Electrospray Preparation and Microwave Absorption Properties of ATO Hollow Micro/Nanospheres

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Abstract. Sb\textsuperscript{3+}-doped SnO\textsubscript{2} (ATO) hollow micro/nanospheres were prepared through electrospray and calcination technique. The influences of the calcination temperatures (500\degree C, 600\degree C, 700\degree C) on the crystal structure, micromorphology and microwave absorbing property of the calcined products were characterized by means of XRD, FT-IR, SEM and vector network analyzer. The results showed that Sb\textsuperscript{3+}-doped SnCl\textsubscript{2}/PVP precursor polymer were smooth spheres with diameters of around 0.35-2.1\mu m. The pure rutile structure of SnO\textsubscript{2} formed at 500\degree C, and the Sb\textsuperscript{3+} entered the lattice of SnO\textsubscript{2}. When the calcination temperature is 500\degree C and 600\degree C, ATO micro/nanospheres appeared to be hollow structure, and the surface were made up of many small particles. When the calcination temperature is 700\degree C, the ATO grains grown up which contained in the micro/nanospheres, and lost the sphere morphology and presented the irregular granular forms. The microwave absorption properties of ATO hollow micro/nanospheres calcined at 600\degree C was the best as the matching thickness was 2mm. The minimum reflectivity can reach -32dB at 10.8GHz, and the frequency band with reflectivity less than -10dB was 9.8-12.2GHz. The minimum reflectivity of ATO hollow micro/nanospheres moved to a low frequency as the matching thickness increased. When the matching thickness was 3mm, the microwave absorption peaks were double, at which the frequency band with reflectivity less than -10dB was widen.

1. Introduction
At present, electromagnetic wave equipment in the frequency range of gigahertz (GHz) has been widely used in civil and military fields. In the civil field, an increasing number of electromagnetic wave devices not only pose a threat to human health, but also cause serious electromagnetic interference (EMI), electromagnetic compatibility (EMC)[1] and other problems. In the military field, stealth technology has become the most important and effective penetration technology means in the three-dimensional modern war integrating land, sea, and air, which is highly valued by the major military powers[2].

SnO\textsubscript{2} is widely studied in metal oxide semiconductor due to its high gap width (E\textsubscript{g}=3.6ev) and low price[3]. Researchers not only study its gas sensitivity and photocatalytic properties, but also develop its applications in new fields, such as electromagnetic wave absorption. In recent years, some literatures have reported that SnO\textsubscript{2}[4-5], antimony-doped SnO\textsubscript{2}[6] and SnO\textsubscript{2} composite materials[7], which are applied in the field of microwave absorption, all show good absorption performance. All these prove that SnO\textsubscript{2} is a kind of absorbing material with great research potential and value.

Wave-absorbing materials not only require strong absorption, but also have the characteristics of thin thickness, light weight and wide absorption frequency band [8-9]. Micro-nano hollow structural
materials have the advantages of ultra-high specific surface area and light weight, and have great potential application value in the field of high-performance absorbing materials. Therefore, in this paper, the precursor Sb$^{3+}$-doped SnCl$_2$/PVP polymer were prepared by electrospray, and the effect of calcination temperature on the microstructure of ATO was discussed, and the microwave absorbing properties of ATO micro/nanospheres were analyzed, which provide some experimental basis for the development of new microwave absorbing materials.

2. Experiment
SnCl$_2$·2H$_2$O and SbCl$_3$ are used for the preparation of ATO micro/nanospheres in accordance with the stoichiometry of n(Sn$^{4+}$):n(Sb$^{3+}$)=10:1 respectively. All the raw materials are dissolved in N,N-dimethyl formamide (DMF) and anhydrous ethanol, and stirred until they are completely dissolved. Add 1g DMF and 1g anhydrous ethanol to each 1mmol of raw material. Take one-third of the mixed solvent mass of polyethylene pyrrolidone (PVP) to the mixed solution and stir it fully, then the electronic spray precursor solution is made.

Electrospray refers to the phenomenon that conductive droplets can be sprayed at high speed under high voltage electrostatic field. The conditions of electrospray are at the voltage of 20kV, the needle of which is the 19G stainlower steel, and the distance between the needle and receiving plate is 20cm, the flow rate is 0.4~0.5mL·h$^{-1}$.

The Sb$^{3+}$-doped SnCl$_2$/PVP precursor polymer after drying are calcinated to 500°C, 600°C and 7000°C for 2h respectively, with the 100°C·min$^{-1}$ heating rate, and then furnace cooling to room temperature. The curves of calcination are shown in Figure 1.

Differential thermal-thermogravimetric analysis(SDT-Q600, America) is used to examine DSC-TGA. X-ray diffraction analysis (XD6, China) is used to examine the phases in samples. The infrared spectrograms of products are studied by using infrared spectrometer, IR (Nicolet-380, America). The morphologies of products are studied by using scanning electron microscopy, SEM (S-4800, Japan). Mix products and paraffin at the mass ratio of 2:1, and make the annular specimen with an outer diameter of 7mm, inner diameter of 3mm and thickness of 2mm by compression molding method. The electromagnetic parameters of annular specimens are studied using vector network analyzer (Agilent-N5242A, America), and the reflectivity curves are calculated by metlab 8 programming, and the microwave absorbing property is analyzed.

3. Results and discussion

3.1. Thermal decomposition process analysis of Sb$^{3+}$-doped SnCl$_2$/PVP polymer (DSC-TGA)
The DSC-TGA curves of Sb$^{3+}$ doped SnCl$_2$/PVP polymer are shown in Figure 2. As can be seen from the figure, the thermal decomposition of Sb$^{3+}$ doped SnCl$_2$/PVP polymer can be divided into three
stages. The first stage is when temperature is below 150°C, the weight loss rate is about 8.17%, which is due to the evaporation of the free water adsorbed on the surface of the polymer and residual solvent. The second stage is when the temperature is between 150~500°C, the weight loss rate is about 53.65%. This is mainly due to the decomposition of PVP and the conversion of SnCl₂ to SnO₂. When the temperature exceeds 500°C, TGA curve tends to level, and the weight loss rate does not change. It indicates that the thermal decomposition process of Sb³⁺ doped SnCl₂/PVP polymer is complete, and SnCl₂ is completely converted to SnO₂.

![Figure 2. TGA curves of Sb³⁺ doped SnCl₂/PVP polymer.](image)

3.2. Phase analysis of ATO hollow micro/nanospheres (XRD)

The XRD pattern of products calcinated at 500°C, 600°C and 700°C for 2h respectively at the heating rate of 100°C·min⁻¹ are shown in Figure 3. Compared with SnO₂ standard PDF card (PDF No: 52-0278), the diffraction peaks of all products obtained after calcination at 500°C and above are the same as the standard SnO₂'. This shows that the pure rutile structure of SnO₂ is all formed when Sb³⁺ doped SnCl₂/PVP polymer are calcinated at 500°C and above. This is consistent with the DSC-TGA analysis.

![Figure 3. XRD patterns of ATO calcined at different temperatures.](image)
The characteristic diffraction peaks of antimony oxide were not observed in the pattern, which may be Sb$^{3+}$ atoms entering into the lattice of SnO$_2$ to form the solid solution. With the increase of calcination temperature, the diffraction peak intensity gradually increases, and the peak shape narrows, which shows that the grain size of ATO increases with the crystallinity improving and the crystal structure being more complete.

3.3. Infrared spectroscopy analysis of ATO hollow micro/nanospheres (FT-IR)

In order to further characterize the structure of ATO, FT-IR is carried out to measure the products obtained after calcination at 500°C, as shown in Figure 4. It has obvious absorption peaks in the vicinity of 650 cm$^{-1}$. This absorption peak is characterized of SnO$_2$[10]. It is found in the infrared spectrum that the absorption peak of O-H stretching vibration that belongs to water molecules at about 3430 cm$^{-1}$ and 1640 cm$^{-1}$[11]. This is because the products have adsorption to the water in the air. And the absorption peak is because of the infrared light spreading in the air at 2360 cm$^{-1}$. Furthermore, it is found in the infrared spectrum that it has no other absorption peak in addition to all the above. So this shows that the metal salts and PVP have completely decomposed after calcination at 500°C, and target ATO is generated.

3.4. Micro morphology analysis of ATO hollow micro/nanospheres (SEM)

The SEM image of Sb$^{3+}$ doped SnCl$_2$/PVP polymer is shown in Figure 5. It is found that a great many of Sb$^{3+}$ doped SnCl$_2$/PVP polymer micro/nanospheres with smooth surface, no cracks and holes, average diameters of around 0.35~2.1 μm are prepared by employing electrospray technology.

Figure 6 shows the SEM images of products after being calcinated at 500°C, 600°C and 700°C respectively. As can be seen from the Figure 6(a) and (b), it is found that the products appeared to be a good spherical shape, and the surface are made up of many small particles after being calcined at 500°C and 600°C. It is show that the particles of the products grow up after being calcined at 600°C, which making the spherical surface denser than those after being calcined at 500°C. The products all have hollow structure and porous surface, most of products are open. According to Figure 6(c), with the increase of calcination temperature, the higher energy makes the "fusion", "swallow" function between the grains become more and more intense. Meanwhile, the higher energy and the faster rate of temperature rise make the PVP to break out of the ATO spheres more violently in the gaseous form. And it eventually loses the spherical morphology and presents the granular form after being calcined at 700°C.
3.5. Microwave absorption properties analysis of ATO hollow micro/nanospheres

The reflectivity of microwave absorbing materials is the comprehensive embodiment of electromagnetic characteristics, electromagnetic wave frequency, the thickness of absorbing coating and other factors[12]. Figure 7 shows the reflectivity of products obtained after calcination at 600°C at different thickness (2mm, 3mm, 4mm, 5mm), and vertical incidence of electromagnetic waves. It can be seen from the figure that when the sample thickness is 2mm or more, there are microwave absorption lower than -10dB in the range of lower than 12GHz. With the increase of the thickness, the position of the minimum reflectance absorption peak gradually moves to low frequency. For a specific monolayer material, the matching frequency ($f_m$) and the matching thickness ($d_m$) of the absorption
characteristic are known. Only when the working frequency and material thickness are all met, the absorption performance presents the best. When the working frequency and material thickness are deviation, the absorption performance will be reduced. When the product of \( f_c \) and \( d_c \) is to a certain value, it meets the impedance matching. Therefore, when the thickness of the material increases, its matching frequency is reduced, and the absorption peak moves to low frequency [13]. The matching thickness of ATO hollow micro/nanospheres is 2mm. The minimum reflectivity can reach -32dB at 10.8GHz, and the frequency band lower than -10dB is 9.8-12.2GHz. In addition, when the thickness is 3mm, the absorption peak lower than -10dB is two, which widens the absorption band.

The hollow structure of ATO hollow micro/nanospheres not only reduces the weight, but also enables more electromagnetic waves to enter the spherical cavity for multiple oscillations and losses. After the consumption of electromagnetic waves, there are still some reflection out, and then, it is into the adjacent spherical cavity continues to be lost, so electromagnetic waves are absorbed more.

![Figure 7. Reflectivity of ATO hollow micro/nanospheres at different thickness.](image)

4. Conclusions

The Sb\(^{3+}\) doped SnCl\(_2\)/PVP polymer with average diameters of around 0.35-2.1\( \mu \)m are fabricated through electrospray. the pure rutile structure of ATO are formed at 500°C and above.

It has a great effect of calcination temperature on the morphology of ATO. When the calcination temperature is 500°C and 600°C, ATO micro/nanospheres appeared to be hollow structure and porous surface and the surface were made up of many small particles. When the calcination temperature is 700°C, the ATO grains grown up which contained in the micro/nanospheres, and lost the sphere morphology and presented the irregular granular forms.

ATO hollow micro/nanospheres are an excellent absorber with light weight and high absorption intensity. The matching thickness of ATO hollow micro/nanospheres is 2mm, at which the microwave absorption properties are fine. The minimum reflectivity can reach -32dB at 10.8GHz, and the frequency band lower than -10dB is 9.8-12.2GHz. This study provides some experimental basis for the development of new microwave absorbing materials with the properties of "thin, wide, light and strong".

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