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An oligo-phenylenevinylene derivative encapsulated in sol–gel silica matrix

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An oligo-phenylenevinylene (OPV) derivative [4,4′-(1,4-phenylenedivinylene)bis(*N*-methylpyridinium iodide)] (OPVD) has been introduced to silica film by a sol–gel process. The X-ray diffraction pattern shows that the crystallization of OPVD can be eliminated in the composite film. Fluorescence spectral results show that the luminescent peak of the OPVD in the composite film undergoes a blue shift at about 80 nm and its emission intensity is enhanced compared with that of OPVD in the solid state. Surface photovoltage spectroscopy (SPS), and electric field induced surface photovoltage spectroscopy (EFISPS) are used to investigate the electron process in the OPVD–SiO_2 heterostructured composite film. The results indicated that silica acted as an electric-passivation layer of OPVD, which can explain the strong blue-shifted emission of OPVD in the composite film.

Introduction

Conjugated oligomers have received great attention during the past few years and have been proved to be one of the most promising candidates for advanced materials due to their unique photo, electro, and magnetic properties.[1–3] Since materials with phenylenevinylene functional groups have important electro-photo properties,[4,5] efforts in the synthesis and study of oligo-phenylenevinylene (OPV) and its derivatives have intensified.[6–9] However, an issue has been addressed in the crystallization of OPV that affects the properties of devices, such as brightness and stability.[10,11] There have been some reports of applications of dispersing OPV in a polymeric matrix.[8,12] But there are few reports on OPV trapped in a sol–gel matrix.

In order to obtain highly luminescent materials, electronic passivation is an important factor. Passivation is the chemical process by which luminescent cluster surfaces are bonded to another material with a larger band gap that acts as a chemical potential for electrons or holes at the interface. This potential confines electrons and holes inside the cluster, which improves the luminescent quantum yield.[13] Recently, CdSe nanoparticles passivated with a ZnS layer were found to be strongly luminescent with a 50% quantum yield at room temperature.[14]

The sol–gel silica material, which has a larger band gap, can be a good substance for passivation. Its matrix has excellent optical properties and photochemical stability. Therefore, some laser dyes were encapsulated in the sol–gel silica matrix in order to improve luminescent properties,[15–17] but very little has been reported on the electronic process between the luminescent molecules and silica. In this paper, we first report the encapsulation of OPVD into silica film. The purpose of this work is the elimination of the crystallization of OPVD by the sol–gel process, and improvement of its luminescence properties. The effect of silica on the luminescence properties was investigated and explained by fluorescence spectroscopy and surface photovoltage spectroscopy, respectively.

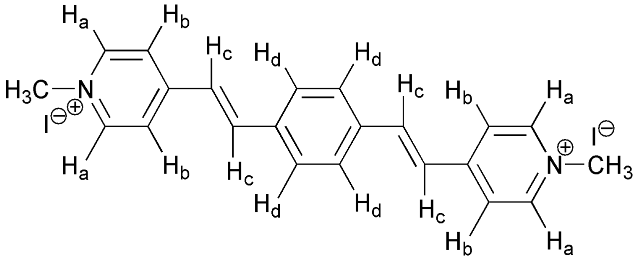
Experimental

The synthesis of OPVD

A typical procedure for the OPVD synthesis is as follows: iodomethane and γ-methylpyridine with molar ratio 1 : 1 were mixed in ethanol under stirring for 0.5 h, then terephthalic aldehyde and the above solution with molar ratio 1 : 2 were refluxed in a NaOH–ethanol solution for 60 min. The precipitate was filtered and recrystallized from isopropyl alcohol to yield a yellow powder. ^{1}H-NMR (400 MHz, CD_3OD), δ 8.67 (4Ha), 7.74 (4H_b), 7.13 (4Hc), 7.46 (4H_d), 2.38 ppm (6H); elemental analysis: calcd for $C_{22}H_{22}N_2I_2$: C 46.48, H 3.90, N 4.93%; found: C 45.72, H 4.01, N 4.91%, which is obtained on PLASMA-SPEC(1)ICP-AES elemental analyses meter. The structure of synthesized OPVD is showed in Scheme 1.

The preparation of OPVD doped composite film

33 g of tetraethoxysilane (TEOS) was dissolved in 22.1 g of terahydrofuran (THF) and refluxed under HCl catalysis (0.75 ml, 2 M) for 2.5 h to obtain the silica sol. 2 ml OPVD–methanol solution (0.5 mg ml^{-1}) and the sol (2 ml) were mixed and stirred for 30 min. The resulting solution concentration is 2.5×10^{-4} M. The transparent OPVD–SiO_2 composite film was



Scheme 1 The molecular structure of OPVD.

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obtained by spin-coating the mixture onto clean quartz substrates at 2000 rpm for 20 s. The thickness of film is *ca.* 1 μm (±50) nm.

Measurement

The X-ray diffraction patterns of the sample were obtained on a Rigaku D/max rA Diffractoneter using the Cu K$_\alpha$ line as radiation source. The UV-vis absorption spectra were measured by using a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were measured by a RF-5301 PC spectrofluorophotometer. The slit width was 3 nm, and the scanning speed was medium. The excitation and emission spectra were background-subtracted and corrected for detector and monochromator tranmission nonlinearities. The surface photovoltage spectra (SPS) were measured with a laboratory-built apparatus described in Ref. 18. Monochromatic light was obtained by passing light from a 500 W Xenon lamp through a double-prism monochromator (Higher and Watts, D300). A lock-in amplifier (Brookdeal, 9503-SC), synchronized with a light chopper, was used to amplify the photovoltage signal. The photovoltaic cell consisted of indium tin oxide (ITO)–sample–ITO.

The surface photovoltage (SPV) effect, a change of the surface-potential barrier caused by illumination, has successfully been applied to the investigation of electron processes in heterostructured composites.[19,20] The generation of photovoltage arises from the creation of electron–hole pairs, followed by the separation and transportation to electrode surface under a built-in electric field (the space-charge layer).

Cyclic voltammetry of OPVD was performed on an HPD-1A Model Potentiometer under nitrogen atmosphere. The electrochemical measurements were carried out in a three-electrode compartment cell with a 0.1 M KCl–water solution, using a SCE electrode as the reference electrode, a platinum disc as the counter electrode and a glassy carbon electrode. The reported cyclic voltammograms were obtained at a voltage-scanning rate of 100 mV s^{-1}.

Results and discussion

Crystallization of OPVD in the SiO$_2$ film was studied by X-ray diffraction. Its X-ray diffraction pattern is shown in Fig. 1a. For comparison, that of OPVD powder is also given in Fig. 1b. It can be seen that the OPVD powder has a certain crystalline character, whereas the OPVD in the silica matrix displays an amorphous state. It suggests that the OPVD dissolved in methanol can also be homogeneously dispersed in the silica sol containing ethanol and THF. After the solvents were evaporated, an OPVD–SiO$_2$ composite film was formed on the substrate. The film exhibits a microporous structure.[21] In such small pores the crystallization of OPVP can be readily avoided.

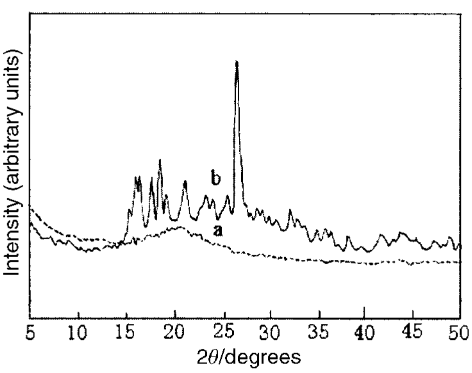


Fig. 1 X-ray diffraction pattern of (a) OPVD–SiO$_2$ composite film and (b) OPVD powder.

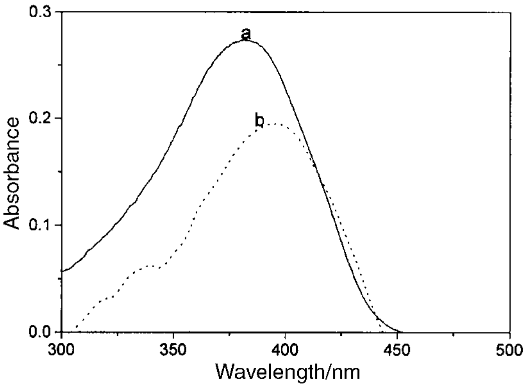


Fig. 2 UV-vis absorption spectra of (a) methanol solution of OPVD (the concentration is 10^{-5} mol l^{-1}), and (b) the OPVD–SiO$_2$ composite film.

Generally, the π–π* transition of molecules is a useful indicator for studying their aggregation behavior. UV-vis absorption spectra of OPVD–SiO$_2$ composite film and OPVD in methanol solution (10^{-5} mol l^{-1}) are shown in Fig. 2. The absorption maximum of sol–gel composite film undergoes a red shift with respect to that in methanol solution. It can be considered that there is little aggregation in the solution, since the concentration of OPVD is rather low. According to Kasha's molecule excitation theory,[22] the observed red shift of the absorption maximum is contributed by the formation of J-aggregates of OPVD in the sol–gel matrix. Meanwhile the shoulder peaks in the shorter wavelength region indicate that H-aggregates have also been formed in the silica cages. The chain torsional angle between adjacent phenylene rings of OPVD, calculated by empirical quantum chemistry method AM1, is about 1.56°. The OPVD molecules of such a structure tend to coplane and this is favorable for formation of H-aggregates. However, different aggregate states of OPVD molecules may be formed due to the interactions between the OPVD molecules and OH groups on the surface of the silica cage with irregular geometrical structure.

The fluorescence spectra of OPVD in powder and OPVD–SiO$_2$ composite film are quite different (see Fig. 3). The spectrum of OPVD in methanol solution shows a monomeric emission at 475 nm. The fluorescence peak of OPVD in the solid state underwent a red shift compared with that of its methanol solution, and the peak of the composite film underwent a blue shift compared with that in the solid state. The 1.56° chain torsional angle of OPVD indicates its coplanar structure. It is reasonable to suppose that such coplanar OPVD crystal molecules are densely packed face to face in the crystal lattice, which can form an excimer,[23] *i.e.*, a complex between an excited state OPVD* and a ground state OPVD upon excitation. The excimer causes a red-shifted emission with respect to monomeric OPVD emission in solution. In the sol–

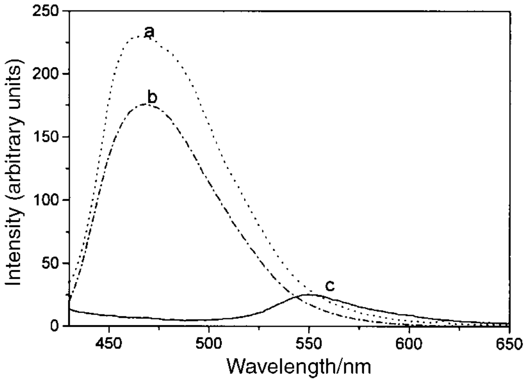


Fig. 3 Fluorescence spectra of (a) OPVD–SiO$_2$ composite film, (b) methanol solution of OPVD, and (c) OPVD powder ($\lambda_{ex}=400$ nm).

gel process, the crystallization of OPVD is eliminated, and OPVD is a disordered blend of different aggregates after being isolated and caged in the sol–gel matrix, so it has a blue-shifted emission. Additionally, non-radiation processes caused by crystal lattice vibration can be dimished owing to the restriction of the crystallization of OPVD, meanwhile the isolation and confinement of OPVD in a silica cage can restrict concentration quenching of OPVD.[24] Therefore, the emission intensity of OPVD in composite film is obviously enhanced and the relative quantum yield increases about 30 times.

The surface photovoltage spectra (SPS) and the electric field induced surface photovoltage spectroscopy (EFISPS) of OPVD in solid and in composite film are shown in Fig. 4 and Fig. 5, respectively. It can be seen that the surface photovoltage (SPV) of OPVD in the solid is much stronger than that of OPVD in composite film. In the crystallization, the OPVD molecules arrange densely, photocreated electrons and holes are mobile in its conduction band and valence band, respectively, so the SPV response is relatively strong. The threshold is about 550 nm. However, when OPVD was trapped in a silica matrix, the crystallization of OPVD was eliminated and OPVD was caged and limited by the SiO_2, so the threshold shifted from 550 to 460 nm, which is consistent with the UV-visible spectra (Fig. 2). These are the reasons for its blue-shifted emission. According to the SPV mechanism, the SPV measurement cell structure is shown in Scheme 2. As an organic semiconductor, the conduction band (*E*c) and valence band (*E*v) of OPVD are at −2.2 and −5.45 eV with respect to the vacuum energy level, respectively, which were obtained by calculation based on the data of electrochemical measurements.[25,26] SiO_2 has a large band gap of 8 eV that makes a barrier on the *E*c and *E*v of OPVD, so it is difficult for the internal photocreated electrons of OPVD to transmit through the thicker SiO_2 and transfer to ITO. Only a few photocreated electrons of OPVD near ITO may pass through the thinner SiO_2 to the ITO surface for the SPV response to take place, so the SPV response is very weak as shown in Fig. 5a. The electron–hole separation is the competitive process with radiative recombination, which results in a strong emission. The mobility of photocreated electrons and holes in the conduction band and valence band of OPVD molecules in crystallization contributes to the electron–hole separation, which makes the SPV response strong but the fluorescence intensity weak. On the other hand, the encapsulation of OPVD in SiO_2, which acts as a passivation layer and confines electron–hole separation is beneficial for the electron–hole radiative recombination, which makes the emission intensity enhance. So the strong blue-shifted emission of OPVD in the composite film caused by passivation and confinement by SiO_2 can also be explained by SPS. The result of SPS is consistent with that of the fluorescence spectra.

From Fig. 5 we can see that the SPV response of OPVD in composite film is enhanced with an external positive electric field. It is because when an external positive electric field (+2.0 V) is applied, the whole energy becomes tilted, thus the wall of potential barrier of the SiO_2 layer becomes thinner, so the photocreated electrons can transport through the SiO_2 and eventually accumulate on the ITO surface, so the SPV response of OPVD is enhanced tremendously as shown in Fig. 5b. The above results indicate that the OPVD is well dispersed in the silica matrix and the electron–holes can transfer under an external positive electric field, so the OPVD–SiO_2 composite system will be significant for organic–inorganic hybrid electroluminescent devices. The silica composite film can improve stability of the devices. The work on this study is in progress.

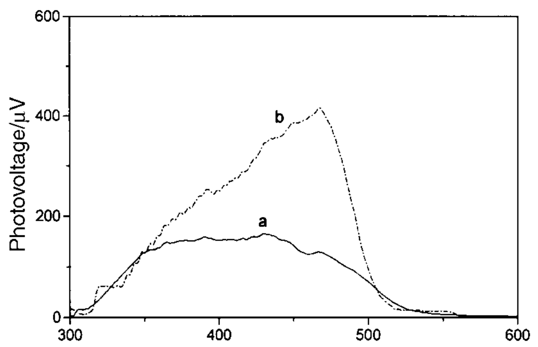


Fig. 4 Surface photovoltage spectra of OPVD powder (a) no external electric field, (b) an external positive electric field (+2.0 V).

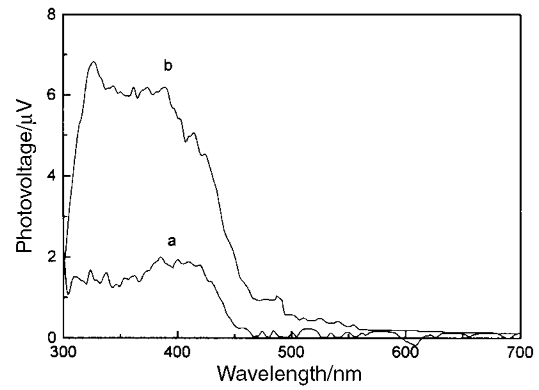
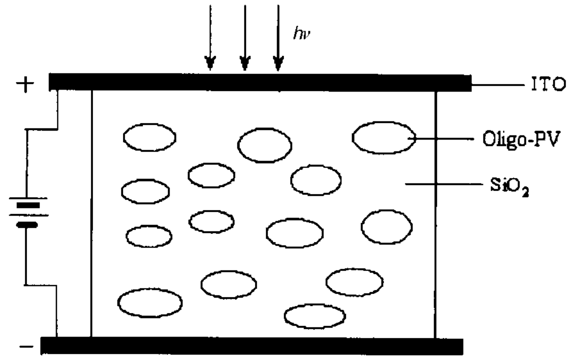


Fig. 5 Surface photovoltage spectra of OPVD–SiO_2 composite film: (a) no external electric field, (b) an external positive electric field (+2.0 V).



Scheme 2 Cell structure for SPS measurement.

Conclusions

An oligo-phenylenevinylene derivative [4,4′-(1,4-phenylenedivinylene)bis(*N*-methylpyridinium iodide)] was introduced to silica film by means of the sol–gel method. This process can eliminate the crystallization OPVD, and the OPVD is well dispersed in composite film. The encapsulation of OPVD in a silica matrix provides a microenvironment for caging and limiting OPVD. Meanwhile the silica as a passivation layer can confine electron–hole separation and contributes to electron–hole radiative recombination, which gives such a composite a strong blue-shifted emission.

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References

1 M. Albota, D. Beljonne and L. L. Brédas, *Science*, 1998, **281**, 1653.

2 Y. Shimoi and S. Abe, *Phys. Rev. B.*, 1994, **72**, 156.

3 Z. Xu, D. Fichou, G. Horowitz and F. Garnier, *Adv. Mater.*, 1991, **3**, 150.

4 V. L. Colvin, M. C. Schiamp and A. P. Alivisatos, *Nature*, 1994, **370**, 354.

5 M. Gao, B. Richter and S. Kirstein, *Adv. Mater.*, 1997, **9**, 802.

6 J. M. Tour, *Chem. Rev.*, 1996, **96**, 537.

7 N. F. Colaneri, D. D. C. Bradley and R. H. Friend, *Phys. Rev. B.*, 1990, **42**, 11670.

8 J. G. Lee, B. Park and H. S. Woo, *Solid State Commun.*, 1997, **102**, 895.

9 T. Goodson, W. J. Li, A. Gharavi and L. P. Yu, *Adv. Mater.*, 1997, **9**, 639.

10 K. Naito, *Chem. Mater.*, 1994, **6**, 2343.

11 J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, *Science*, 1996, **273**, 884.

12 V. Gebhardt, A. Bacher, M. Thelakkat and D. Haarer, *Adv. Mater.*, 1999, **11**, 119.

13 A. P. Alivisatos, *Science*, 1996, **271**, 933.

14 M. A. Hines and P. G. Sionnest, *J. Phys. Chem.*, 1996, **100**, 468.

15 T. Suratwala and Z. Gardlund, *Chem. Mater.*, 1998, **10**, 199.

16 Francisco del Monte and David Levy, *Chem. Mater.*, 1995, **7**, 292.

17 T. Suratwala and Z. Gardlund, *Chem. Mater.*, 1998, **10**, 190.

18 D. J. Wang, W. Liu and T. J. Li, *Huaxue Tongbao*, 1989, **10**, 32; B. H. Wang, D. J. Wang, L. Zhang and T. J. Li, *Thin Solid Film*, 1997, **293**, 40.

19 J. Jin, L. S. Li, Y. Li, D. J. Wang and T. J. Li, *Langmuir*, 1999, **15**, 4565.

20 G. Yu, C. Zhang and A. J. Heeger, *Appl. Phys. Lett.*, 1994, **64**, 1540.

21 Y. Wei, D. L. Jin, T. Z. Ding, W. H. Shih, X. H. Liu, S. Z. D. Cheng and Q. Fu, *Adv. Mater.*, 1998, **3**, 313.

22 M. Kasha, *Radiat. Res.*, 1963, **20**, 55.

23 P. F. Van Hutten, V. V. Krasnikov and G. Hadzhoannou, *Acc. Chem. Res.*, 1999, **32**, 257.

24 A. David, L. David and R. Renate, *J. Phys. Chem.*, 1984, **88**, 5956.

25 Y. Wang, A. Suna and W. Manler, *J. Chem, Phys.*, 1987, **87**, 7315.

26 J. A. Osaheni and S. A. Jenekhe, *Chem. Mater.*, 1995, **7**, 672.