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Investigation of solution processable albumen–$BaTiO_3$ nanocomposite and its application in high-*k* films

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ABSTRACT

Albumen and $BaTiO_3$ nanoparticles are employed to make solution processable nanocomposite for high permittivity films. The nanoparticles are modified with poly(acrylic acid) molecules to achieve homogeneous dispersion in albumen aqueous solution and made into films by drop casting. The dielectric constant and loss tangent of albumen–$BaTiO_3$ nanocomposites are investigated as the function of volume fraction of $BaTiO_3$. The nanocomposites exhibit maximum relative permittivity of 52 and good dielectric stability over a wide range of frequency, while the loss tangent is below 0.05 even at high $BaTiO_3$ loading of 80 vol%. The dielectric constants of nanocomposites with lower volume fractions (<41 vol%) are in good agreement with the Lichtenecker-Logarithmic model.

1. Introduction

Solution processable and printable electronic materials are undergoing rapid development in recent years due to its potential applications in large area, flexible and low cost electronics compared to traditional silicon-based electronics. As one of the most important constituents in the family of printable electronic materials, solution processable high-*k* dielectric materials have attracted much attention because there are not many suitable materials available [1]. Among the few materials that have been developed, polymer–nanoparticle composites have emerged as the favorite because of their high dielectric constant, good mechanical properties and solution processability at ambient temperature and pressures [2,3]. Extensive work has been reported on high permittivity polymer nanocomposites formed from traditional synthetic polymer such as poly(methyl methacrylate) [2], poly(4-vinylphenol) [4], polystyrene [5], polyetherimide [6], poly(vinylidene fluoride) [7], and poly(vinyl alcohol) [8].

To increase the dielectric constant of a polymer–nanoparticle composite, the normal strategy is to increase the volume ratio of nanoparticles which are of high dielectric constant. However, one issue for such a strategy is the increased leakage current compared to pure polymer film. The other issue is the difficulty to obtain homogeneous dispersion of high volume content of nanoparticles which act as fillers in a polymer matrix [1].

In a nanocomposite, polymer usually occupies the majority of the volume, which has a great influence on its permittivity. For example, according to the Lichtenecker mixture law (Eq. (1)) [9], permittivity of the nanocomposite with 30% volume ratio of nanoparticular filler will increase 30% if the dielectric constant of polymer matrix changes from 4 to 6. However, very few work were reported in the direction of improving permittivity through using higher *k* polymers, partly because it is not easy to alter the permittivity of most synthetic polymers [10].

In this work, albumen, which is known to have high dielectric constant [11,12], is selected as the polymer host and $BaTiO_3$ nanoparticles are employed as the inorganic filler to form solution processable nanocomposite which is then applied to make high-*k* dielectric films. The $BaTiO_3$ nanoparticles are functionalized with poly(acrylic acid) molecules to ensure their proper dispersion and good stability in albumen aqueous solution. Thin films have been deposited by drop-casting the solution form of albumen–$BaTiO_3$ nanocomposite on ITO glass substrates and their dielectric properties versus frequency and volume ratio of $BaTiO_3$ nanoparticles have been investigated. It is found that the permittivity of nanocomposite films increases with the increase of $BaTiO_3$ and reaches maximum of 52 at the $BaTiO_3$ content of 80 vol%, while the loss tangent is maintained at about 0.05.

2. Experimental

2.1. Materials

$BaTiO_3$ with an average size of 70–90 nm is purchased from Alfa-Aesar. Albumen is taken from ordinary chicken eggs.

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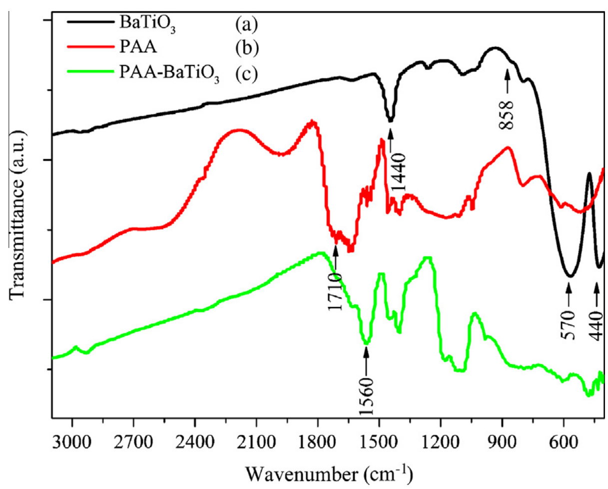

Fig. 1. FT-IR spectra of (a) pure $BaTiO_3$, (b) pure PAA and (c) PAA–$BaTiO_3$.

Poly(acrylic acid) (PAA, Mw ≈ 3000) is purchased from Aladdin-Reagent. All other solvents are analytical grade and used without further purification. The substrate on which thin films are deposited is ITO-coated glass slides which are ultrasonic cleaned in acetone, isopropyl alcohol and deionized water, and then exposed to oxygen plasma for 2 min prior to use.

2.2. Preparation of albumen–$BaTiO_3$ nanocomposite films

0.4 g PAA and 0.4 g ammonium hydroxide (ca. 25 wt%) dissolved in 1 mL water is added to $BaTiO_3$ nanoparticle aqueous dispersion (0.2 g/5 mL). The mixture is ultrasonic treated for 10 min and stirred at 95 °C for 3 h. The PAA-modified $BaTiO_3$ particles are separated by centrifugation and washed with dilute ammonia solution (pH ≈ 9.4) alternately. The washed precipitate is dispersed into ammonia solution (pH ≈ 9.4) with the assistance of ultrasonication. The original albumen aqueous solution (ca. 12.8 wt%) from chicken eggs is stirred for 2 h at 20 °C, and then the precipitate in the albumen is isolated by centrifugation (8000 rpm for 10 min below 15 °C). Aqueous solution with 5 wt% PAA–$BaTiO_3$ is added into 1.6 wt% albumen aqueous solution with vigorous stirring and a few seconds of ultrasonication to obtain homogeneous suspension. The resultant suspension is drop-casted on a clean ITO glass and then heated at 100, 120, 140 °C for 10 min in turns. Finally, the films are cooled down to room temperature naturally. A series of nanocomposite films with different $BaTiO_3$ contents (80, 56, 41, 34, 25 and 13 vol%) are prepared.

2.3. Characterization

The Fourier transform infrared (FTIR) spectra of the $BaTiO_3$, PAA and PAA–$BaTiO_3$ are recorded on FTIR spectroscopy (Nicolet NEXUS 6700), after the samples are prepared in the pellet form by mixing the powder with KBr (Aldrich, 99%, FTIR grade). The $BaTiO_3$ nanoparticles are characterized using transmission electron microscopy (TEM; HRTEM, FEI Tecnai G2 S-twin) for particle sizes. The colloidal stability of the $BaTiO_3$, nanoparticles is characterized using Zeta-potential measurements and dynamic light scattering (Malvern zeta meter, Nano ZS).

The cross-sectional morphology of albumen–$BaTiO_3$ films is observed using scanning electron microscopy (SEM, Hitachi S-4800). Dimension 3100 AFM (Veeco, CA, USA) was used in AFM imaging. For dielectric analysis, the top electrodes are prepared using silver paste. The measurements are carried out in the frequency range of 10 kHz to 10 MHz at room temperature, using Keithley Instruments Model 4200 Capacitance Voltage Unit. The permittivity of the samples is calculated from the capacitances, thicknesses and the top electrode areas. Step profiler (Veeco, Dektak 150) is used to measure the thicknesses of the composite films. At least seven individual measurements are carried out to determine the dielectric parameters of the composite films.

3. Results and discussion

The surface chemistry of $BaTiO_3$ nanoparticles with and without PAA treatment are characterized by FT-IR spectra and compared in Fig. 1. The bands at ca. 570 and ca. 440 cm^{-1} are the absorption of the Ti—O vibration modes in the $BaTiO_3$ compound [3,13]. The peaks around 1440 and 858 cm^{-1} are assigned to C=O stretching and out of plane deformation of CO_3^{2-}, respectively [14–16]. The strong absorption peak at 1710 cm^{-1} is ascribed to the free C=O stretching vibration in the PAA spectrum (Fig. 1b). For surface-modified $BaTiO_3$ nanoparticles by the PAA, the prominent peak at 1710 cm^{-1} disappeared, and a new peak at 1560 cm^{-1} which is attributed to anti-symmetric stretching vibrations of COO—Ba appeared (Fig. 1c). These results clearly confirm that the PAA are not physically but chemically bonded to the surfaces of the $BaTiO_3$ nanoparticles, through the formation of a carboxylic acid–metal salt structure [17,18].

The PAA-modified $BaTiO_3$ nanoparticles dispersed in the aqueous solution have an average particle size of 70–90 nm as seen from Fig. 2, which is close to the primary nanoparticle size (Fig. 2b). The zeta potential of PAA-modified $BaTiO_3$ nanoparticles dispersion liquid is −37 mV. In contrast, the unmodified nanoparticles aggregate too quickly to measure the zeta potential and DLS

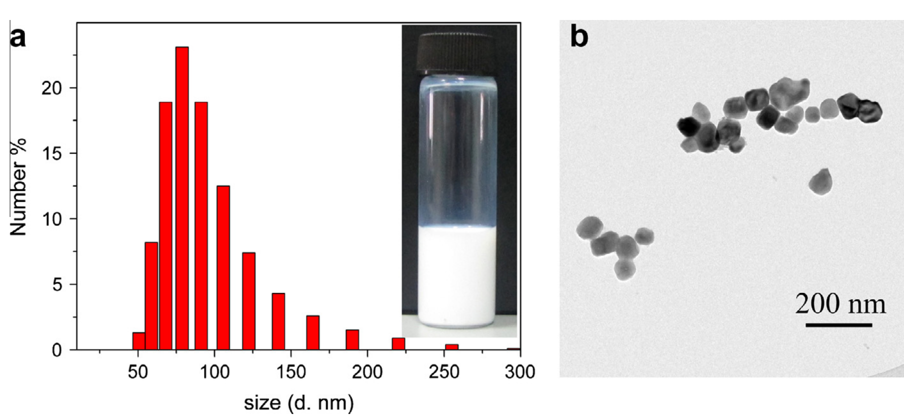

Fig. 2. (a) DLS size distribution of PAA-modified $BaTiO_3$ nanoparticles, the insert is the photo of the PAA-modified $BaTiO_3$ aqueous solution and (b) the TEM image of raw $BaTiO_3$ nanoparticles.