

PREPARATION OF NANOMETER TiO_2 ORGANIC SOLUTION —EFFECT OF ORGANIC SILOXANE ON SOL PROPERTIES*

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Abstract A homogeneous longtime stabilized transparent nanometer TiO_2 organic solution was obtained by means of the simultaneous hydrolysis and co-polycodensation of tetrabutyltitanate (TBT) and methacryloxypropyltrimethoxysilane (MAPTMS) by the sol-gel process. The particle size of nanometer titanium dioxide was controlled by use of bifunctional silanes, such as diphenyldimethoxysilane (DPDMS), diphenyldiethoxysilane (DPDES) and dimethyldiethoxysilane (DMDES). The effect of TiO_2 content in the solution on the refractive index of system was discussed in detail. The result shows that the refractive index of solution increases linearly with TiO_2 content. The refractive index of the three hybrid nanometer materials attained 1.6053, 1.5846 and 1.5346, respectively. The size of nanometer particles was characterized by TEM and the particle diameter thus obtained is in the range of 20–90 nm. FT-IR spectra of the materials show that the Ti—O—Si bond is formed.

Keywords Nanometer titanium dioxide, Tetrabutyltitanate, Refractive index, Hybrid materials, Siloxane

INTRODUCTION

Along with the development of single-ingredient material, composition material and gradient material, hybrid material will become the fourth era material. These hybrid materials can be synthesized by situ-scatter polymerization, the commixture process, the insertion method and the sol-gel process separately. Hybrid material prepared by sol-gel has excellent application prospects due to its good mechanical, optical, heat-resistant properties, and other mechanical performance. The transparent hybrid material of poly(styrene-co-maleic anhydride)/ SiO_2 has been synthesized and the transparency in the range of 500–800 nm wavelengths reached up to 80%^[1]. The preparation of poly(styrene-co-maleic anhydride)/ TiO_2 transparent hybrid material has been studied^[2]. In addition, poly(methylmethacrylate)/titanium dioxide-silica hybrid material with excellent heat-resistant performance has appeared^[3, 4].

However, the refractive index performance of hybrid materials has been discussed much less than other properties. Transparent high refractive index organic/inorganic hybrid materials have been prepared by incorporating a functional oligomer of poly(arylene ether phosphine oxide) with titanium tetraisopropoxide by the sol-gel process^[5, 6], and the refractive index of these materials exhibits a linear relationship with titanium oxide content.

Using simultaneous hydrolysis and co-polycodensation between $\text{Ti}(\text{OC}_4\text{H}_9)_4$, (TBT) and methacryloxypropyltrimethoxysilane (MAPTMS), transparent organic silica/ TiO_2 hybrid materials were prepared in this work. The effect of these components on the size of formed hybrid nanometer materials and the relationship between titanium oxide content and their refractive index of this system were discussed.

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EXPERIMENTAL

Materials

TBT and *n*-butanol were available from Shanghai Chemical Reagent Co. MAPTMS was obtained from Chemical Plant of Wuhan University. DPDMS, DPDES and DMDDES were obtained from Fine Chemical Plant of Zhejiang. All reagents were used directly without any purification.

Preparation of Hybrid Materials

A mixture of TBT, MAPTMS and DPDMS (or DPDES, DMDDES) was placed in a three-necked flask. Then a theoretical amount of 2 mol/L aqueous solution of HCl was added dropwise into the flask. The reaction was carried out and stirred for 4–5 h continuously at room temperature. Finally the reaction mixture was placed in a beaker and covered with a plastic film. After standing for one or two days, several holes were pricked in the film. The mixture was dry at room temperature for one week and then heated at 60°C under vacuum for two days to expel any residual solvent. A yellowish and transparent hybrid material was obtained.

Measurements

The transparency of the hybrid materials in organic solvent was measured by a UV-Vis spectrophotometer with 1 cm sample-cell and at 540 nm wavelength. The refractive index of the materials was measured by an Abbe refractometer at room temperature. The FT-IR spectrum of the nanometer TiO_2 was recorded on an Impact 420 FT-IR spectrometer. The TEM micrograph of the hybrid materials/organic solution was measured by a JEM-100 CXII electron microscope.

RESULTS AND DISCUSSION

Mechanism of Reaction

The key step in preparing organic siloxane/ TiO_2 nanometer hybrid materials is to control the simultaneous hydrolysis and co-polycondensation between TBT and organic silane^[3]. In order to prepare a stable sol system, it is necessary to decrease the number of hydroxyl groups on the particles surface and to depress the condensation activity of TBT hydrolyte as low as possible. Siloxane with aryl groups can stabilize the sol system, because these groups could be assembled on the surface of these nanometer particles and reduce the reactive activity between surface hydroxyls. Figure 1 shows a model of the nanometer particle.

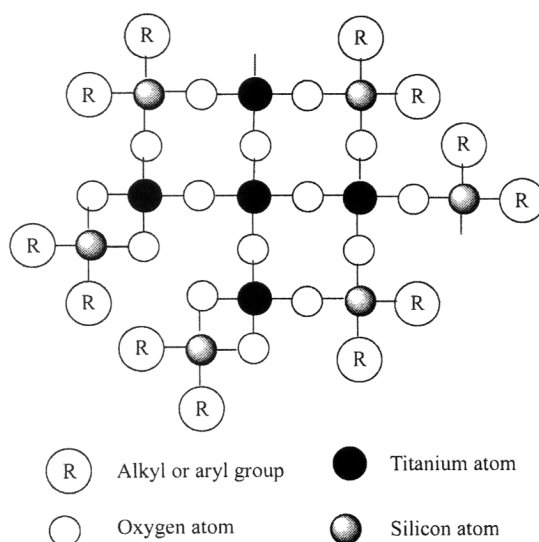


Fig. 1 Model of nanometer TiO_2

Effect of Organic Siloxane Content on Stability of Sol

It was known that when the size of a material's particles is smaller than the wavelength of visible light the material looks transparent. The UV-Vis spectrum of the sol solution is shown at Fig. 2; the TiO₂ sol prepared is a transparent solution. The transparency of the sol is higher than 90% when the wavelength of light is above 500 nm and is lower than 50% below a wavelength of 400 nm. In order to compare the particle size of synthesized sol systems, visible light of 540 nm was selected to measure the transparency of the sol in this work.

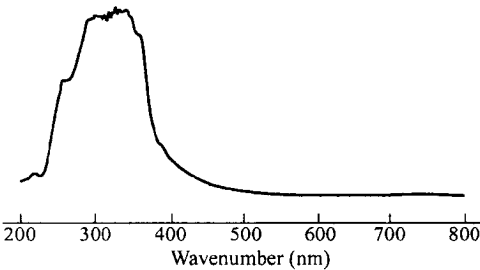


Fig. 2 UV-Vis spectrum of nanometer TiO₂ sols

When the equivalent of TBT is equal to that of MAPTMS, *n*-butanol is used as solvent and the equivalent number of HCl/H₂O was half of that of TBT and MAPTMS. The effect of the mole ratio of DPDMS, DPDES, DMEDES and MAPTMS on the stability and transparency of the sol is shown in Table 1.

Table. 1 The effect of mole ratio of DPDMS, DPDES, DMEDES and MAPTMS on the stability of sol

Run	Silane	MAPTMS/Silane (mol)	Transparency of sol (%)	Character of sol	Gelation time of sol (day)
V	MAPTMS		83	Achromatic and transparent	15
P1	DPDMS	4.0:1	84	Ditto	> 30
P2	DPDMS	1.5:1	78	Ditto	> 30
P3	DPDMS	1:1.2	79	Ditto	> 30
P4	DPDMS	1:1.6	80	Ditto	> 30
P5	DPDMS	1:3.0	61	Little precipitate	–
Q1	DPDES	4.0:1	82	Achromatic and transparent	> 30
Q2	DPDES	1.5:1	84	Ditto	> 30
Q3	DPDES	1:1.2	82	Ditto	> 30
Q4	DPDES	1:1.6	82	Ditto	> 30
Q5	DPDES	1:3.0	66	Little precipitate	–
R1	DMEDES	4.0:1	80	Achromatic and transparent	> 30
R2	DMEDES	1.5:1	84	Ditto	15
R3	DMEDES	1:1.2	83	Ditto	15
R4	DMEDES	1:1.6	83	Ditto	15
R5	DMEDES	1:3.0	67	Little precipitate	–

As shown in Table 1, when silane was added to the system, not only was the transparency of sol decreased, but the gelation time of sol was also prolonged. It is suggested that DPDMS and DPDES can be assembled on the particles surface of titanium dioxide, because these compounds have two reactive functional groups and two phenyl groups with large volume. This will result in higher stabilization of the sol system and smaller particle size of the nanometer materials (as P1, Q2 and V sample films). But when the organic silane content is too high, the transparency and stability of the sol system become worse. It is known that the equivalent number of DPDMS, DPDES or DMEDES is two, while the equivalent number of MAPTMS is three, and the reactivity of

DPDMS, DPDES or DMDES is lower than that of MAPTMS. When DPDMS, DPDES or DMDES are hydrolyzed with TBT in place of MAPTMS, the co-polycondensation ability of these hydrolytes with TBT hydrolyte was lower than that of MAPTMS hydrolyte. This can result in larger particles and lower transparency of the sol system.

TEM of Sol Films

TEM micrographs of nanometer titanium dioxide are shown in Figs. 3–6.

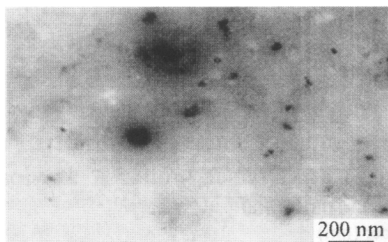


Fig. 3 TEM micrograph of P2 gel

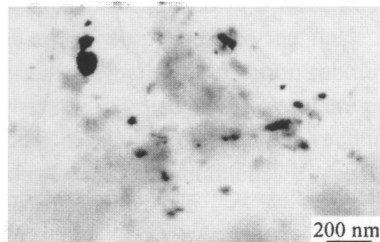


Fig. 4 TEM micrograph of Q1 gel



Fig. 5 TEM micrograph of R2 gel

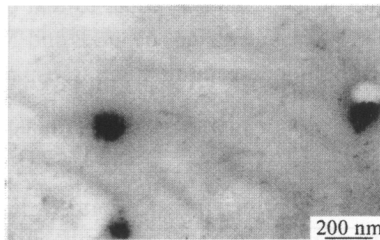


Fig. 6 TEM micrograph of V gel

The particle diameters of P2, Q1, R2 and V samples are in the range of 20–30 nm, 25–35 nm, 50–60 nm and 70–90 nm, respectively. It was known that the phenyl groups on the DPDMS and DPDES possess larger volume, which can control the size of the particles, while DMDES with the smaller methyl group is difficult to control in size, resulting in larger size of R2 than that of P2 or Q1.

FT-IR Spectra of the Sol

Figure 7 shows the FT-IR spectra of nanometer materials synthesized by using hydrolysis and co-polycondensation of TBT with MAPTMS and DPDMS, DPDES and DMDES. The absorption peaks at $1717\text{--}1720\text{ cm}^{-1}$ in the FT-IR spectra of P, R and Q samples are the characteristic absorption peaks of C=O group, and the band at 939 cm^{-1} is the stretching vibration peak of Ti—O—Si. It is suggested that the co-polycondensation between TBT hydrolyte and siloxane hydrolyte has taken place with the formation of Ti—O—Si bond

Effect of Nanometer TiO_2 Content in Sol System on Its Refractive Index

The relationship between refractive index and titanium dioxide content in the sol solution can be seen in Fig. 8.

The refractive index of sol systems shows a linear increase with the increase of TiO_2 content. Four linear equations for the four sol systems are as follows:

$$\text{V: } n_d = 1.378 + 0.647x$$

$$\text{P4: } n_d = 1.3622 + 1.179x$$

$$\text{Q4: } n_d = 1.3675 + 1.123x$$

R4: $n_d = 1.3777 + 0.57x$

where x is titanium dioxide content in the sols.

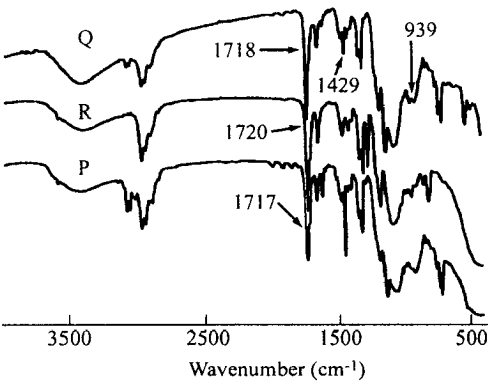


Fig. 7 FT-IR spectra of P, Q and R samples

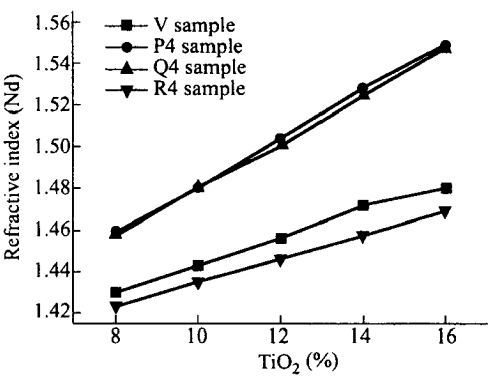


Fig. 8 Influence of TiO₂ content on refractive index

The maximal titanium dioxide contents in V, P4, Q4 and R4 samples are 24.98%, 20.62%, 19.33% and 27.47%, respectively and their corresponding refractive indexes are 1.5398, 1.6053, 1.5846 and 1.5346, respectively. The results showed that when DPDMS and DPDES were added to the sol system, their refractive index would be increased, but when DMDDES was added to the system, the opposite result was obtained because the molar refractive index of phenyl group is higher than that of methyl group. This means that the phenyl group favors increasing the refractive index of these hybrid materials.

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