Study on Hollow Silica Nanoparticle Composite Materials and Their Dielectric Properties

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Abstract

Hollow particles have attracted much attention because of their low dielectric constant. Compared with large-sized hollow particles, there are still many problems in applying nano-sized hollow particles in low dielectric materials. In this work, the shell structure and the effect of water content on the dielectric properties of hollow silica nanoparticles (HSNPs) were studied. HSNPs with different shell structures were synthesized to discuss the structural changes affecting dielectric properties. HSNPs with large differences in water adsorption were synthesized, and the effect of water absorption on dielectric properties was evaluated. Additionally, the influence of surface roughness on dielectric measurements was considered, leading to a new approach to characterizing material surfaces. This study provides valuable insights into advancing nano-sized hollow particle materials in future electronic applications.

Keywords: hollow nanoparticles, silica, composite, dielectric properties.

1. Introduction

The development direction of the communication and semiconductor industries, such as 6G communication, features high-frequency and high-rate signal transmission. However, signal transmission loss and heating problems under high frequency need to be solved urgently. Many studies have shown that the dielectric constant and dielectric loss of materials are important factors affecting the signal transmission speed and heating loss under high frequency[1]. Low dielectric constant and low dielectric loss materials can solve the above problems.

At present, low dielectric constant materials can be mainly divided into three types: fluorine-containing materials, non-fluorine-containing materials, and porous materials. As the element with the strongest electronegativity, fluorine has a very low polarity, and fluorine-containing materials are considered one of the ideal choices for preparing low dielectric constant materials. However, since organic fluoride (PFAS) is almost unavoidable in its preparation process, such materials are extremely difficult to degrade and have cumulative biological toxicity, greatly limiting their application[2].

Hollow particles have the characteristics of low density, low thermal conductivity, high specific surface area, and so on[3, 4]. Hollow particles can achieve a lower dielectric constant without involving fluorine in manufacturing. Therefore, hollow particle composites have attracted attention as a more ideal technical route. There have been many studies on hollow particle low dielectric constant materials, and some results have been achieved[5, 6]. Till now, most of the current research has focused on Micro-sized hollow particles[7]; nano-sized hollow particle composite low dielectric materials have the features of good performance uniformity and lower theoretical dielectric constant, which are the future development direction. However, many problems remain in the low dielectric constant research of nano-sized hollow particles. such as poor reproducibility of results and inconsistency between results and theoretical calculations. The reason may be due to the structure of the nanoparticles themselves and the interface characteristics. Therefore, in this work, we discuss the influence of the structure of hollow silica nanoparticles (HSNPs) on the dielectric properties.

2. Effect of the shell structure of hollow silica nanoparticles on the dielectric constant

The shell structure of HNSPs can be the main factor influencing dielectric properties. Therefore, HSNPs with different shell structures were synthesized by template method, and the schematic diagram is shown in **Fig.1**. The template particles were coated with tetraethoxysilane (TEOS) to form silica shells. After dissolving the internal $CaCO_3$ with hydrochloric acid,

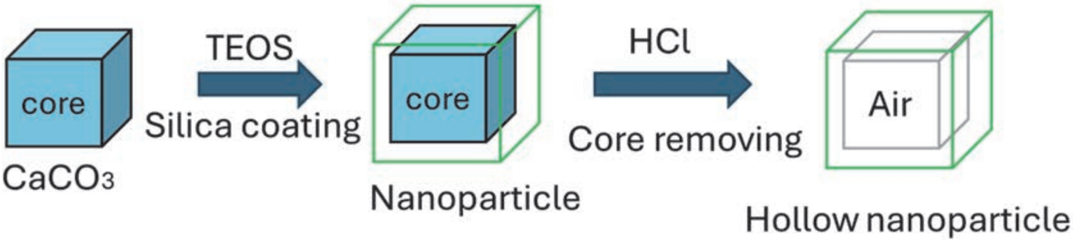

Fig.1 Fabrication process of Hollow silica nanoparticles (HSNP).

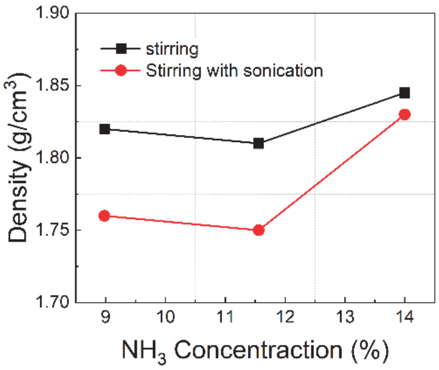

Fig.2 Effect of ultrasonic irradiation on the density of hollow particle shells density of hollow particle shells. *(J. Soc. Powder Technol., Japan*, 61 (2024) 672-679

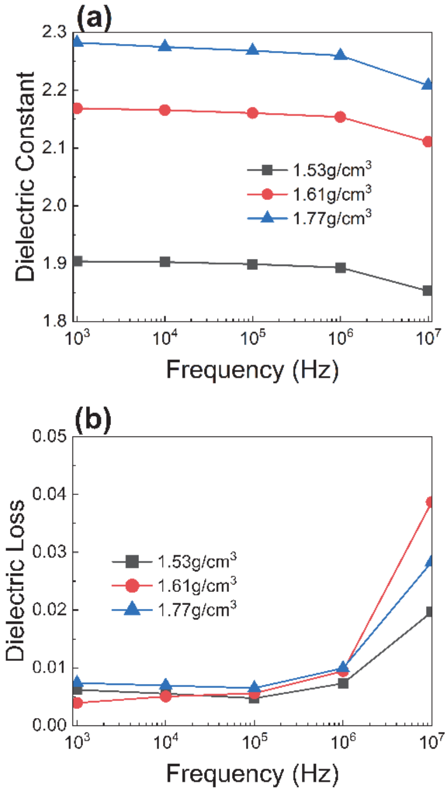

Fig.3 (a) The dielectric constant of HSNP/PI composite films with varying shell densities. (b) The dielectric loss of HSNP/PI composite films with varying shell densities.*J. Soc. Powder Technol., Japan*, 61 (2024) 672-679

the HSNPs were washed with water and alcohol. The shell density of HSNPs was changed by using ultrasonic irradiation during silica polymerization, while the TEOS amount controlled shell thickness. **Fig.2** shows shell density measurements of the synthesized particles using the Helium displacement method. HSNP made with ultrasonic irradiation and stirring had a higher density than those made with stirring only, indicating that ultrasonic irradiation increases shell density. During the hydrolysis and condensation of TEOS, ultrasonic waves create micro-jets that break unstable chemical bonds. This increases cross-linking and forms a stronger, denser shell[8].

Fig.3 shows the dielectric constant and dielectric loss of composite films with different HSNP shell densities. Due to the decrease in the shell density of HSNP, the atomic density and -OH group density of the HSNPs shell are reduced, thereby reducing the electronic polarization density and dipole polarization density of the material, reducing the dielectric constant and dielectric loss of HSNP[9, 10].

Fig.4 shows the dielectric constant and dielectric loss of HSNP/PI composite films with varying HSNP shell thickness. As the shell thickness decreases, the dielectric constant decreases. Thinner shells reduce the silica volume ratio and increase the air content of HNSP, likely lowering the dielectric constant. Hydrogen bonds between silica -OH groups and PI of C=O groups may restrict polymer chain vibration, reducing molecular motion in high-frequency electric fields and lowering dielectric loss.

3. Effect of adsorbed water of hollow silica nanoparticles on dielectric properties

HSNPs have a higher specific surface area than large-sized particles, and their adsorption properties are significantly improved. For silica nanoparticles, especially hollow particles, the hydroxyl groups on their surface will adsorb more water molecules, considerably increasing the dielectric properties. In previous testing, the dielectric properties of HSNP/PI composites can be influenced by water molecules in the air. This is because the dielectric constant of water (about 80) is much higher than that of silica (4.2) or polyimide (4.0), making even small amounts of water significantly affect the dielectric constant. Therefore, it is crucial to study the impact of hygroscopicity on material properties. In this work, HSNPs with multi-layer shell structures were prepared using the Polyacrylic acid (PAA) template method, which was used to prepare hollow particles with significant differences in water absorption characteristics to study the effect of water on the dielectric properties of materials. **Fig.5** shows TEM and EDS images of the HSNPs. After washing, the distribution of carbon changed, indicating a shift in the PAA distribution. Part of the PAA from inside the particles moved to the silica shell's outer surface, forming a PAA/SiO_2/PAA structure, as illustrated in **Fig.6**.

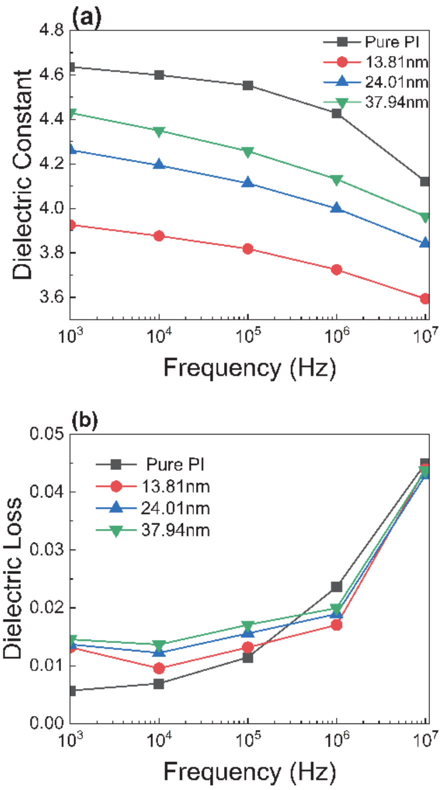

Fig.4 (a) The dielectric constant of HSNP/PI composite films with different HSNP shell thickness. (b) The dielectric loss of HSNP/PI composite films with different HSNP shell thickness.(*Adv. Powder Technol.*, 36 (2025) 104854)

Fig.7 compares the changes in water vapor adsorption capacity under different hollow particle shell structures. The water sorption capacity of nanoparticles with PAA is much higher than that of silica hollow particles due to PAA's hydrophilic -COOH groups, which adsorb more water molecules[11]. Additionally, water molecules are absorbed between the PAA molecular chains, further increasing water absorption. As a result, the water sorption ability of PAA composite hollow silica nanoparticles is enhanced[12].As the water content in the particles increases, the degree of polarization and dielectric relaxation in the alternating electric field will also increase. Therefore, the dielectric constant and

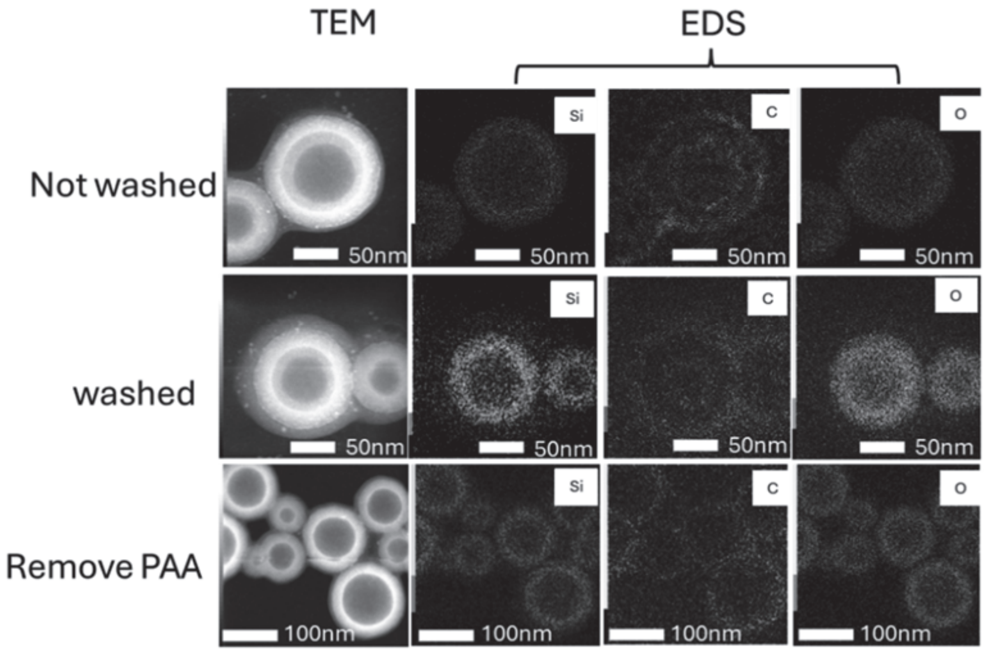

Fig.5 The transmission electron microscope (TEM) images and Energy spectrum scanning mapping (EDS) of HNSP contain various PAA contents.(*Coatings*, 14 (2024) 829.)

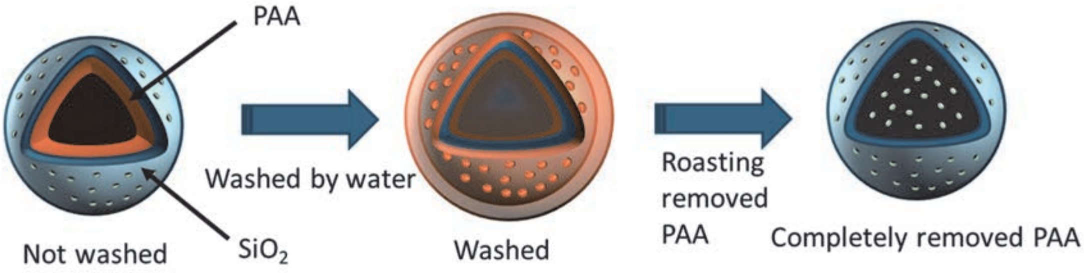

Fig.6 Shell Structural change diagram of composite hollow silica nanoparticles (*Coatings*, 14 (2024) 829.)

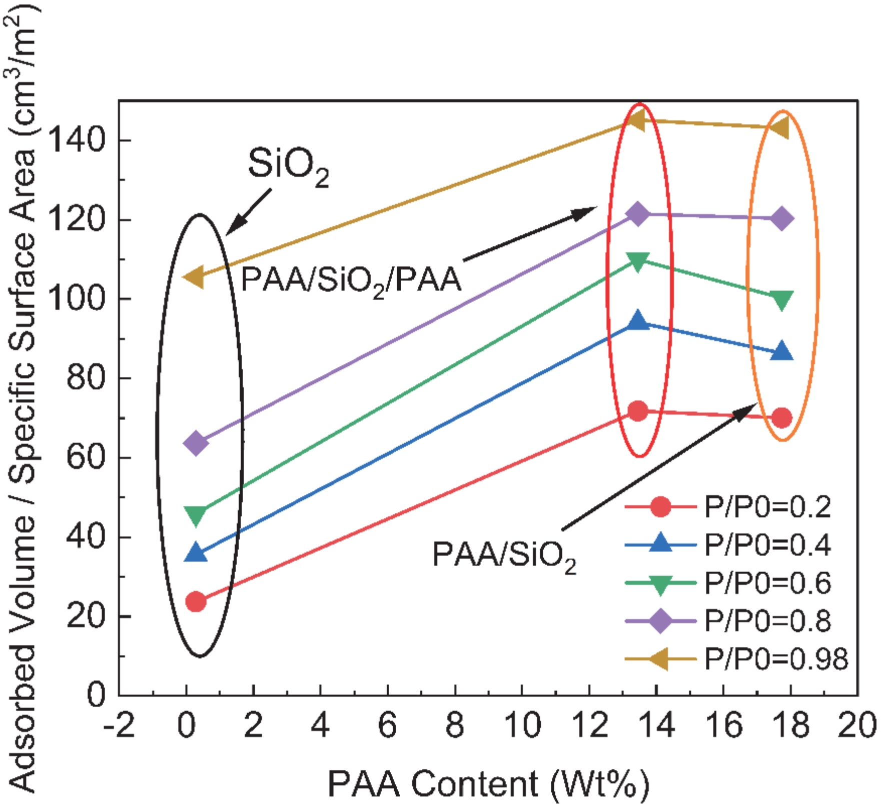

Fig.7 Comparison of water vapor adsorption capacity in different shell structures of hollow nanoparticles (SiO_2, SiO_2/PAA, and PAA/SiO_2/ PAA). (*Coatings*, 14 (2024) 829.)

dielectric loss of the composite particles and their resin composite films will increase[13]. These findings can be found in **Fig. 8**.

4. Determination method of the dielectric constant of the concave-convex surface of nanoparticle composite film

In the dielectric constant measurement, the test data often fluctuates. After repeated confirmation, we inferred that this was caused by the unevenness of the test sample surface. When HSNP is dispersed in PI, due to the agglomeration of HSNPs, it will cause agglomeration protrusions on the material surface, which will affect the final dielectric constant test results. To verify our expectation, composite films with subtle surface variations were prepared by modifying the surface of solid silica nanoparticles (OX50) and adjusting their dispersibility in a polyimide matrix. The dispersion state of the particles is regulated by adjusting the density of the particle surface modification group (3-Aminopropyl) triethoxysilane (APTES) and controlling the agglomeration size of the particles in polyimide. The preparation process is shown in **Fig. 9**.

Fig.10 shows SEM images of the films, revealing reduced particle agglomeration after modification. As the modifier content increases, particle dispersion improves, consistent with laser microscope observations. EDS mapping of Si elemental further confirms better particle distribution and reduced agglomeration, aligning with the SEM results.

Fig.11(a) shows the effect of the particle dispersion state on the dielectric constant. As the degree of particle

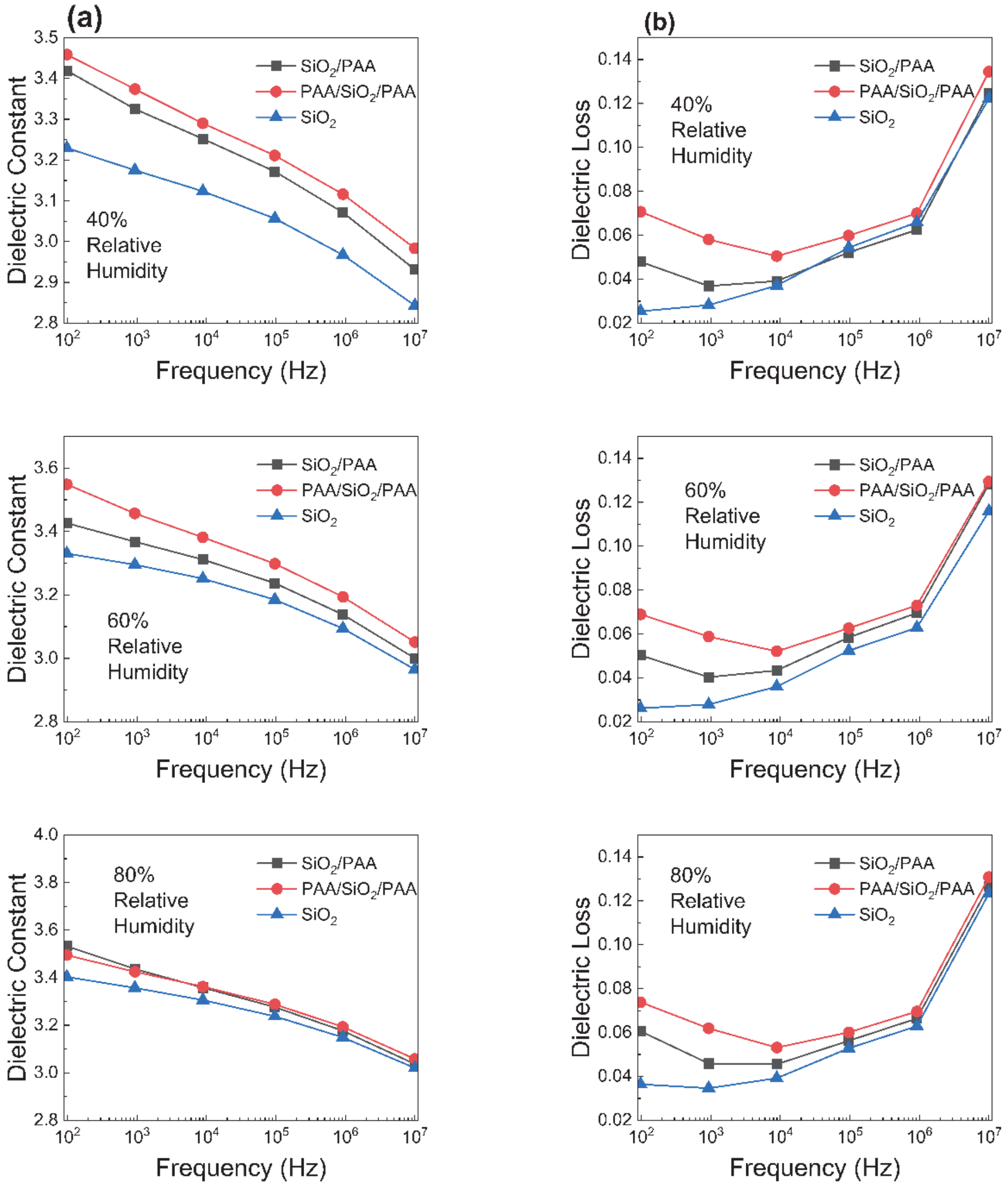

Fig.8 (a)The dielectric constants of HSNP composite films with different shell structures. (b)The dielectric loss of HSNP composite films with different structures.

modification increases, agglomeration in the matrix decreases, and the size of protrusions on the material surface decreases, resulting in a smoother composite surface. This reduces the void volume between the electrode and the sample (shown in **Fig. 11(b)**), resulting in a higher measured dielectric constant.

As a result, it can be determined that the subtle concave and convex state of the sample surface will significantly impact the dielectric constant test results. At the same time, this relationship between the dielectric constant and the particle surface can be used as a new test method to characterize the subtle differences in the material surface.

5. Conclusions

In this study, the shell structure of HSNPs and the effect of the hygroscopicity of HSNPs on the dielectric properties were clarified. The shell structure of HSNP significantly influences the dielectric constant. Lowering the shell density or thickness can reduce the dielectric constant. The adsorbed water of HSNPs also significantly affects their dielectric constant and dielectric loss.

Reducing the adsorbed water of HSNPs can significantly reduce their dielectric loss. In addition, the relationship between the roughness of the material and the dielectric constant test result is established. Based on this model, the evaluating method of the material surface smoothness by using the dielectric constant is proposed These findings provide technical guidance for applying

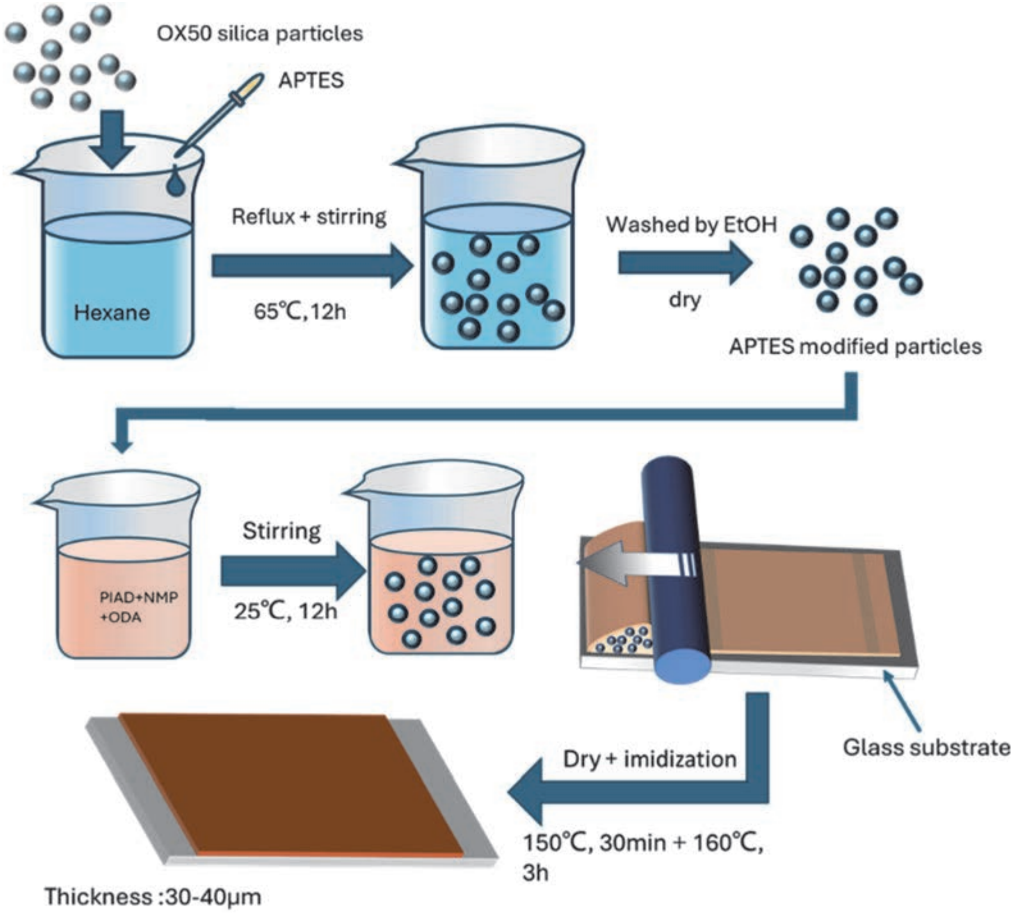

Fig.9 Diagram of silica nanoparticle /PI composite film

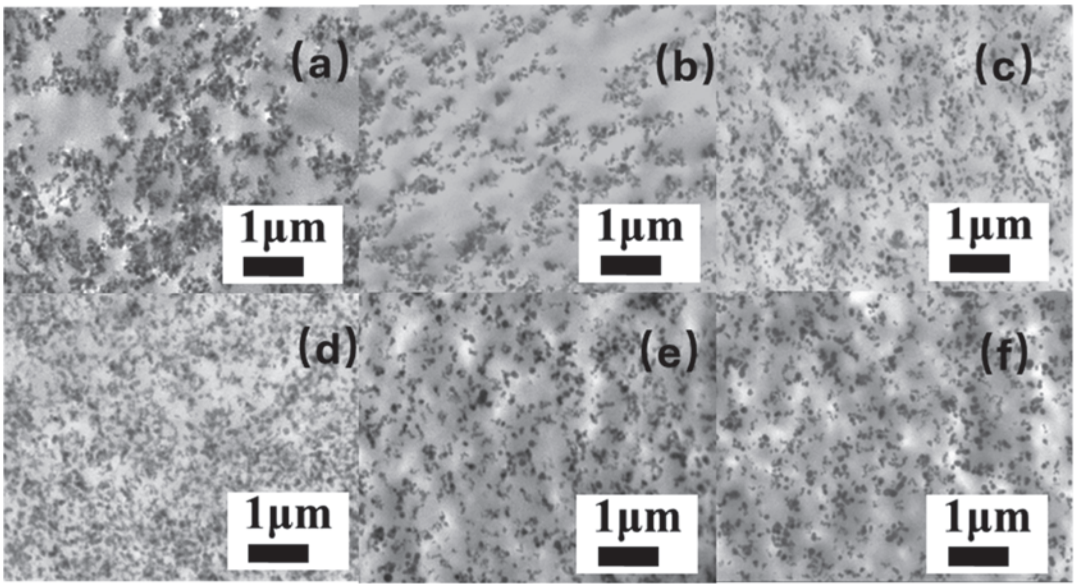

Fig.10 The Scanning electron microscope (SEM) images of silica nanoparticle/PI composite film of which the modifier content of the particle is (a = 0, b = 0.005, c = 0.01, d = 0.02, e = 0.04, f = 0.08ml/g)

nano-size hollow particle materials in low-dielectric materials.

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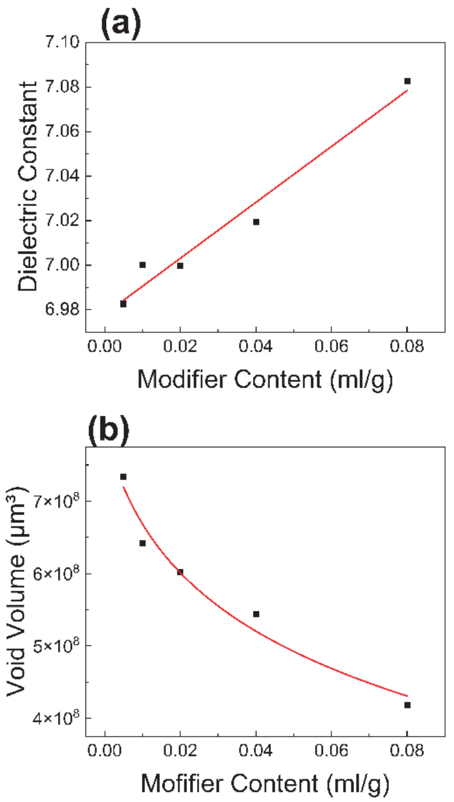

Fig.11 (a) The dielectric constant of polyimide composite films made by particles with different modifier contents (at 100KHz). (b) Measurement results of void volume between the polyimide composite films and electrode. (Reprinted from Surface Engineering 38 (2022) 789-796. Copyright © 2025 Sage Publication)

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