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Original Article

# Exciting low-field dielectric tunability in clamshell

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ABSTRACT

The dielectric properties and dielectric tunability of the nacreous part of the clamshell were investigated. Microstructure characterizations reveal that the sample shows a "brick-and-mortar" structure composed of aragonitic $CaCO_3$ regions and bimacromolecule regions separated by transition regions consisting of crystalline particles surrounded by amorphous area. A ferroelectric-like dielectric tunability behavior was observed and an exciting dielectric tunability of 79% was achieved at 400 °C and 500 Hz within a small field increment of 34 V/cm. Such a low field scale for dielectric tunability near 80% rivals all known tunable dielectrics. Both thermally and electrically activated hopping motion of oxygen vacancies in the multilayered structures of the clamshell leads to the exciting low-field dielectric tunability. Our results dramatically expand the dielectric tunable materials and offer a facile way to achieve superior dielectric tunability in bio-multilayered materials.

## 1. Introduction

Nonlinear dielectric materials (NDMs) characterized by the strong dependence of permittivity on the applied dc electric field have attracted tremendous interest due to their potential applications in electrically tunable microwave devices [1–4]. Ferroelectric materials due to their reversible polarization are the most important and widely investigated NDMs. However, most of the ferroelectric NDMs showing high tunability are lead-based ones and their high tunability requires a large dc electric field in the order of $10^3$–$10^6$ V/cm [5–8]. These shortcomings strongly stymie their practical applications. In this case, researchers turn to search for non-ferroelectric NDMs [9–12]. It had been reported that different causes, such as Maxwell-Wagner (MW) relaxation [9], Langevin effect [13], percolation threshold model [14], charge ordering or so-called electronic ferroelectricity [15,16], etc., that can contribute to the dielectric tunability in non-ferroelectric NDMs. Among these causes, the MW relaxation is associated with Schottky barrier that can be easily depressed by a small dc bias [17] giving rise to superior nonlinear dielectric property of the tested sample. Appealing dielectric tunability caused by MW relaxation can be achieved at a low field in the order of $10^2$ V/cm [10]. Since the MW relaxation is associated with interfaces between two layers with different conductivities and dielectric constants, this provides heuristic hint to improve dielectric tunability in multilayered thin film system. Earlier theoretical [18,19] and experimental [20,21] studies had truly revealed high dielectric constant and excellent dielectric tunability in $BaTiO_3/SrTiO_3$ superlattice. In recent years, tunable ferroelectricity was even reported in artificial tri-layer supperlattices comprised of non-ferroic components [22] and excellent micro-wave dielectric tunability was reported in Ruddlesden-Popper $Sr_{n+1}Ti_nO_{3n+1}$ films [23].

The above fact underscores the vital role of interfaces on the dielectric tunability in multilayered films. Compared to the artificial structures, biomaterials (suck as nacre, wood, and bone) possess intrinsic hierarchically layered architecture after the lengthy natural evolution. This architecture renders the biomaterials a remarkable mechanical strength and toughness [24] and triggers a burst of biomimetic designs [25]. Here, we reported on the dielectric properties of clamshell. Exciting dielectric tunability was achieved in the order of tens of V/cm, which rivals all known tunable dielectrics.

## 2. Experimental details

The clam was achieved from Chaohu, Anhui province. Nacreous part of the clamshell was used as samples. Phase purity of the sample was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer (Rigaku Smartlab Beijing Co, Beijing, China) with Cu *Kα* radiation. Thermogravimetry (TG, STA449F3, Germany Netzsch Corporation, Selb, Germany) measurement was employed to detect the decomposition temperature of the clamshell. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo-Fisher ESCALAB 250Xi

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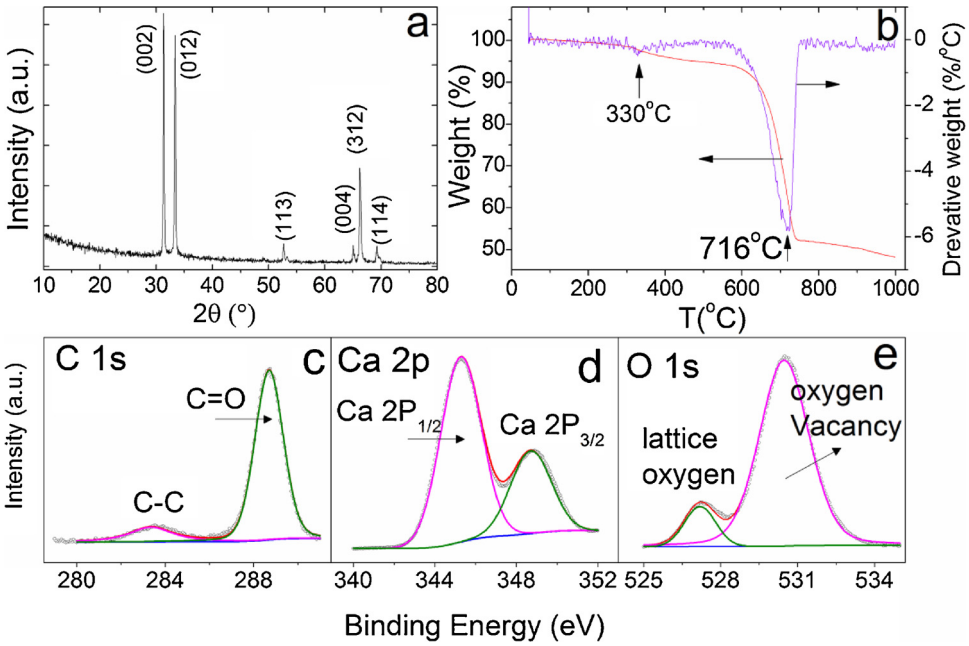


**Fig. 1.** (**a**) XRD pattern of the clamshell sample obtained at room temperature. (**b**) TGA mass loss and corresponding derivative mass loss curves of the sample. (**c-e**) High-resolution XPS spectra of C 1 s (**c**), Ca 2p (**d**), and O1 s (**e**).

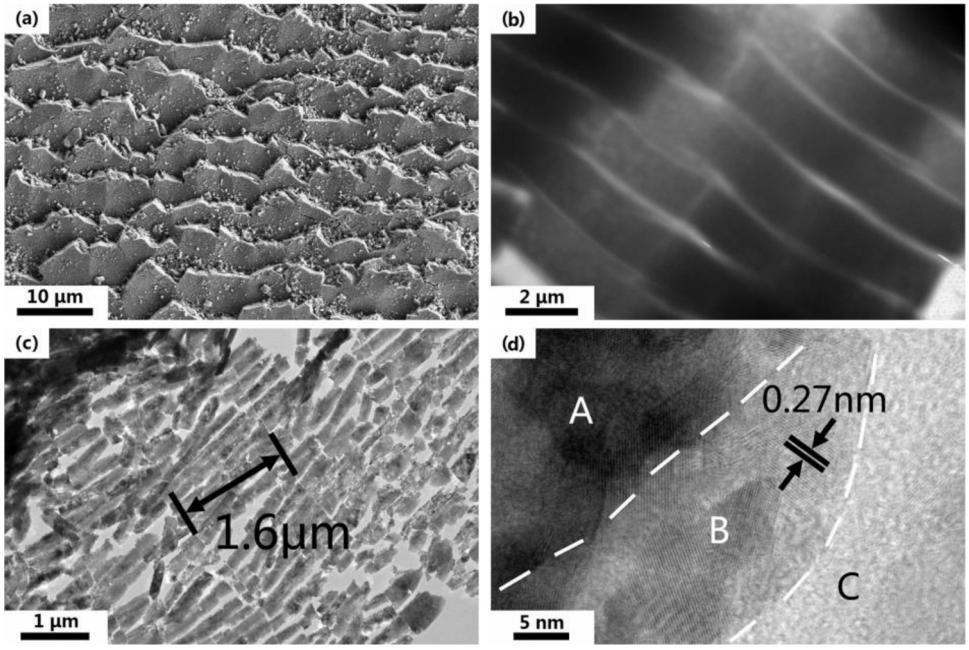


**Fig. 2.** (**a**) SEM image of the sample. (**b**,**c**) TEM images of the layered structure with different resolutions. (**d**) High-resolution TEM image of the interface between two layers.

using using mono Al Kα source with 1486.6 eV exciting energy and 650 μm spot size. The morphology of the sample was examined by a scanning electron microscope (SEM, HITACHI S4800) and a transmission electron microscope (TEM, JEOL JEM-2100) with an acceleration voltage of 200 kV. Dielectric properties were measured using a Wayne Kerr 6500B precise impedance analyzer (Wayne Kerr Electronic Instrument Co., Shenzhen, China) with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Partulab Co., Wuhan, China). The amplitude of ac measuring signal was 100 mV rms. Electrodes were made by printing silver paste on both sides of the disk-type samples.

## 3. Results and discussion

### 3.1. XRD, thermal, and XPS experiments

Fig. 1(a) shows the XRD pattern of the sample, the diffraction peaks are in good agreement with JCPDF Card: No. 41-1457. The calculated lattice parameters of $a = 4.962$ nm, $b = 7.968$ nm, $c = 5.744$ nm. The results of thermal measurement presented in Fig. 1(b) reveal two-setp mass losses: a weak mass loss of ~ 3% in the temperature range of 320 to 500 °C and a remarkable mass loss of ~ 41% from 560 to 745 °C. The first one was reported to be due to the desorption of the structural water, while the latter one was caused by the decarbonation of $CaCO_3$