Synthesis and Photocatalytic Activity of Submicron Strontium Titanate in Soluble Polymer System

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Abstract. Recently, micro-nano-strontium titanate photocatalytic materials have been one of the research hotspots because they can degrade organic pollutants. In the work, 200-400 nm strontium titanate powder was synthesized by soluble polymer (PEG) system and low-temperature direct precipitation method. Studies showed that the concentration of PEG and the degree of polymerization had a significant effect on the particle size of the powder. At the same time, the work studied the photocatalytic properties of the obtained strontium titanate powder, discussing the effect of particle size of strontium titanate on its photocatalytic activity.

1. Introduction
These strontium titanate, a kind of perovskite-type composite oxide, is a new type of high-quality electronic ceramic material and photocatalytic material[1-6]. The low-temperature precipitation method was used to obtain strontium titanate powder with good uniformity of crystal particles between 200 and 400 nm with SrCl₂·6H₂O and TiCl₄ as precursors in polyethylene glycol (PEG) system at different polymerization degrees. We investigated the effect of PEG concentration and degree of polymerization on the particle size of strontium titanate powder and its photocatalytic activity.

2. Experiment
2.1. Synthesis of strontium titanate powder
A certain amount of saturated cerium chloride hexahydrate solution and a certain amount of PEG were added to the reactor, and a certain amount of TiCl₄ solution was slowly added under 75 °C water bath and stirring. The pH of the mixed solution was controlled at pH=13 with sodium hydroxide, and the powder was washed with deionized water after heating in a water bath for 4 hours. Meanwhile, the circulating water multi-purpose vacuum pump was used for suction filtration. Repeat washing and suction filtration until there was no Cl⁻ in the filtrate. The powder was dried for 3 h, and then calcined in a muffle furnace at 750 °C for 3 h. The PEG polymerization degree was 2,000, and the strontium titanate powder obtained under the condition of a concentration of 5 g/L was marked as STOPEG2000-5.

The surface morphology of the sample was observed using a Japanese Hitachi S-4800 scanning electron microscope, and the surface of the sample was sprayed with gold to eliminate charge accumulation. Set the emission current to 10 μA, and the acceleration voltage to 3.0 kV.

2.2. Photocatalytic performance evaluation of strontium titanate powder
The photocatalytic properties of strontium titanate powder were evaluated by methyl orange. A certain amount of methyl orange standard solution and our synthesized strontium titanate sample were added to the quartz reactor. After ultrasonic mixing, the photocatalytic experiment was carried out with TU1202 UV transillumination station UVC (254 nm) as the ultraviolet light source under stirring and a certain air flow rate. The reaction time was 0.5, 1, 1.5 and 2 h. After centrifugation, the solution was analyzed by colorimetric method. The concentration of methyl orange was determined by absorbance at 468 nm of ultraviolet-visible spectrophotometer, calculating the photocatalytic degradation rate of methyl orange solution.

The reagents used in this experiment were of analytical grade, and water was obtained by two-stage reverse osmosis.

3. Results and discussion

3.1. Effect of PEG concentration on the particle size of strontium titanate powder

We synthesized strontium titanate powder with PEG2000 at concentrations of 1, 5 and 10 g/L, respectively. Fig. 1 shows the SEM of the powder. The particle size statistics of 1,000 powder particles are counted by SEM image, and Fig. 2 shows the particle size distribution statistics. The particle sizes of STO\textsubscript{PEG2000-1}, STO\textsubscript{PEG2000-5} and STO\textsubscript{PEG2000-10} are 325, 240 and 415 nm, respectively. The particle sizes are relatively uniform in normal distribution. The synthesized strontium titanate belongs to submicron powder.

The experimental results showed that the strontium titanate powder particles decrease first and then increase with the increased PEG concentration. We speculate that when the PEG concentration is low, the formed strontium titanate crystal particles are incompletely encapsulated. The protection effect is not good, so the particle size is relatively large. When the amount of PEG increases to an appropriate concentration, PEG is ideal for the protection of strontium titanate grains, which can effectively prevent grain growth and agglomeration. When the PEG concentration rises, a large amount of hydrogen bonds can be generated due to the hydroxyl groups among the polyol compounds\cite{7}. The bridging action between the hydrogen bonds of the PEG causes them to aggregate, which makes the size of the strontium titanate particles become large.

3.2. Effect of PEG degree of polymerization on the particle size of strontium titanate powder
Under the condition of PEG concentration of 5g/L, PEG1000, PEG2000 and PEG4000 were used as protective agents, respectively. Fig. 3 shows the SEM of the synthesized strontium titanate powder, and Fig. 4 shows the particle size distribution statistics. The experimental results showed that the crystals of the three samples were spherically monodisperse, and the average particle size of STO_{PEG1000-5} was 293 nm. The average particle size of STO_{PEG2000-5} was 240 nm, with good uniformity of the particle sizes of the two samples in normal distribution. The average particle size of STO_{PEG4000-5} was 332 nm, but the uniformity of particle sizes was significantly reduced. The effect of PEG concentration on the particle size of strontium titanate was similar. Under the same concentration conditions, the polymerization degree of polyethylene glycol had no linear relationship with the particle size of strontium titanate powder. Rather, as the degree of polymerization of PEG increased, the average particle size of strontium titanate powder increased after decrease.

This phenomenon can be explained by the increase in the number of -(CH₂CH₂O)ₙ-units in the PEG molecule and the in situ formation of pseudocrown structure encapsulated by -(CH₂CH₂O)ₙ- with the high degree of polymerization. As the -(CH₂CH₂O)ₙ-chain is short in PEG1000 molecules with low degree of polymerization, a single molecule cannot form a complete pseudocrown ether structure. When pluralities of molecules encapsulate the pseudocrown ether, the interaction between the molecules is small with incomplete encapsulation of the strontium titanate particles. It cannot prevent the entropy effect of the high surface energy of the strontium titanate particles, thereby causing particle agglomeration and growth\[8\]. When the degree of polymerization of PEG is large, it may be due to the decrease in PEG monomer at the same mass/volume concentration and uneven encapsulation of strontium titanate. It makes the decreased distribution uniformity of particle size and the increased particle size. Thus, the molecular configuration of the protective agent is an important factor affecting the size of the strontium titanate particles.

### 3.3. Photocatalytic performance of strontium titanate powder

Methyl orange was used as a photocatalytic evaluation of strontium titanate. Fig. 5 and Table 1 show the photocatalytic experimental data of the synthesized strontium titanate powder. At the same time, as a comparison, we prepared a strontium titanate powder (φ=24 μm) obtained by oxalic acid coprecipitation without macromolecular polymer protection and a strontium titanate powder synthesized by a sol-gel method of acetic acid chelating agent (φ=301 nm) for photocatalytic experiments\[9-11\]. The results were grouped in Fig. 5 and Table 1.
According to the experimental results, the photocatalytic activity of the strontium titanate powder obtained under the PEG system was significantly better than that of the oxalic acid method and the sol-gel method. The synthesis of strontium titanate photocatalyst with PEG as a protective agent is more promising.

The experimental results showed that STOPEG2000-5 had the highest photocatalytic degradation rate and the best activity, and the degradation rate exceeded 93% at 2h. The photocatalytic degradation rate of STOPEG1000-5 was relatively poor, and the degradation rate did not exceed 80% at 2h. The photocatalytic degradation rate of STOPEG4000-5 could reach about 90%. The degree of polymerization of polyethylene glycol had a significant effect on the photocatalytic activity of strontium titanate powder, and it was not linear. As the degree of polymerization of PEG increased, the photocatalytic activity of strontium titanate powder first increased and then decreased.

Fig. 6 shows the relationship between the particle size of strontium titanate powder and photocatalytic activity. STOPEG2000-5 has the smallest average particle size and the highest photocatalytic degradation rate. The average particle size of STOPEG4000-5 is larger than that of STOPEG1000-5, and the photocatalytic degradation rate of the former is higher than that of the latter. It indicates that there is no simple linear relationship between the average particle size and the photocatalytic degradation rate. The photocatalytic degradation rate of STOPEG2000-5 is the highest because of its small crystal size\(^{[12-14]}\). The specific surface area is large, and more active sites are reacted, thereby improving the photocatalytic activity.
activity. Although the average particle size of STOPEG4000-5 is larger than that of STOPEG1000-5, the degradation rate of the former is nearly 10% higher than that of the latter.

![Figure 6. Relationship between the particle size of STO and photocatalytic activity](image)

Some of the PEG is adsorbed on the surface of the strontium titanate crystal during the washing through the low-temperature precipitation method. In the subsequent calcination process, PEG evaporates at a high temperature, so there are many pores on the surface of the crystal, and the porous material is favorable for the improvement of photocatalytic performance. Since the addition of large polymerization degree PEG makes the pore density larger, STOPEG4000-5 has a higher average particle size than STOPEG1000-5, but the photocatalytic performance of the former is still better than the latter.

For the strontium titanate samples synthesized under different PEG concentrations, the same particle size and photocatalytic activity do not show a linear relationship. When the PEG concentration is large, the obtained strontium titanate powder has a large particle size, which is caused by the agglomeration of the strontium titanate grains from the bridging action of hydrogen bonds[15]. The agglomerated strontium titanate crystal grains have more pores, thus with better photocatalytic activity.

4. Conclusions

(1) A series of spherical and monodisperse strontium titanate powders were synthesized by low-temperature precipitation method using soluble polymer (PEG) as protective agent. The particle sizes were mainly distributed between 200 and 400 nm, rare for crystals smaller than 200 nm and larger than 400 nm. The strontium titanate powder synthesized by the method has good photocatalytic activity.

(2) As the concentration of polyethylene glycol increased, the particle size of the sample crystal increased after decrease. We briefly analyzed the factors affecting the particle size of strontium titanate powder by PEG concentration and degree of polymerization.

(3) Studies showed that PEG concentration and degree of polymerization were critical to the photocatalytic performance of the synthesized strontium titanate, which has been discussed in the work.

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