

Keggin 结构钴取代硅钨酸盐聚苯胺掺杂材料的合成及性质

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摘要: 以 Keggin 结构钴取代杂多硅钨酸盐异构体 $\alpha, \beta_i\text{-K}_{6-n}\text{H}_n[\text{SiW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot x\text{H}_2\text{O}$ ($\beta_i = \beta_1, \beta_2, \beta_3$) 为掺杂剂, 采用固相合成法制备了 4 种聚苯胺掺杂材料。用元素分析、红外光谱、紫外-可见光谱、SEM、X-射线粉末衍射、热重分析等对材料进行了表征, 测定了材料的热稳定性、荧光性和导电性。实验结果表明: 合成的掺杂态聚苯胺新材料具有较好的热稳定性、荧光性和导电性, 室温电导率为 $7.5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$, 每种掺杂材料都有一个荧光发射峰, 其发光中心来自于掺杂态聚苯胺极化子能带与价带之间的跃迁。

关键词: 聚苯胺; 硅钨酸盐异构体; Keggin 结构; 荧光性; 导电性

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Synthesis and Properties of Polyaniline Doped with Cobalt Substituted Silicotungstate Isomers in Keggin Structure

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Abstract: The polyaniline hybrid materials doped with cobalt substituted silicotungstate isomers $\alpha, \beta_i\text{-K}_{6-n}\text{H}_n[\text{SiW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot x\text{H}_2\text{O}$ ($\beta_i = \beta_1, \beta_2, \beta_3$) have been prepared. The materials were characterized by elemental analysis, IR spectroscopy, UV-Vis, scanning electron microscopy (SEM), TG and X-ray powder diffraction (XRD). Fluorescence and conductivity of the materials were determined. The results indicate that $\text{SiW}_{11}\text{Co/PANI}$ have better thermal stability, fluorescence and conductivity; the conductivity of the materials is $7.5 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at room temperature. Each of the polyaniline hybrid materials has one emission spectrum from the transition of the electrons between exciton band (produced due to doping) and valence band.

Key words: polyaniline; silicotungstate isomer; Keggin structure; fluorescence; conductivity

Inorganic-organic hybrid materials have received increasing attention over the last few years as a result of their specific properties^[1,2]. These new materials have both the advantages of organic materials (such as light weight, flexibility and good malleability) and of inorganic materials (such as high strength, heat stability and chemical resistance).

Conductive polyaniline as a new material of functional polymer attracts more and more attention because of its simple synthesis method, particular doping mechanism, excellent environmental stability, as well as wide application. The conducting state is usually obtained through p-doping of the chains, which takes place with the incorporation into the polymer the

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charge balancing anions. Therefore, aniline polymerizes in the presence of oxidizing agents and under acidic media to yield the protonated/oxidized form of emeraldine in its conducting state. In recent years, the research of HPA in this field has been very active^[3,4]. Physico-chemical properties of heteropoly complexes can be modulated by changing their chemical environments. The best method to do this at the moment is to replace some atoms by transition metal atoms. Polyaniline is one of the most interesting conducting polymers due to its environmental stability, ease in preparation, exciting electrochemical, optical and electrical properties and possible applications in rechargeable batteries, microelectronics devices, biosensors, electrochromic displays and chemical sensors. In this paper, we report the preparation of polyaniline doped with cobalt substituted silicotungstate isomers. Elemental analysis, IR, UV-Vis, SEM, XRD and TG were used to characterize the polyaniline. The conductivity of the polyaniline doped with $\alpha, \beta_i\text{-K}_{6-n}\text{H}_n[\text{SiW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot x\text{H}_2\text{O}$ ($\beta_i = \beta_1, \beta_2, \beta_3$) was also studied and the fluorescence was found.

1 Experimental

1.1 Instrument and reagents

All chemicals used were analytical grade. The aniline was distilled twice under vacuum. Leeman Lab ICP emission spectrometer and PE2400CHN element analyzer were used. FTIR studies were carried out on Spectrum-One FTIR spectrophotometer with KBr pellets. The UV-Vis absorption spectra were obtained with Tu-1901 UV spectrophotometer. XRD patterns were recorded on BD90 XJ 10-60N X-ray diffraction spectrometer with monochromatized Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm, power 35 kV \times 20 mA). A FEISIRION scanning electron microscope (SEM) was employed to observe the morphology of the hybrid polyaniline by the heteropoly acid material. TG measurements were carried out on SII Prayis Diamond thermal analyzer under a constant nitrogen flow with the scanning rate of 10.0 $^{\circ}\text{C} \cdot \text{min}^{-1}$. The conductivity was measured using a standard four-probe technique. Disk shape samples were prepared from powders using 20 MPa pressure at

room temperature. The photoluminescence spectra were recorded with an F-4500 apparatus.

1.2 Synthesis

1.2.1 Synthesis of silicotungstate isomers

$\alpha, \beta_i\text{-K}_{6-n}\text{H}_n[\text{SiW}_{11}\text{Co}(\text{H}_2\text{O})\text{O}_{39}] \cdot x\text{H}_2\text{O}$ (noted $\alpha, \beta_i\text{-SiW}_{11}\text{Co}$; $\beta_i = \beta_1, \beta_2, \beta_3$) were synthesized according to the literature^[5] and examined by polarography and IR spectroscopy.

1.2.2 Polyaniline doped with $\alpha, \beta_i\text{-SiW}_{11}\text{Co}$ (noted $\alpha, \beta_i\text{-SiW}_{11}\text{Co/PANI}$)

Freshly distilled aniline (2 mL) and acetic acid (1 mL) was put in a mortar and frozen at -20 $^{\circ}\text{C}$ for 20 min; then $\alpha, \beta_i\text{-SiW}_{11}\text{Co}$ (5 g) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (3 g) were added into the mortar, furbishing for *ca.* 30 min until the color of the solid being changed to black-green and then washing with distilled water until pH = 7. The powder obtained was dried under vacuum at 50 $^{\circ}\text{C}$ for 48 h. Empirical formula and elemental anal. (%), for $\alpha\text{-(C}_6\text{H}_{4.5}\text{N)(SiW}_{11}\text{Co)}_{0.0743}$: W 39.72, C 19.05, H 1.20, N 3.70; for $\beta_1\text{-(C}_6\text{H}_{4.5}\text{N)(SiW}_{11}\text{Co)}_{0.0781}$: W 40.19, C 18.34, H 1.15, N 3.56; for $\beta_2\text{-(C}_6\text{H}_{4.5}\text{N)(SiW}_{11}\text{Co)}_{0.0763}$: W 39.97, C 18.67, H 1.18, N 3.63; for $\beta_3\text{-(C}_6\text{H}_{4.5}\text{N)(SiW}_{11}\text{Co)}_{0.0801}$: W 45.76, C 20.36, H 1.28, N 3.96.

2 Results and discussion

2.1 IR spectra

The IR spectra of the materials are shown in Fig.1. The intensity ratio of the absorption at 1589 cm^{-1} for quinoid ring and at 1501 cm^{-1} corresponding to benzene ring is more than 1 in IR spectra of polyaniline base. The bands in the range of 1200~1400 cm^{-1} are C-N stretching bands of an aromatic amine^[6]. The characteristic band of polyaniline base is N=Q=N stretching band at 1166 cm^{-1} . The IR spectra will change after polyaniline is doped with cobalt substituted silicotungstate isomers; 1589 cm^{-1} band shifts slightly to the lower frequency, 1501 cm^{-1} band keeps the same in the main and the relative intensities ratio of 1589/1501 cm^{-1} decreases. These indicate that the doping occurs in $-\text{N}=$, benzene ring increases and quinonoid ring decreases; the band at *ca.* 1142 cm^{-1} is the characteristic band of the protonated state^[7], showing that the protonation of the polyaniline molecule; the bands in the range

of $700 \sim 1\,100\text{ cm}^{-1}$ corresponding to characteristic vibrations of the heteropoly acid appear^[8], suggesting that the insertion of molecules of heteropoly acid into

the molecules of polyaniline. The IR frequencies including assignments of the polyaniline are listed in Table1.

Table 1 IR spectra of polyaniline/SiW₁₁Co

(cm⁻¹)

Samples	N=Q=N	N-B-N	C-N	Q-NH ⁺ -B	W-O _d	Si-O _a	W-O _b -W	W-O _c -W
α -SiW ₁₁ Co/PANI	1 575	1 485	1 303	1 147	957	911	879	791
β_1 -SiW ₁₁ Co/PANI	1 575	1 485	1 303	1 146	956	909	878	790
β_2 -SiW ₁₁ Co/PANI	1 569	1 483	1 304	1 143	956	910	879	790
β_3 -SiW ₁₁ Co/PANI	1 575	1 485	1 304	1 147	956	911	878	792
α -SiW ₁₁ Co					958	889	796	728
β_1 -SiW ₁₁ Co					959	903	878	796
β_2 -SiW ₁₁ Co					960	904	874	791
β_3 -SiW ₁₁ Co					959	899	876	619
PANI	1 589	1 501	1 303	1 166				

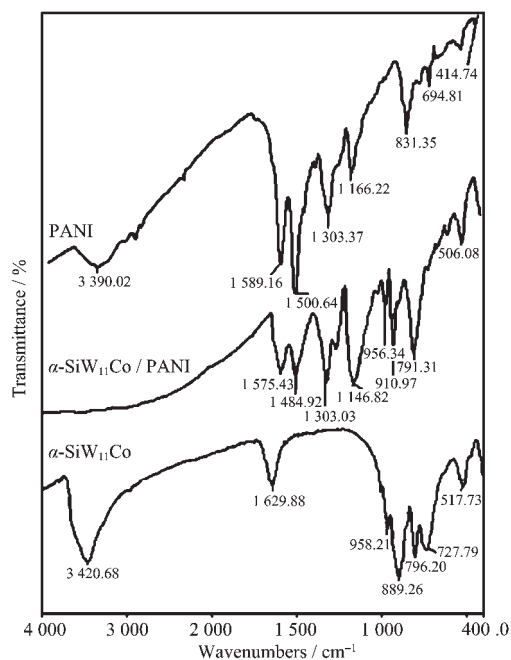


Fig.1 IR spectra of different samples

2.2 UV-Vis spectra

Fig.2 shows the UV-Vis absorption spectra of polyaniline doped with α, β_i -SiW₁₁Co. For the intrinsic polyaniline, the band at 630 nm can be attributed to π_b - π_q^* electronic transition of quinone and benzene units^[9]. In the polyaniline doped with α, β_i -SiW₁₁Co, two new bands at about 450 and 860 nm appear. These two bands should be the characteristic absorption of the doped states of polyaniline, which may be attributed to the polaron absorption^[10]. Moreover, two stronger bands at about 190 nm and 260 nm appear in UV range of

polyaniline doped with α, β_i -SiW₁₁Co; the band at 260 nm is the characteristic band of heteropoly acid, and we can deduce that the band must be attributed to charge transfer band of $O_b/O_c \rightarrow W^{[11]}$. The appearance of bands at about 190, 260, 450 and 860 nm shows that polyaniline molecule has been protonated effectively by α, β_i -SiW₁₁Co. The UV-Vis absorption spectra data of polyaniline doped with α, β_i -SiW₁₁Co are listed in Table 2.

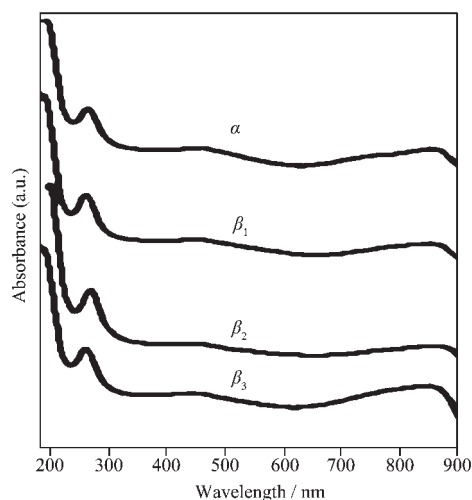


Fig.2 UV-Vis spectra of polyaniline doped with α, β_i -SiW₁₁Co

Table 2 Data of UV spectra of polyaniline/SiW₁₁Co (nm)

Samples	O _d →W	O _b /O _c →W	Polaron absorption	
α -SiW ₁₁ Co/PANI	191	264	452	856
β_1 -SiW ₁₁ Co/PANI	191	263	459	866
β_2 -SiW ₁₁ Co/PANI	193	262	456	866
β_3 -SiW ₁₁ Co/PANI	191	263	453	860

2.3 XRD patterns

The X-ray diffraction patterns of the intrinsic polyaniline, α -SiW₁₁Co and polyaniline doped with α -SiW₁₁Co are shown in Fig.3. There are two very broad overlapping halos and some ordered crystalline peaks in the X-ray diffraction pattern of the polyaniline prepared in the presence of α -SiW₁₁Co. These peaks are different from those of polyaniline base and α -SiW₁₁Co. No peak from any crystalline form of heteropoly acid can be observed, indicating the insertion of the heteropoly anion unit into the polymer matrix. The peak at $2\theta=7.43^\circ$ ($d=1.189$ nm), which is close to the distance of polymer repeat unit with relatively distinct Bragg reflections. This indicated that the PANI doped α -SiW₁₁Co was ordered in short distance.

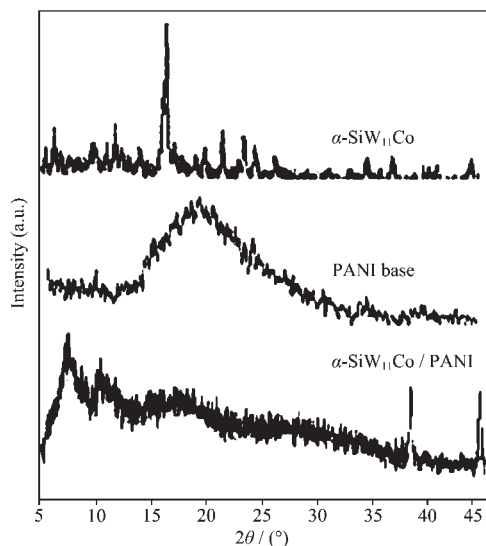


Fig.3 XRD patterns of different samples

2.4 Scanning electron microscopy (SEM)

Fig.4 shows a SEM photograph of the material. The image shows the microporous nature of the material. We conclude that the heteropoly acid anions have been incorporated in the bulk of the hybrid materials.

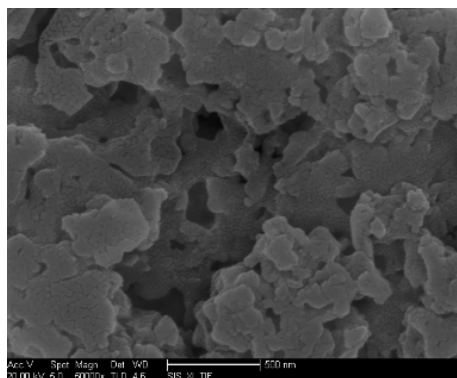


Fig.4 SEM of polyaniline doped with β_1 -SiW₁₁Co

2.5 Fluorescence

We monitored the solid materials with the strongest emission wavelength and excited them at the strongest excitation wavelength. Fig.5 gives the fluorescence emission spectra of the polyaniline doped with α, β_1 -SiW₁₁Co. For the polyaniline doped with α -SiW₁₁Co, when excited under 300 nm, the material shows broad band emission of 400~580 nm with a peak at 490 nm (Fig.5a). For polyaniline doped with β_1 -SiW₁₁Co, when excited under 430 nm, the material shows broad band emission of 560~760 nm with a peak at 603 nm (Fig.5b). For polyaniline doped with β_2 -SiW₁₁Co, when excited under 470 nm, the material shows broad band emission of 650~800 nm with a peak at 706 nm (Fig.5c). For polyaniline doped with β_3 -SiW₁₁Co, when excited under 270 nm, the material shows broad band emission of 350~550 nm with a peak at 419 nm (Fig.5d). Because the intrinsic polyaniline has no fluorescence, according to the excitonic luminous mechanism, we conclude that the luminescence center comes from the electronic transition between exciton band (produced due to the doping) and valence band^[12]. Obviously, the polyaniline molecule synthesized has conjugated transition; moreover, the rigidity and

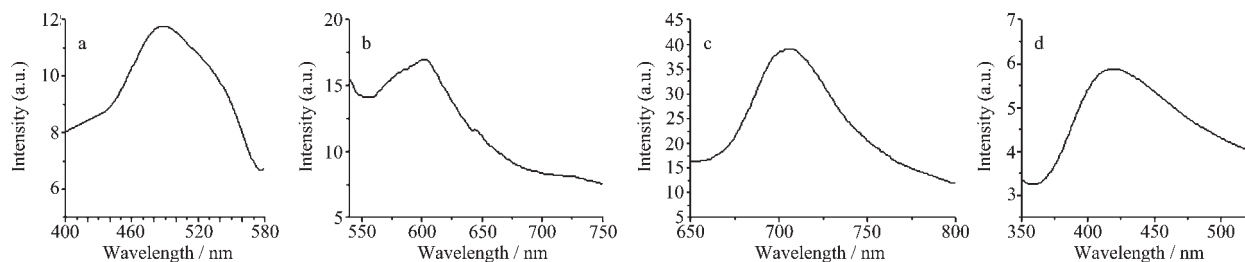


Fig.5 Emission spectra of doped polyaniline (a) α -SiW₁₁Co/PANI; (b) β_1 -SiW₁₁Co/PANI; (c) β_2 -SiW₁₁Co/PANI; (d) β_3 -SiW₁₁Co/PANI

coplanarity of the polyaniline molecule has been improved. The results show that the properties of the fluorescence of the polyaniline/ α,β -SiW₁₁Co are different. The reason why the α,β -SiW₁₁Co/PANI has different emission wavelength is that the substituted elements in silicotungstate are in different positions. It suggests that the effects of heteropoly acid isomers on the fluorescence are different. In other words, changing positions of substituted elements in silicotungstate may improve the fluorescence of doped polyaniline.

2.6 Thermal behavior

Fig.6 shows the results of the thermogravimetric measurements in a nitrogen atmosphere for the polyaniline doped with α -SiW₁₁Co. TG curve shows that the materials undergo three-stages weight loss: the first stage occurs in the range of 26.8~115.3 °C with 5.49% mass loss, which is the loss of surface water molecules; the second occurs in the range of 266.8~576.4 °C with 17.28% mass loss and the third stage occurs in the range of 650~870 °C with 18.66% mass loss. The weight loss at about 266.8 °C is the beginning of degradation of polyaniline molecule, because the spectra of IR at 270 °C keeps stable basically (Fig.7b). The weight loss at about 650 °C is due to the degradation of polyaniline molecule backbone and heteropoly acid molecule backbone, which is indicated by the IR spectra of the polyaniline when the material is heated at 660 °C for 60 min (Fig.7c).

TG curve of the polyaniline base [13] indicates that there are two steps of mass loss. The first stage occurs in the range of 50~160 °C, which is the loss of surface

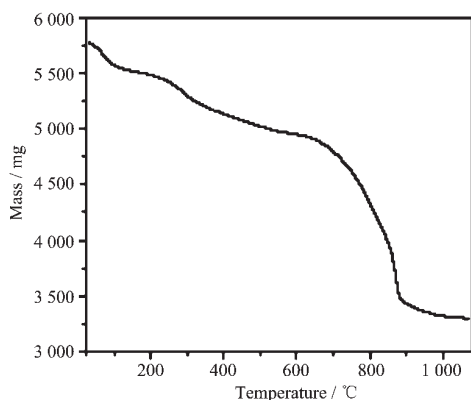


Fig.6 TG curves of polyaniline doped with α -SiW₁₁Co

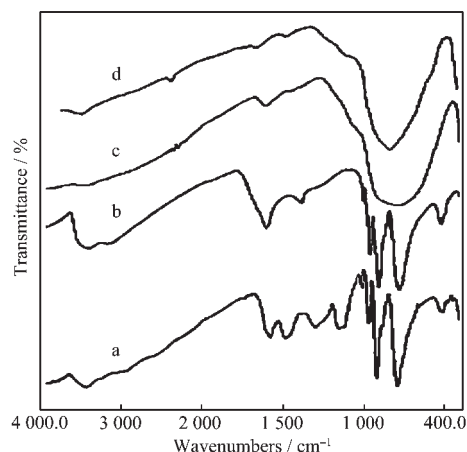


Fig.7 IR spectra of polyaniline, treated by heating at (a) 120 °C, (b) 270 °C, (c) 660 °C and (d) 750 °C

water molecules; the second stage occurs in the range of 250~700 °C, the weight loss at about 250 °C is the beginning of degradation of polyaniline molecule. The thermal analysis shows that the thermal stability of polyaniline doped with α -SiW₁₁Co is higher than that of polyaniline base.

2.7 Conductivity

It is well known that polyaniline base is insulator with the conductivity in the order of 10^{-12} S·cm⁻¹, and the heteropoly acid is insulator with the conductivity in the order of 10^{-3} ~ 10^{-4} S·cm⁻¹ [8], and its protonation gives rise to an increase of several orders of magnitude in the electronic conductivity. Here the conductivity of all materials at room temperature is α -SiW₁₁Co/PANI: 1.63×10^{-2} S·cm⁻¹, β_1 -SiW₁₁Co/PANI: 7.25×10^{-2} S·cm⁻¹, β_2 -SiW₁₁Co/PANI: 6.02×10^{-2} S·cm⁻¹ and β_3 -SiW₁₁Co/PANI: 5×10^{-2} S·cm⁻¹, respectively. The results indicate that the title materials have good conductivity. Comparing with polyaniline doped with H₃PMo₁₂O₄₀ and H₄PMo₁₁VO₄₀, the conductivity of polyaniline doped with α,β -SiW₁₁M is higher than that of polyaniline doped with H₃PMo₁₂O₄₀ and H₄PMo₁₁VO₄₀ (H₄PMo₁₁VO₄₀/PANI: 4.78×10^{-4} S·cm⁻¹; H₃PMo₁₂O₄₀/PANI: 1.34×10^{-2} S·cm⁻¹ [14]). This result indicates that the conductivity of polyaniline doped with transition metal substituted silicotungstate is higher than that of polyaniline doped molybdenum-containing heteropolyacid.

3 Conclusion

Four poly aniline doped with cobalt substituted

silicotungstate isomers were synthesized by using solid-state synthesis method. The UV-Vis, IR and XRD results confirm the existence of Keggin anions. The thermal analysis indicates that $\text{SiW}_{11}\text{Co/PANI}$ has better thermal stability. SEM shows that the materials have microporous nature. The materials exhibit excellent proton conductivity; the proton conductivity is $7.25 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ at room temperature (20°C). The spectra data indicate that polyaniline doped with α, β - SiW_{11}Co has the property of fluorescence which comes from transition between exciton band (producing due to doping) and valence band.

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