High permittivity polymer embedded with Co/ZnO core/shell nanoparticles modified by organophosphorus acid

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The Co/ZnO core/shell nanoparticles-filled polymer poly(vinylidene fluoride) (PVDF)-based composites (0-3 connectivity) are fabricated, in which the core/shell structure for preventing Co particles from agglomeration is prepared by a simple wet chemistry procedure. At the same time, the N,N-di(phosphonomethyl)iminoacetic acid (DPMIAA) is used to modify the core/shell surface. High dielectric permittivity and low leakage current are achieved for the DPMIAA-modified Co/ZnO core/shell nanoparticle-PVDF composite, which shows good homogeneity, no cracks, and fine mechanical flexibility. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2819089]

Ferroelectric polymers, such as poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene [P(VDF-TrFE)], have been intensively studied for their applications in transducers, capacitors, etc.[1–4] Polymers are flexible, easy to process with low temperature, and possess high dielectric breakdown field and low leakage current.[4] However, the dielectric permittivity is usually lower than ten at room temperature.[5] Raising the dielectric permittivity of PVDF-based polymer is a key issue while retaining the low leakage current. Particulate-filled (0-3 connectivity) polymer-based nanocomposites have been widely studied due to their easy fabrication process and low cost.[6–8] Firstly, much work was done on nanocomposites of polymer and ferroelectric nanoparticles.[8] However, usually high volume ($>50\%$) nanoparticles will be incorporated in order to achieve high dielectric permittivity, thus deteriorating the mechanical quality.[9] Secondly, high permittivity polymer can also be fabricated using conductive fillers (e.g., metal particles).[7–9] Nevertheless, the as-prepared composites have large leakage current due to aggregation of the conductive particles. In order to avoid such aggregation, an insulator/semiconductor barrier layer of high resistivity is desired to prevent the conductive particles from connecting with each other.[10] On the other hand, the simple solution incorporation of nanoparticles in a polymer matrix generally leads to poor quality because of the poor interfaces between the particles and matrix and also leads to the inhomogeneity or cracks. It is thus preferred to modify the surface of nanoparticles so that they can be homogenously distributed in the polymer matrix.[6,11–13] A good dispersion of ceramic fillers in epoxy matrix using a phosphate ester as the surfactant was achieved by Rao and Wong[7] while Kim *et al.* employed {2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphonic acid and pentafluorobenzyl phosphonic acid to modify BaTiO$_3$ nanoparticles and obtain high dielectric permittivity of up to 40.[14] It is believed that some surfactants, such as phosphate esters and oligomers thereof, can improve the dispersion of nanoparticles in host polymers and, consequently, the overall quality of the nanocomposite.

In this paper, we report the synthesis of PVDF polymer filled with randomly dispersed Co/ZnO core/shell nanoparticles, i.e., the Co/ZnO core/shell-PVDF composites. The Co cores are coated with ZnO shells in order to avoid the Co particle agglomeration. The phosphonic acid ligands are used to modify robustly the ZnO shell surface. We will report the preparation of homogenously dispersed and noncracked Co/ZnO-PVDF composites with high dielectric permittivity and low leakage current.

The Co/ZnO core/shell nanoparticles of average diameter of 100 nm were synthesized by a simple wet chemistry procedure.[15] In a typical experiment, 0.05 mol CoCl$_2$·6H$_2$O and 0.075 mol citric acid monohydrate were dissolved in 100 ml absolute ethanol. After stirring at 60 °C for 6 h, Zn(NO$_3$)$_2$·6H$_2$O was added and the solution was stirred for another 2 h. Subsequently, with the evaporation of ethanol at 80 °C and heating of the residual at 350 °C in air for 3 h, then the xerogel was reduced in H$_2$ at 450 °C for 4 h. Figure 1(a) shows the phase identification by x-ray powder diffraction (XRD), indicating perfect lines corresponding to Co and wurtzite ZnO. The morphology of the Co/ZnO core/shell nanoparticles was examined by transmission electron microscopy (TEM), as shown in Fig. 1(b). Clear and high contrast between the Co cores and ZnO shells is seen and the shell is of ~15 nm thick.

The N,N-di(phosphonomethyl)iminoacetic acid (DPMIAA) (phosphonic ligand) with the 95/5 V/V ethanol/H$_2$O mixture as solvent was mixed with Co/ZnO nanoparticles (0.5 mmol ligand/g Co/ZnO) in the standard
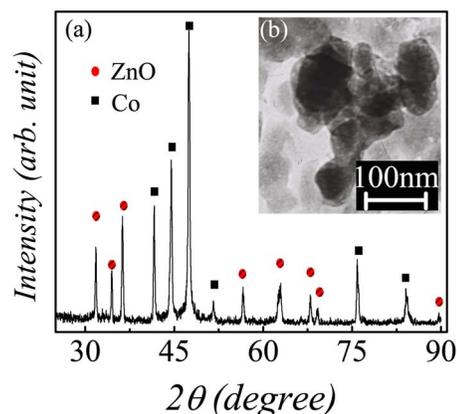

FIG. 1. (a) XRD pattern and (b) TEM image of the as-prepared Co/ZnO core/shell nanoparticles.

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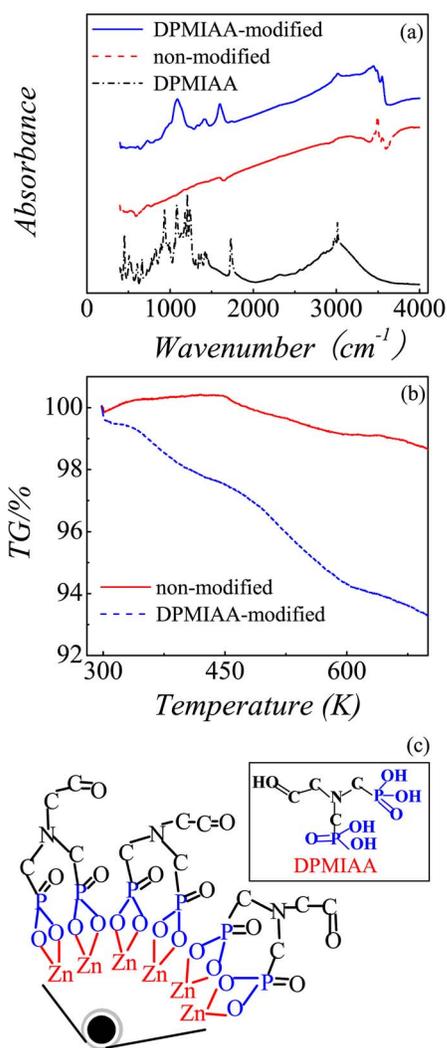
FIG. 2. (Color online) (a) FTIR spectra of DPMIAA, nonmodified Co/ZnO core/shell particles, and DPMIAA-modified Co/ZnO core/shell nanoparticles. (b) TGA spectra of the nonmodified and DPMIAA-modified Co/ZnO core/shell nanoparticles. (c) Proposed surface structure of Co/ZnO core/shell after modification with DPMIAA.

FIG. 3. SEM morphology of the polished surfaces of the composites with (a) DPMIAA-modified and (b) nonmodified Co/ZnO core/shell particles.

sequence.[14] The modified Co/ZnO nanoparticles were characterized using Fourier transform infrared (FTIR) (Nexus 870) spectroscopy and thermogravimetric analysis (TGA). The PVDF precursor solutions (5 wt %) were prepared by dissolving PVDF in dimethylformamide (DMF). The modified and nonmodified Co/ZnO nanoparticles were dispersed into the organic solvent of DMF with PVDF with a mass ratio of 1:10 was ultrasonicated at a power of 100 W for 1 h. The precursor solution was dropped on the glass substrate and then dried at 60 °C under vacuum for 12 h. For the electrical testing, gold electrodes (3 mm in diameter) were coated on both faces of the films with vacuum ionic sputtering.

We first come to look at the effect of the surface modification. Figure 2(a) gives the FTIR spectra of the Co/ZnO particles, DPMIAA and the modified Co/ZnO particles, respectively. The P–O and P=O stretching absorption regions between wave numbers 1300 and 800 cm^{-1} could be examined for DPMIAA. The modified Co/ZnO particles also show evidently strong absorption in this region, but the nonmodified Co/ZnO particles do not. In addition, the strong C–H stretching absorptions (3000 cm^{-1}) for the modified
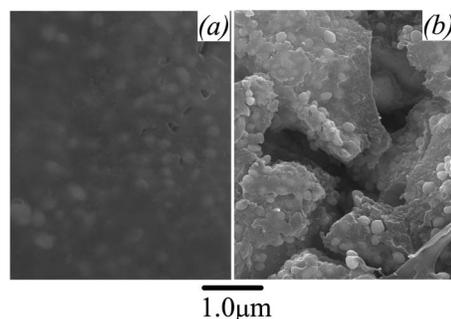
Co/ZnO particles were also observed, indicating the binding of DPMIAA. The stretching absorption peak at 1600 cm^{-1} may originate from the carbonyl group in DPMIAA. For DPMIAA, the corresponding P=O and P–O bonds are located at 1147–1294, 1078, and 880–940 cm^{-1}, respectively. However, the changes of P=O and P–O can be observed for the modified Co/ZnO particles, which may be attributed to the stretching of Zn–O–P, suggesting that the majority of the ligand bound to the surface takes a tridentate form, involving all three oxygen atoms.[14,16,17] The structure of a typical modified Co/ZnO nanoparticle is schematically shown in Fig. 2(c). The gray region represents the modified layer, the white region is the ZnO shell, and the black area is the Co core. It illustrates the surface modification of the Co/ZnO nanoparticles with DPMIAA (the proposed chemical structure at the interface is shown), while the original structure of DPMIAA is also given in Fig. 2(c) for comparison. In short, these changes are consistent with previous FTIR studies of phosphonic acids bound to TiO$_2$ and ZrO$_2$ surfaces, which were interpreted as evidence of the tridentate binding.[16,17] The phosphonic ligand bound to the Co/ZnO surface shows high stability against solvolysis, remaining bound after extensive washing. These results proved the relatively high and robust surface coverage of the Co/ZnO nanoparticles by DPMIAA. To confirm the robust surface coverage, we performed the TGA of the nonmodified and modified Co/ZnO nanoparticles, respectively, shown in Fig. 2(b). A significant weight decrease was observed for the modified Co/ZnO sample and the weight loss is ~5.7% upon heating above 600 K. However, the weight loss for the nonmodified Co/ZnO sample is only about 1%.[13] The weight loss corresponds to a surface coverage of phosphonic ligand, given the theoretical presuppose of a monolayer mantle.[17]

With the effective surface coverage with DPMIAA, we investigate the particle dispersion in the polymer matrix. For the present work, only a small volume (~10%) of Co/ZnO nanoparticles is embedded into the PVDF matrix, benefiting to retain the excellent mechanical performance of PVDF. The microstructures of the modified and nonmodified samples are checked using scanning electron microscopy (SEM), as shown in Figs. 3(a) and 3(b), respectively, noting that the imaging areas are the surfaces of the polished samples. The modified sample shows dense microstructure with homogeneously dispersed Co/ZnO nanoparticles in the PVDF matrix, while that for the nonmodified sample is cracked with clearly aggregated Co/ZnO particles. This observation illustrates two effects. One is that the surface modification by DPMIAA improves the interfacial property between the particles and matrix, probably the interfacial adhesion by chemi-
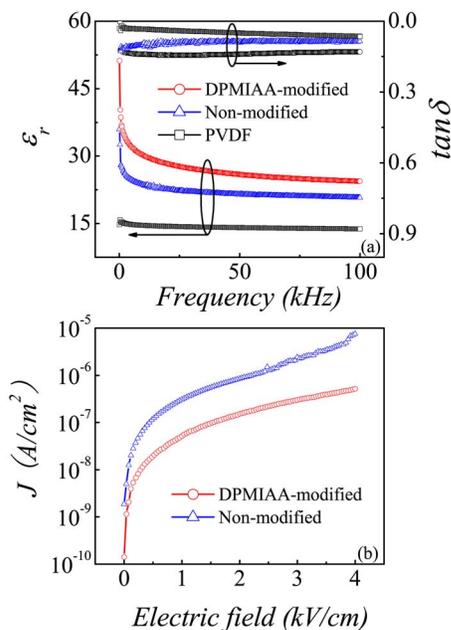
FIG. 4. (Color online) (a) Variation of ε_r with frequency f for pure PVDF sample, PVDF composites, respectively, with nonmodified and DPMIAA-modified Co/ZnO core/shell particles and (b) dc leakage current of PVDF composites respectively with nonmodified and DPMIAA-modified Co/ZnO core/shell particles.

cal binding. The other is that the surface modification can improve the homogeneity of the particles in the matrix. One understands the underlying physics. Generally, polymer and inorganic materials have very different surface energies and a homogeneous dispersion of one phase in the other is difficult due to the incompatibility between them. This incompatibility can be overcome by the surface modification of the inorganic materials with phosphonic ligands, such as DPMIAA, as well demonstrated,[14] and confirmed here for the Co/ZnO nanoparticle-PVDF composite. The molecular-level bridges between the Co/ZnO particles and PVDF lead to the considerable improvement of the compaction and homogeneity of the microstructures. In contrast, for the nonmodified sample, the cracks and inhomogeneity seem to be the outcome of such an incompatibility, revealing the importance of the DP-MIAA modification for synthesizing high quality PVDF composite.

Finally, we demonstrate the enhanced electrical properties of the as-prepared composite samples, measured by using HP4194 impedance analyzer and HP4140B. Figure 4(a) presents the variation of dielectric permittivity (ε_r) and loss factor (tan δ) with frequency for three samples: pure PVDF, nonmodified Co/ZnO-PVDF composite, and modified Co/ZnO-PVDF composite, respectively. It is seen that ε_r for all samples decreases with frequency. While the nonmodified Co/ZnO-PVDF composite has its ε_r twice over that of pure PVDF, the value of ε_r for the modified composite is even three times higher than that of pure PVDF. The maximal ε_r for the modified composite reaches up to 51. The maximal tan δ is only 0.14, much lower than those composites with conductive fillers (0.18–0.5) and even much lower than the polymer/ceramic composites.[15] The slightly higher tan δ of the modified sample than the nonmodified one is possibly due to the response of phosphonic ligands bound to the Co/ZnO surface to external ac signal. Regarding the leakage current, as shown in Fig. 4(b), we can see that the modified

sample has much lower leakage than the nonmodified one (more than one order of magnitude).

The reason responsible for the improved electrical property of the modified sample is as follows. First, the reduced leakage current is attributed to the surface modification by DPMIAA, which provides an efficient surface passivation depressing the mobility of charge carriers associated with the surface of Co/ZnO nanoparticles. In addition, the concentration of ionizable hydroxyl groups on the nanoparticle surface is minimized due to the passivation layers.[14] Second, the ZnO shell may also play as a barrier layer against the conduction due to the direct contact of Co particles, although ZnO is a semiconductor. The high dielectric permittivity of the modified and nonmodified samples is evidently ascribed to the fact that the conducting particles are isolated by the thin dielectric layers to form microcapacitors, thus preferring the enhancement of the effective capacitance. Furthermore, the homogeneous dispersion of the Co/ZnO nanoparticles in the matrix benefits to the even higher dielectric permittivity and low leakage, which are reasonable results.

In conclusion, the Co/ZnO core/shell nanoparticles-filled polymer (PVDF)-based composites are fabricated. High dielectric permittivity and low leakage current are achieved in the PVDF polymer embedded with the DPMIAA-modified Co/ZnO core/shell nanoparticles. Simultaneously, the composite shows good homogeneity, no cracks, and fine mechanical flexibility. These enhanced properties may allow more capability of PVDF polymers as smart functional materials for applications.

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