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Study on the fluorescence properties of benzopyrylium salt in Ti-HMS

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Abstract

Benzopyrylium salt S-2 (2,4-diphenyl-5,6,7,8-tetrahedro-1-benzopyrylium perchlorate) was introduced into the channels of mesoporous molecular sieves Ti-HMS with different Ti content by impregnation method. The fluorescence properties (excitation, emission and lifetime) of S-2 in these sieves have been studied. The results indicated that S-2 molecules interact with the isolated framework Ti^{4+} on the internal surface of Ti-HMS and the amount of S-2 introduced increases with the increasing of isolated titanium content. The observed biexponential decay can be interpreted in terms of two absorbed site, the isolate Ti site and the silanol site. The S-2 molecules absorbed on the Ti site have longer lifetime.

Keywords: Ti-HMS; Benzopyrylium salt; Impregnation method; Fluorescence; Biexponential decay; Isolated Ti^{4+}

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1. Introduction

Energy problem is one of the three largest problems faced all over the world in the 21st century. While solar energy is the most inexpensive and easily available energy resource. So in recent years, photoinduced electron transfer in heterogeneous hosts with various dyes (dye-sensitized electron transfer) has been widely studied towards finding chemical processes that are capable of conversion and storage of light energy or designing molecular systems that can mimic photosynthesis [1–4]. The reason is that encapsulation into molecular sieves not only modifies the molecular and photochemical properties of organic molecules [5], but also increases the lifetime of the photogenerated radical ions and improves the efficiency of photo-electricity conversion [1]. However, development of photoinduced electron transfer requires clarifying the photophysical and photochemical properties about organic molecules incorporated in the host. Therefore, in this paper, we demonstrated the fluorescence properties of benzopyrylium salt S-2 in Ti-HMS with different

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titanium content. Pyrylium, benzopyrylium and thiapyrylium compounds are widely used as sensitizers in photographic materials and photosemiconductors [6], fluorescence indicator [7], photocatalyst [8,9] and so on. Study on their photoluminescence in Ti-HMS may provide useful information for taking advantage of solar energy.

2. Experimental section

2.1. The synthesis of molecular sieves Ti-HMS

HMS-type molecular sieves with different Ti contents were synthesized according to Pinnavaia TJ and coworkers [10]. That is, Ti-HMS were prepared by acid hydrolysis of Ti(*iso*-$OC_3H_7)_4$:$Si(OC_2H_5)_4$ mixture in alcoholic solutions using dodecylamine (DDA) as a template. In a typical synthesis, a clear solution of $Si(OC_2H_5)_4$ (1.00 mol) and Ti(*iso*-$OC_3H_7)_4$ (0.01 mol) in ethanol (6.54 mol) and isopropanol (1.00 mol) was added to a stirred solution of DDA (0.27 mol) and HCl (0.02 mol) in water (36.3 mol). Allowing the resulting gel to age for 18 h at ambient temperature afforded the crystalline templated products. All these samples were filtered, washed thoroughly with water, dried at ambient temperature and calcined at 823 K for 5 h.

2.2. Inclusion of benzopyrylium salt into Ti-HMS

Calcined Ti-HMS molecular sieves (100 mg) were heated at 200 °C for 6 h to remove water adsorbed on the surface, then at once transferred to a flask and allowed to cool to room temperature under N_2 atmosphere. Benzopyrylium dye (shown in Fig. 2) solution (5 ml) of desired concentration was added into the flask; after 24 h, the solids were filtered and washed thoroughly with the solvents until the solution was clear, which indicated that the dye molecules attached to the external surface of Ti-HMS have been removed. Then the samples were dried for characterization.

2.3. Characterization

The mesoporous molecular sieves Ti-HMS were characterized by powder X-ray diffraction (XRD) in the low-angle range. XRD measurements were carried out with a Rigaku D/MAX-2550 diffractometer using Cu Kα radiation within the scattering angle 2θ range of 1.2–10°, typically run at a voltage of 40 kV and current of 100 mA. Excitation, emission spectra and fluorescence lifetimes of S-2 in Ti-HMS were measured by using Edinburgh FLS920 combined fluorescence lifetime and steady state spectrometer with time-correlated single-photon counting unit. The lifetimes were calculated from the decay curve by using the least-square method. All the measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD

The XRD patterns of the mesoporous molecular sieves Ti-HMS obtained in the present study are depicted in Fig. 1. It can be seen that all materials exhibit well-defined 100 reflections, and the relatively well-defined pattern is typical of HMS as described by Pinnavaia TJ and coworkers [10]. And there are some differences between the (100) diffraction peaks of 1%Ti-HMS, 2% Ti-HMS and 10%Ti-HMS. The intensities decrease and their peaks become broader with the Ti content increasing in the samples, suggesting that the mesoporous structures of Ti-HMS become less uniform upon the introduction of Ti into the framework and the hexagonal lattice is destroyed. The contents of titanium in the present samples are not quantified and just the values calculated from the raw materials.

3.2. Fluorescence spectra and fluorescence lifetime

Fluorescence technique has been widely used in studying the organic molecules in microenvironment [11]. By using steady state and time resolved fluorescence technique, extensive insights have been provided to analyze the interaction between the organics and support or the effect of environment on the excited state of organic molecules.

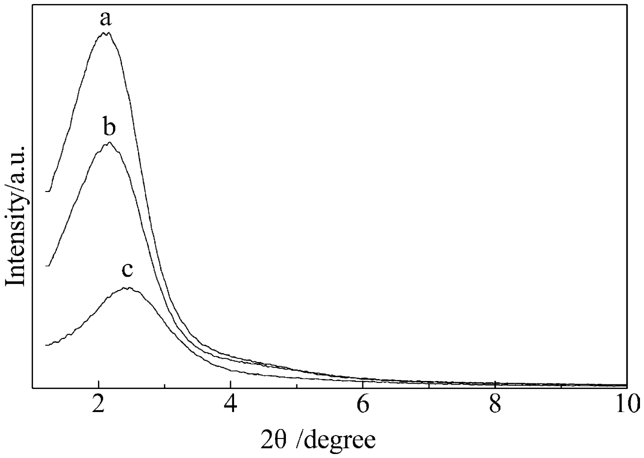

Fig. 1. Powder XRD patterns of Ti-HMS: (a) 1%Ti-HMS; (b) 2%Ti-HMS; (c) 10%Ti-HMS.

And the excited state lifetime is an important factor in photoinduced electron transfer.

The emission and excitation spectra of S-2 in Ti-HMS are illustrated in Fig. 3(A) and (B), respectively. The emission spectra are obtained by exciting at respective maximum excitation wavelength and the excitation spectra are obtained by emission at respective maximum emission wavelength. For comparison, the emission of S-2 in HMS is also given in Fig. 3(A). The fluorescence decay profiles of S-2 in Ti-HMS are shown in Fig. 4. The fluorescence data and lifetime data are listed in Table 1.

It can be known from Table 1 that the maximum emissions of S-2 in Ti-HMS are at about 435 nm, blue shifting about 20 nm compared with that in HMS, which indicates that S-2 molecules interact with Ti^{4+} [12]. Most of the Ti atoms in the Ti-HMS samples occupy site-isolated positions within the silica framework, expect for high Ti content sample 10%Ti-HMS, where some of the Ti species may be present in an octahedrally coordinated environment, while in low Ti content sample, such as 1%Ti-HMS, highly dispersed fourfold coordinated Ti species are found and play the role of effective adsorption sites [13]. On the other hand, the S-2 cation is very stable,

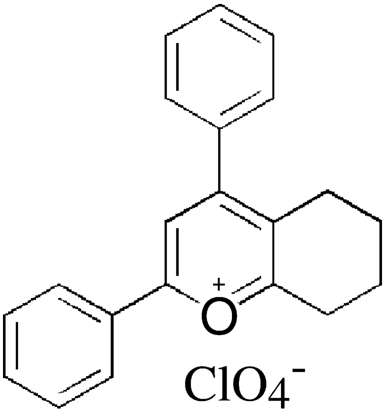

Fig. 2. Molecular structure of S-2.

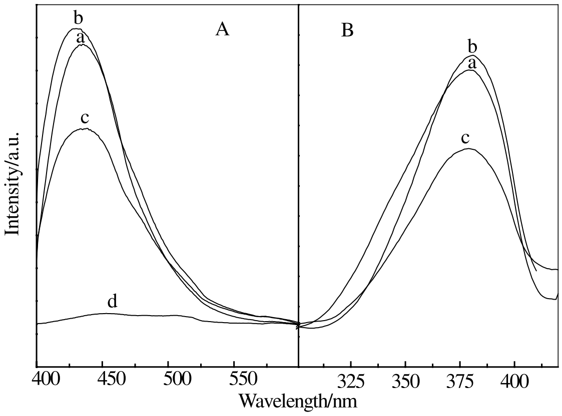

Fig. 3. Emission (A) and excitation (B) spectra of S-2 in Ti-HMS: (a) 1%Ti-HMS; (b) 2%Ti-HMS; (c) 10%Ti-HMS; (d) HMS.

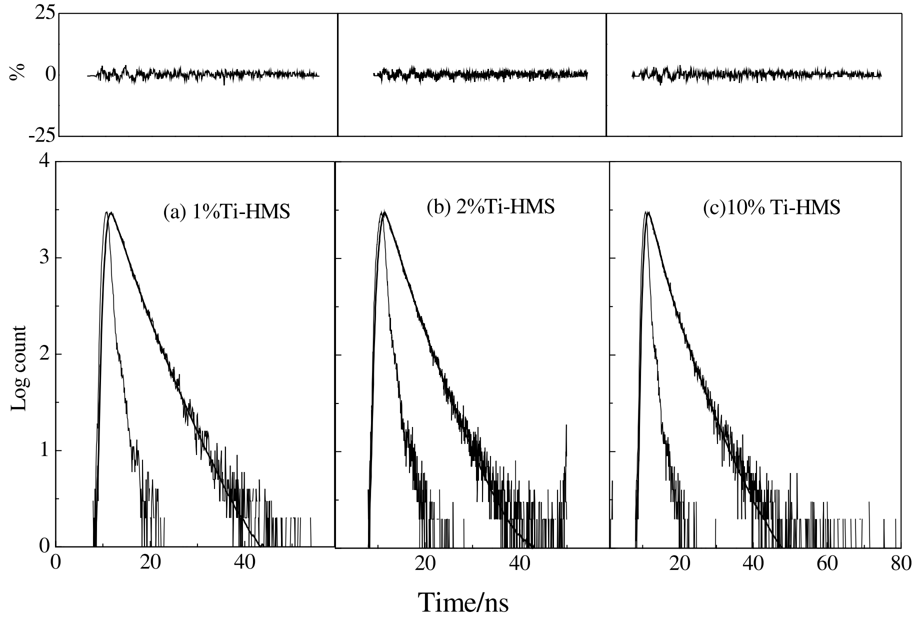

Fig. 4. Fluorescence decay profiles of S-2 in Ti-HMS: (a) 1%Ti-HMS; (b) 2%Ti-HMS; (c) 10%Ti-HMS.

indicating that the single electron is in the plane of heterocyclic ring. So the interaction of S-2 with Ti-HMS should be the coordination between the lone-pair electron of oxygen atom in S-2 structure and the isolate framework Ti^{4+} in the internal surface [14]. The blue shift of the maximum emission of S-2 in Ti-HMS can be explained by the change in the π-conjugation due to the interaction with Ti^{4+}, the transition energy increases with a decrease of π-conjugation [12] and so the emission shifts to blue.

The intensity of emission is related to the amount of chromophore and the excited state lifetime. The higher the intensity, the more the chromophore and the longer the excited state lifetime. From Table 1, it can be seen that the amounts of two forms (discussed later) are almost the same (50%), so the more of isolated framework Ti^{4+}, the more of S-2 molecules introduced into the channels of molecular sieves. Therefore, we see in Fig. 3(A) that the intensity of S-2 in HMS is far lower than that in Ti-HMS, and the intensity of S-2 in 2%Ti-HMS is higher than that in 1%Ti-HMS and 10%Ti-HMS. Of course, the S-2 molecules absorb on the surface of TiO_2, but the lifetime will become very short due to the electron transfer from singlet state of S-2 molecules to the conduction band of TiO_2 [15], and the emission cannot be measured at room temperature because there is no emission by using the commercial TiO_2 (P25) as the host.

Table 1
The fluorescence data of S-2 in Ti-HMS

Host	$\lambda_{max,ex}$ (nm)	$\lambda_{max,em}$ (nm)	τ_1 (ns)	τ_2 (ns)	χ^2
1%Ti-HMS	379	435	2.084 (0.513)[a]	3.963 (0.487)	1.160
2%Ti-HMS	381	430	1.869 (0.508)	3.651 (0.492)	1.063
10%Ti-HMS	379	438	1.929 (0.548)	4.530 (0.452)	1.173
HMS	379	454			

[a] The amplitudes are given in parentheses.

Fig. 4 shows that all S-2 in Ti-HMS are found to exhibit biexponential decay, irrespective of the content of titanium, viz, 1%, 2% and 10%. The two lifetimes are designated as τ_1 (short) and τ_2 (long). Biexponential decay has been interpreted from the monomer–dimer equilibrium [16], or existing two types of components [17]. But for the present study, the results could not be interpreted by the former because there is no emission and excitation of the aggregate ($\lambda_{\max,em} = 560$ nm and $\lambda_{\max,ex} = 330$ nm) in Fig. 3(A) and (B). And the S-2 molecules cannot have two types of components for its rigid structure. Kano et al. [18] suggest that two types of existing state, in solution and absorbed on surface, account for the biexponential decay. Similarly, two types of absorbing state may interpret our results: (i) S-2 molecules absorb on the isolated surface Ti^{4+} site, the oxygen atom in S-2 molecules coordinates with the isolate Ti^{4+} doped into the framework of Ti-HMS and (ii) S-2 molecules absorb on the silanol site, the oxygen atom in S-2 molecules forms hydrogen bond with the hydrogen atom of the silanol of silica framework just as that in the HMS. For the (i) form, the S-2 molecules are tightly fixed and become more rigid, moreover electron transfer from the S-2 molecules to the d orbit of Ti existed, so the excited state of the (i) form is more stable than that of the (ii) form, namely, the τ_1 belongs to (ii) form and τ_2 belongs to (i) form.

4. Conclusions

S-2 molecules are introduced into the channels of Ti-HMS with different titanium content. The fluorescence results indicate that the S-2 molecules interact with isolated framework Ti^{4+} in the internal surface. The biexponential decay can be interpreted in terms of two absorbed site, the isolate Ti site and the silanol site. In one absorb site, the oxygen atom in S-2 molecules coordinates with the isolate Ti^{4+} in the internal surface, and in the other, the oxygen atom in S-2 molecules forms hydrogen bond with the hydrogen atom of the silanol of silica framework. The presence of isolate titanium in the framework of molecular sieves eases the introduction of S-2 molecules and the lifetime of S-2 absorbed on the Ti site has been prolonged.

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