gen level is essential and urgent. Up to date, the quantification of oxygen relies on four major methods: (a) the classical Winkler titration; (b) electroanalytical; (c) pressure-based detection; (d) optical methods [7]. Compared with other detection approaches, optical oxygen sensors possess many advantages, including high sensitively, fast response, no analyte consumption, strong anti-interference ability [8,9], which make it of great significance to the development of optical oxygen sensors.

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In recent years, large amount of luminescent complexes have been prepared for oxygen sensing [10–16]. Metal organic frameworks (MOFs), which are defined as a class of inorganic-organic hybrid materials formed by the self-assembly of transition metal ions or clusters and organic linkers [17]. MOFs have attracted plenty of attention since their characteristics of high surface area, tunable and various structures, unique photoelectric properties, etc. [18,19]. Luminescent MOFs, as a class of MOFs, have drawn a lot of attention for their potential application in light devices [20–22], chemical sensing [23–27], drug delivery [28–30], medical imaging [31,32] and so on. According to previous reports, there are many ways to generate luminescence MOFs, including the introduction of lanthanide ions. Lanthanide ions can emit sharp but weak luminescence and the luminescent intensity can be enhanced by “antenna effect” [33]. Based on this, lanthanide ions encapsulated luminescent MOFs could be a good platform for optical detection. The luminescent intensity of lanthanide ions emission in MOFs is always decreasing with the increasing oxygen concentration. The mechanism for this phenomenon may be that oxygen molecular can cause the deactivation on triplet-state organic ligands, thus affecting the energy transfer between Lanthanide ions and ligand [34]. Recently, a promising oxygen sensing material has been prepared in which Sm^{3+} was doped into TiO_2 [35]. Different with lanthanide ions encapsulated MOFs, the luminescent intensity of this material is enhancing with the increase of oxygen content.

As far as we know, most of oxygen sensing approaches are depend on the luminescence of one transition, which is susceptible to environmental interferences like fluctuations in the light source intensity [36,37], leading to inaccuracy in quantification. Two-emission or multi-emission luminescent materials can solve this problem effectively. By monitoring the luminescent intensity ratio of different emission under various stimuli, the materials can be good sensing platforms for their characteristic of self-calibrating [38,39]. Based on the above mentioned, we try to assemble the $\text{Sm}^{3+}@TiO_2$ with lanthanide ions encapsulated MOFs, so we can get ratio-dependent oxygen sensing material.

In this paper, Bio-MOF-1 is chosen as a host material for its low toxicity, water-stability and high specific surface area [40]. Tb^{3+} is introduced to Bio-MOF-1 via cation exchange method and then the optical properties of $\text{Tb}^{3+}@Bio-MOF-1$ towards oxygen are investigated. $\text{Sm}^{3+}@TiO_2$ is assembled with $\text{Tb}^{3+}@Bio-MOF-1$ by the assistance of IPTES and TTA [41,42]. Subsequently, oxygen-sensing properties of as-prepared hybrid is explored after spreading the complex on ethanol, which shows that the luminescent intensity of Tb^{3+} decreases with increasing oxygen content while the luminescent intensity of Sm^{3+} enhances, suggesting that it can be used as a promising ratio-dependent oxygen sensing material.

2. Experimental section

2.1. Materials and reagents

All the reagents (A.R.) were obtained commercially and used without further purification. $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving europium/samarium oxide in concentrated nitric acid/hydrochloric acid followed by evaporation and vacuum drying. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, adenine, biphenyl-4,4-dicarboxylic acid (BPDC), N,N-dimethylformamide (DMF), 2-Thenoyltrifluoroacetone (TTA), 3-isocyanatopropyltriethoxysilane (IPTES) are purchased from Aldrich. Nitrogen and oxygen are both 99.999% pure.

2.2. Physical characterization

Scanning within the 2θ range of 5–50°, a Bruker D8 diffractometer using $\text{Cu K}\alpha$ radiation with 40 mA and 40 kV was employed to

obtain the PXRD patterns. Using KBr pellets, FTIR spectra were collected in the range of 4000–400 cm^{-1} on a Nexus 912 AO446 spectrophotometer. Excitation and emission spectra of the samples were measured on an Edinburgh FLS920 spectrophotometer using a 450 W xenon lamp as excitation source. Thermogravimetric analysis (TGA) was measured using a Netzsch STA 449C system with a heating rate of 5 °C/min. The morphologies of the samples were recorded on a Philips XL-30 scanning electron microscope (SEM). Oxygen sensing experiments were carried out with the assistance of Edinburgh FLS920 spectrophotometer and a homemade gas mixer.

2.3. Synthesis of bio-MOF-1 and $\text{Tb}^{3+}@Bio-MOF-1$

Bio-MOF-1 was prepared as Nathaniel's report [40]. adenine (0.125 mmol, 0.0169 g) and zinc acetate dihydrate (0.375 mmol, 0.0823 g), 4,4'- biphenyl dicarboxylic acid (BPDC) (0.25 mmol, 0.0605 g), nitric acid (1 mmol), DMF (13.5 ml), water (1 ml) were mixed well in a 20 ml of vial and heated at 130 °C for 24 h and then cooled down to room temperature. After washing with DMF for several times, the yield was dried under vacuum at 80 °C for 6 h, then we can get Bio-MOF-1. Tb^{3+} was introduced to Bio-MOF-1 via cation exchange method. 30 mg of Bio-MOF-1 were soaked into the DMF solution of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (5 mL, 10 mmol) for 3 days. The product was collected by centrifugation and washed with DMF for several times to remove the residual Tb^{3+} . After drying under a vacuum at 80 °C for 6 h, $\text{Tb}^{3+}@Bio-MOF-1$ was finally obtained.

2.4. Synthesis of $\text{Sm}^{3+}@TiO_2$

$\text{Sm}^{3+}@TiO_2$ was prepared referring to Marko's paper [35]. The ratio of Sm^{3+} and TiO_2 are increased to 10%. $\text{Ti}(\text{OC}_4\text{H}_9)_4$ solution in butanol was used as precursor. Methanol solution of Sm^{3+} can be obtained by dissolving $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ into methanol. After mixing the two solutions well, distilled water was added to the mixture drop to drop while stirring and then we can obtain white precipitate. The precipitate was dried using vacuum rotator and then calcined at 800 °C for 2 h, so we can get Sm^{3+} doped TiO_2 .

2.5. Assembly of $\text{Sm}^{3+}@TiO_2-\text{Tb}^{3+}@Bio-MOF-1$

Tb^{3+} was introduced to Bio-MOF-1 via cation exchange method. $\text{Tb}^{3+}@Bio-MOF-1$ we prepared is labeled as product 1. For functionalization, the as-synthesized $\text{Tb}^{3+}@Bio-MOF-1$ (0.2 g) was dispersed in 50 mL of THF and then 0.6 mL of IPTES was added into the abovementioned mixture. Furthermore, the mixture was heated at reflux for 20 h under argon gas and the obtained complex (labeled as product 2) was dried under vacuum. In product 2, IPTES was successfully connected to $\text{Tb}^{3+}@Bio-MOF-1$. subsequently, TTA (0.1 mmol, 0.0222 g) was dispersed in 50 ml of THF and then NaH (0.2 mmol, 0.0048 g) was added, after the mixture was heated at reflux for 2 h under argon gas, product 2 (0.2 mmol, ≈ 0.7000 g) was added and heated at reflux for 12 h under argon gas, after centrifugation and drying under a vacuum at 80 °C for 6 h, we can get product 3, there is a common reaction of IPTES and TTA. Since that carbonyl in TTA can react with Sm^{3+} , we can finally get the target product. product 3 (0.5000g) was dispersed in ethanol and the pH was adjusted to 7–8, the ethanol solution of $\text{Sm}^{3+}@TiO_2$ (0.0500g) was added, the mixture was stirring at room temperature for 10 h, after centrifugation and drying under a vacuum at 80 °C for 6 h, the final hybrid $\text{Sm}^{3+}@TiO_2-\text{Tb}^{3+}@Bio-MOF-1$ was finally obtained. The more detailed parts are exhibited in Fig. S1.

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