四针状氧化锌晶须的氧化硅包覆改性

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摘 要: 通过并流中和法对 T-ZnOw 进行氧化硅包覆改性, 改善了与有机高分子材料的相容性。利用红外光谱、X 射线衍射、扫描电子显微镜、激光粒度分析等手段对包覆后的 T-ZnOw 进行了表征, 探讨了 pH 值、陈化时间、温度以及 SiO2 包覆量对包覆效果的影响。结果表明: 晶须表面成功包覆了非晶态硅氧化合物; 包膜后的 T-ZnOw 粒径减小, 分散性能大幅度提高; 实现均匀完整包覆的最佳工艺条件为: 包膜 pH=9~10, 陈化时间 5 h, 反应温度 90 ℃, SiO2 包覆量 10%(质量分数)。

关键词: 四针状氧化锌; 晶须; 二氧化硅; 包覆改性

Tetrapod-like Zinc Oxide Whisker Modified via Silica Cladding

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Abstract: Tetrapod-like zinc oxide whisker (T-ZnOw) was clad with SiO2 by a simultaneous neutralization method to improve its compatibility with organic polymeric materials. The structure of ZnOw cladded with SiO2 was characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and particles size distribution, respectively. The influences of pH value, gelling time, cladding temperature and SiO2 amount on the cladding performance were investigated. The results show that the surface of T-ZnOw is clad with amorphous SiO2 layer. Its particles size decreases and the dispersity of T-ZnOw clad with SiO2 improves after cladding. The homogeneous and full cladding of T-ZnOw can be obtaning under the optimized process condition (i.e., pH of 9–10, modification time of 5 h, reaction temperature of 90 ℃, and the mass fraction of SiO2 as 10%, mass fraction).

Keywords: tetrapod-like zinc oxide; whisker; silicon dioxide; cladding

1 Introduction

Tetrapod-like zinc oxide whisker (T-ZnOw) is a regular three-dimensional structure material in the family of whisker1–2. It can be used to prepare new composites with function integration due to its unique structure, high strength, high modulus, heat resistance, antibacterial and antistatic, semiconductor, and other superior properties3–11. However, it is quite difficult to add the T-ZnOw as an inorganic oxide into organic polymer matrixes such as rubber. This is because 1) the surface energy of the T-ZnOw particles is rather high and easy to aggregate, leading to the unevenly particle dispersion in polymers12–14, and 2) the surface of T-ZnOw appears hydrophilic and oleophobic, showing strong polar and lacking binding force between nonpolar rubber substrate naturally, resulting in prolonged mixing duration15 and its malfunction16. It is thus necessary for the improvement of the cohesion between T-ZnOw and polymer to modify the surface of T-ZnOw with organic binders.

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Some researchers directly disposed whisker with a coupling agent \[14, 17\]. However, it is difficult to bond T-ZnOw with other groups due to its chemical stability, resulting in the ineffective coupling. Kim et al. \[19–25\] reported that the surface properties could be improved by cladding SiO\(_2\) layer on the surface of TiO\(_2\) nanoparticles. After the modification, TiO\(_2\) nanoparticles can form bond between coupling agent with silicon-oxygen bond \[18\], thereby improve the modification effect and enhance the compatibility between organic materials.

In this work, a compact silica layer was coated onto the surface of T-ZnOw by a simultaneous neutralization method using sodium silicate as a cladding agent and sulfuric acid as a neutralization agent. Also, the effect of the modification parameters on the cladding performance was investigated.

2 Experimental

2.1 Materials

T-ZnOw (AR, Chengdu Jiaotong Jingyu Technology Co., Ltd.), Na\(_2\)SiO\(_3\) (AR, Tianjin Alum Chemical Reagent Factory), and concentrated sulphuric acid (AR, Shanghai Shenxiang Chemical Reagent Co., Ltd.) were used in the experiments.

2.2 Preparation

T-ZnOw was added into deionized water when 0.1 mol/L Na\(_2\)SiO\(_3\) solution as a cladding agent was used. The pH value of the suspension was adjusted to 9–10. The suspension was dispersed by ultrasound for 20 min. After that, the suspension was put into a water bath at 80 °C. Na\(_2\)SiO\(_3\) solution and 1% H\(_2\)SO\(_4\) solution were then added into the suspension with the SiO\(_2\) and T-ZnOw ratio of 5% (mass fraction) under stirring. The dropping rate of H\(_2\)SO\(_4\) solution was adjusted to ensure the pH value of the suspension of 9–10. After the insulation and aging for 2 h, the suspension was filtered and washed. Finally, T-ZnOw modified with SiO\(_2\) cladding was obtained after dried at 120 °C and ground.

2.3 Characterization

The surface bonding, phase constitution and chemical components of the cladding samples were characterized by a model 100 Fourier transform infrared spectrometer (Perkin Elmer Co., USA). The particles size and zeta potential of samples were determined by a model Nano-ZS90 zeta potential/particle sizer (Malvern Co. Ltd., UK). The phase composition of the samples was determined by a model XD-3 X-ray diffractometer (Purkinje General Instrument Co., China). The scanning electron microscopy images of the samples were obtained by a model JSM–6330F, by a field emission gun scanning electron microscope (JEOL Co., Japan).

3 Results and discussion

3.1 Parameters for cladding

3.1.1 pH value  Sodium silicate and dilute sulphuric acid solution were simultaneously added into scattered zinc oxide whisker aqueous solution. Sodium silicate can hydrolyze into single molecule orthosilicate at a certain pH value \[26\], forming a sol. The generated active silicon sol is immediately absorbed on hydroxyl of whisker surface, forming nucleation site, which is a physical absorption process. Theoretically, in the whole range of pH value, the relationship between logarithm of silicic acid solution gel time and pH value looks like a complete “N”\[27\]. The fastest rate of silica gel occurs as pH<2 and pH>7–8 and the slowest rate appears as pH=2–4 and pH>9. When the clad polymeric silicic acid rate is so great that active silicic acid self-nucleation occurs and then a number of small spherical SiO\(_2\) particles depositing on the whisker surface form, resulting in nucleation being clad. However, controlling the formation of silicic acid and slower polymerization rate can favor the gradual deposition on the whisker surface to form a film clad, finally obtaining a continuously homogeneous compact-silicon layer.

The pH value also has an effect on the dispersion of T-ZnOw. Since small T-ZnOw particles easily aggregate, it is necessary for the dispersion of T-ZnOw to add a dispersant into the suspension at a certain pH value. In the case, the surface of each particle can be clad. Otherwise, enveloping on the whisker aggregates will greatly affect the quality of capsule. Here, we use sodium silicate as a dispersant, which can be absorbed on whisker surface to form the double-electric layer. This layer can produce the Coulomb repulsion between the particles, hindering the particle aggregation. Consequently, particles can be dispersed homogeneously\[28\]. Figure 1 shows the zeta potentials of T-ZnOw at different pH values. Clearly, the maximum absolute value of zeta potential is at pH value of 8–10. When the zeta potential is greater, the particles will have less opportunity to collide, aggregate and sediment\[29\]. The dispersion of whisker will reinforce, and it is advantageous to envelope. The optimum pH value for cladding is 9–10.

![Fig. 1](image-url)  Zeta potentials of T-ZnOw at different pH values

3.1.2 Aging time  Figure 2 shows the FTIR spectra of pure T-ZnOw and clad T-ZnOw at different aging time.
Compared to pure T-ZnOw, a strong absorption peak appears at 1 024.7 cm$^{-1}$ after cladding, which corresponds to Si–O–Si asymmetrically stretching vibration absorption peak\(^2\), shifting to a lower wave number. This indicates that the presence of certain interaction between T-ZnOw and SiO$_2$ layer. An absorption peak at 508.0 cm$^{-1}$ also appears after cladding, which may be overlaid each other of Zn–O characteristic absorption peak at 538.6 and 507.3 cm$^{-1}$, and Si–O symmetrically stretching vibration absorption peak appears at 471.0 cm$^{-1}$\(^2\). After cladding, an absorption peak at 1 024.7 cm$^{-1}$ appears for all the cases, which corresponds to Si–O–Si peak. The absorption peak becomes gradually more intense with the increase of aging time. It is seen that the significant change occurs at the aging time of 2–3 h. In this case, the peak becomes sharper and then the peak changes slowly. This shows that at the initial aging stage, silica sol is constantly absorbed onto whisker surface. During the formation of the layer, the layer growth rate becomes slower, which is mainly because the concentration of silicic acid solution gradually decreases.

![Fig. 2 FTIR spectra of T-ZnOw at different aging time](image)

Table 1 shows the average diameter of T-ZnOw at different aging time. The particles size in the solution could reflect the dispersion of the particles. If the average particles size is smaller, the particles dispersion will be more homogeneous\(^2\). Particles size reduces greatly after cladding, and slowly decreases with the increase of aging time. This illustrates that at the initial aging stage, activated silicic acid rapidly absorbs to the whisker surface and changes its surface molecular properties, thus leading to the small reduction of whisker size. The whisker size becomes the smallest at the aging time of 5 h or 6 h.

![Fig. 3 FTIR spectra of T-ZnOw cladding at different temperatures](image)

3.1.3 Temperature for cladding Figure 3 shows that the FTIR spectra of cladding test results at different temperatures. At 40 $^\circ$C, Si–O–Si asymmetrically stretching vibration area does not appear the corresponding peak, indicating that the temperature is rather low and silicic acid gel speed is so slow. When the temperature is lower than 40 $^\circ$C, it is difficult to form the layer. At 50 or 60 $^\circ$C, Zn–OH asymmetrically bending vibration peaks at 988.4 and 867.3 cm$^{-1}$ are weak or even disappear, and a weak Si–O–Si peak appears at 1 024.7 cm$^{-1}$, showing that whisker surface is attached to active silicic acid, but the cladding effect is poor. At 70 or 80 $^\circ$C, Si–O–Si vibration peak at 1 024.7 cm$^{-1}$ becomes more intense, and an absorption peak appears at 784.5 cm$^{-1}$, which corresponds to Si–O symmetrically stretching vibration\(^2\). The rate of silicic acid gelation becomes greater when the temperature increases. At 90 $^\circ$C, Si–O peak becomes more obvious, and Si–O–Si absorption peak is more intense. The content of SiO$_2$ on whisker surface is greater and silicon film can grow more compactly.

![Table 1 Average diameter of T-ZnOw at different aging time](image)

<table>
<thead>
<tr>
<th>Gelling time/h</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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</thead>
<tbody>
<tr>
<td>Average diameter/nm</td>
<td>2.137</td>
<td>2.006</td>
<td>1.962</td>
<td>1.936</td>
<td>1.933</td>
</tr>
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</table>
Table 2 Average diameter at different cladding temperatures

<table>
<thead>
<tr>
<th>Temperature/℃</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average diameter/nm</td>
<td>4.415</td>
<td>3.486</td>
<td>2.818</td>
<td>2.461</td>
<td>2.137</td>
<td>1.994</td>
</tr>
</tbody>
</table>

3.1.4 SiO₂ content

Figure 4 shows the FTIR spectra of T-ZnOw with different SiO₂ contents. Clearly, Si–O–Si absorption peak gradually enhances at 1 024.7 cm⁻¹ when SiO₂ cladding content increases. When the content reaches 10%, Si–O stretching vibration absorption peak appears at 784.5 cm⁻¹, and the peak intensity increases with increasing the content. When SiO₂ content is low, most of the acid and hydroxyl on whisker surface react, leading to a poor cladding growth. As a result, the surface is not completely clad. As the SiO₂ cladding content increases, Si–O on whisker surface and silicate condense to form Si–O–Si bond. The bond clad a thin silicon layer on whisker uniformly and the layer starts to grow, which will make the nature of molecules surface change apparently and reduce the interparticle van der Waals forces. Consequently, the particle aggregation can be eliminated effectively [30]. In Fig. 6, a multilayer cladding process appears at SiO₂ content of more than 10%.

Table 3 Average diameter with different SiO₂ contents

<table>
<thead>
<tr>
<th>Mass fraction/%</th>
<th>5.0</th>
<th>7.5</th>
<th>10.0</th>
<th>12.5</th>
<th>15.0</th>
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<tr>
<td>Average diameter/nm</td>
<td>2.137</td>
<td>2.475</td>
<td>2.537</td>
<td>2.563</td>
<td>2.888</td>
</tr>
</tbody>
</table>

3.2 Surface structure analysis

Figure 5 shows the XRD patterns of T-ZnOw and SiO₂/T-ZnOw. The diffraction peaks intensity and peaks width of both samples before and after cladding are similar. No apparent diffraction peak appears after modification and no characteristic diffraction peaks of SiO₂ occur. The correlatively characteristic peaks of silicon appear in the modified samples, which indicates that the interaction between whisker surface and SiO₂ exists. Based on the infrared analysis and XRD results, SiO₂ film formed on the surface of T-ZnOw is an amorphous silicon-oxygen compound.

3.3 Analysis of cladding effects

Figure 6 shows that the SEM micrographs of T-ZnOw with SiO₂ contents of 5.0% (mass fraction, the same below) and 15.0%. Clearly, when the content is 5.0%, the cladding on whisker surface is compact and uniform. The cladding layer is completely covered, but it is rather thin. When the content is 15.0%, the cladding is heterogeneous, and there emerges a large number of irregularities. This shows that when SiO₂ content is too great, silicic acid firstly nucleates homogeneously on whisker surface, and then absorbs active silica to form micelle particles and irregular homopolymers. Active silicon absorbing on whisker surface is rather few due to the nuclear-clad inhibiting film cladding. As a result, the surface coverage rate is rather low. Therefore, to obtain a more complete cladding and prevent homogeneous nucleation, SiO₂ content should be controlled at approximately 10.0%, which is consistent with the results of FTIR analysis.

4 Conclusions

1) T-ZnOw clad with SiO₂ layer was obtained using a simultaneous neutralization method. The FTIR analysis showed that the interaction between the cladding layer and whisker surface exists. The XRD results indicated that SiO₂ layer formed on the surface of T-ZnOw was an amorphous silicon-oxygen compound. The surface properties of whisker changed and the particles size reduced after cladding.
2) At the pH value of 9–10, the gelation rate of silicic acid could be slow, and T-ZnOw was dispersive, which was advantageous to clad.

3) The T-ZnOw compact silicon film cladding could be obtained under the optimum condition (i.e., pH of 9–10, modification time of 5 h, reaction temperature of 90 ℃, and the SiO₂ content of 10.0%). The whisker surface could be clad completely and uniformly under the optimum condition.

References:


