

PVDF based all-organic composite with high dielectric constant

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Received: 14 October 2007 / Revised version: 4 December 2007 / Accepted: 4 January 2008
Published online: 19 January 2008 – © Springer-Verlag 2008

Summary

High dielectric constant copper phthalocyanine oligomer (o-CuPc) was chemically grafted to poly(*p*-chloromethyl styrene) (PCMS) to improve its dispersibility in PVDF. From SEM results, the size of o-CuPc-g-PCMS particles in the blend of poly(vinylidene fluoride) (PVDF) and o-CuPc-g-PCMS (o-CuPc-g-PCMS/PVDF) was about 70nm, less than 1/7 the size of o-CuPc in o-CuPc/PVDF. In addition, o-CuPc-g-PCMS in o-CuPc-g-PCMS/PVDF showed much improved dispersibility. Both of the improvements obviously enhanced the electric properties of the composite. The dielectric constant of o-CuPc-g-PCMS/PVDF was more than 325 (100Hz), which was about 7 times higher than that of o-CuPc/PVDF. The dielectric constant at high frequencies (~1MHz) was also high (~130).

Introduction

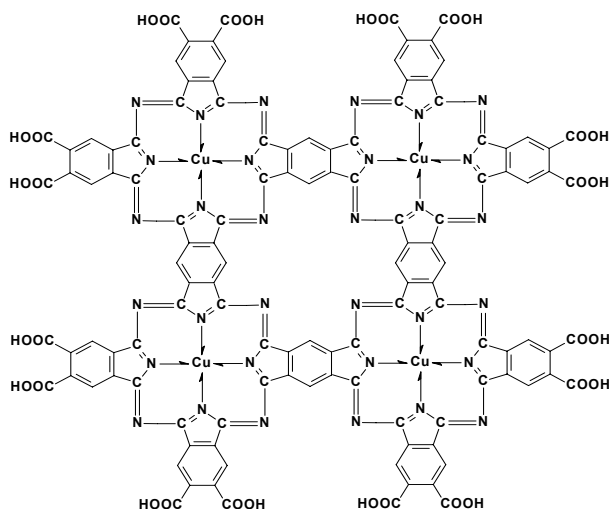
Electroactive polymers (EAPs) who give significant shape or size changes responding to external electrical stimulation play important roles in electromechanical fields such as high performance sensors, actuators, micro-electrical-mechanical system (MEMS) and artificial muscles. These kinds of materials have been pursued with great enthusiasm for years [1-5]. How to raise the electric energy density in these EAPs is crucial for electromechanical devices to generate high elastic energy densities as the input electric energy density (U_E) is always less than the output mechanical energy density (U_M) according to the law of conservation of energy. To obtain a high electric energy storage density device, we can either improve the electric field (E) or dielectric constant (K) of the material. However, the limit to the supply of high electric field makes people pay more attention to the dielectric constant. The dielectric constant of most polymers is less than 10. By adding dielectric ceramics into certain polymer matrixes, as lots of researchers did, the dielectric constant of the composite could reach 100 which was much higher than most of polymers. However, the unsatisfied dielectric constant, poor interface property and seriously increased elastic modulus of the composites restrict the application in electromechanical fields [6-8].

An all-organic composite of o-CuPc and poly(vinylidene fluoride-trifluoroethylene) with high dielectric constant (100 at 100Hz) has been developed [1]. The dielectric constant of the composite is enhanced by o-CuPc (with a K higher than 10^5) [9] because of the easy displacement of the electrons in o-CuPc under electric fields through the highly conjugated π -bonds within the entire sheet like molecule. This all-organic composite can generate high elastic energy density and large strain at a lower electric field. However o-CuPc particles are susceptible to be agglomerated in the polymer matrix and the size of them reaches almost $1\mu\text{m}$ which restricts the electric properties such as breakdown field and dielectric constant of the composite. To overcome this shortage, *Wang* used a chemical method to graft o-CuPc to poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) chains which causes the decrease of the o-CuPc size to about 100nm and the dielectric constant was greatly promoted to 175 (100Hz) [10, 11]. However the synthetic procedure was complex and there was still great potential to improve dielectric constant. By grafting o-CuPc to PCMS in our work, the improvement of dispersion and decrease of size level of o-CuPc-g-PCMS in PVDF was achieved, and the improved electric properties of the o-CuPc-g-PCMS/PVDF composite were obtained.

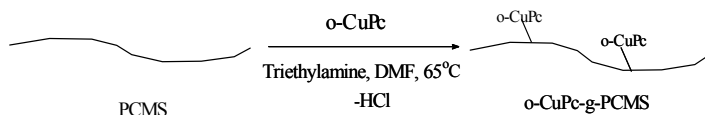
Experimental

Materials

The o-CuPc (Scheme 1) was synthesized following a procedure reported in ref [12]. PCMS (97%) was purchased from Aldrich and used without further purification. Triethylamine (TEA) was dried with NaOH and distilled before use. Dimethylformamide (DMF) was dried with CaH_2 followed by distillation in vacuo prior to use. The PVDF with a weight-averaged molecular weight of 400,000 was purchased from Shanghai 3F Company, China. Other reagents were analytical grade without further purification.



Scheme 1. Chemical structure of the o-CuPc



Scheme 2. Schematic drawing of the synthesis of o-CuPc-g-PCMS

Synthesis of o-CuPc-g-PCMS

Scheme 2 shows the synthetic route to o-CuPc-g-PCMS. A 100mL three-neck round-bottom flask fitted with a magnetic stirrer, a thermometer and a condenser was used as the reactor. PCMS (0.5g) and TEA (3.0mL) was added to a solution of o-CuPc (0.5g) in DMF (40mL), and then stirred at 65°C for 12 hours under nitrogen. After the grafting reaction, the TEA and DMF were removed by reduced pressure distillation. The mixture was washed with methylene dichloride to remove unreacted PCMS, if any, followed by distilled water to remove triethylamine hydrochloride. The final product was dried in vacuo at 50°C.

Preparation of films for electric tests

Films were prepared using solution cast method. For the o-CuPc-g-PCMS/PVDF film, PVDF was dissolved in DMF, and then a proper amount of o-CuPc-g-PCMS was added to the solution and ultrasonically stirred for 2 hours. Afterward, the solution was poured onto a clean glass slide and dried in air at 70°C for 5 hours, then in vacuo at 50°C for 12 hours to remove DMF. Finally, the films were annealed at 120°C for 12 hours and slowly cooled to room temperature. For the o-CuPc/PVDF film, the procedure was the same as that of o-CuPc-g-PCMS/PVDF. The typical thickness of the film was 30-40µm. For the electric characterization, the films were cut into small pieces of 10×10mm, and circular gold electrodes with 2.5mm radius were sputtered in the center of both surfaces.

Characterization

FT-IR spectra were recorded with a Bruker Vector-22 FT-IR spectrometer. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to determine the graft ratio of o-CuPc in o-CuPc-g-PCMS. The unreacted o-CuPc in samples for test was removed by washing o-CuPc-g-PCMS with 0.1mol/L of NaOH aqueous solution, followed by distilled water to get rid of NaOH. The resulting product was dried in vacuo at 50°C, and then was decomposed with a mixed solution of 70% nitric acid and 70% perchloric acid at a volume ratio of 5 to 1. After all of the liquids were slowly evaporated off, the organic components were burned up in a crucible. The residues were diluted by 5% nitric acid to a 10mL solution, and the metal contents were measured by a Jarrell-Ash J-A1100. For thermal analysis, a Perkin-Elmer DSC-2C calorimeter was used to characterize thermal transitions of the composites at heating rate of 20°C/min. LEO1550 was used to observe the rupture face of the composite film. The film had been cooled in liquid nitrogen below T_g before broken. X-ray study was carried out using a D8Advance X-ray generator with a copper target in the range of 3°-90°, $\lambda=1.5406\times 10^{-10}$ m. For the characterization of frequency dependence of the dielectric properties, an Agilent 4194A Impedance

Analyzer was used in the range from 100Hz to 10MHz. The dielectric constant K of the film is calculated by the formula of a parallel plate capacitor as $K=Ct/\varepsilon_0A$, where C is the capacitance of the capacitor, ε_0 is the vacuum dielectric permittivity, A is the area of the electrode and t is the thickness of the capacitor.

Results and discussion

Synthesis and characterization of o-CuPc-g-PCMS

Carboxyl groups (-COOHs) in o-CuPc (shown in Scheme 1) can react with PCMS in the presence of TEA. TEA acts as an acceptor to take in resulting hydrochloric acid from the solution consequently the esterification is promoted. The FT-IR analysis of o-CuPc and o-CuPc-g-PCMS is shown in Figure 1. The absorption band at 1767cm^{-1} corresponds to carbonyl band of an ester linkage, which proves the successful esterification. The strong absorption band at 1717cm^{-1} corresponds to the stretching vibration of carbonyl group of -COOH, indicating some unreacted -COOHs in o-CuPc-g-PCMS. As the figure shows, o-CuPc-g-PCMS still keeps the characteristic peaks (1100 , 1130 , 450 and 1510cm^{-1}) in o-CuPc.

According to the ICP-AES analysis, the unreacted o-CuPc after the grafting process was removed by NaOH aqueous solution. The results showed as much as 96.8% o-CuPc was grafted with PCMS.

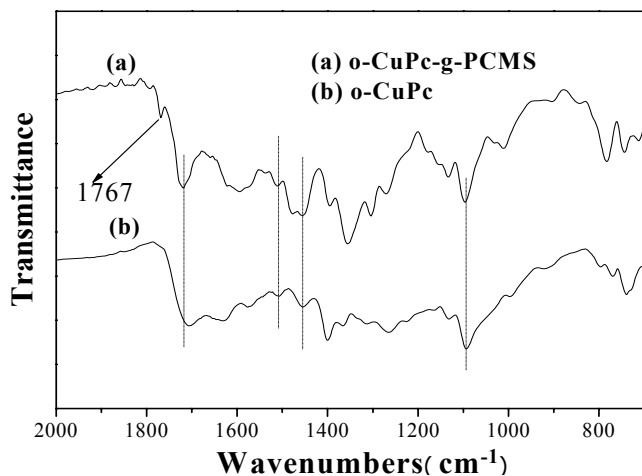


Figure 1. FT-IR spectra of o-CuPc and o-CuPc-g-PCMS

Microstructure of o-CuPc and o-CuPc-g-PCMS in PVDF

Figure 2 shows the SEM of rupture faces of o-CuPc/PVDF and o-CuPc-g-PCMS/PVDF. The o-CuPc and o-CuPc-g-PCMS particles have nearly spherical shape in both of the composites. The size of o-CuPc in o-CuPc/PVDF is more than 500nm (Figure 2(a)), and in o-CuPc-g-PCMS/PVDF composite the o-CuPc-g-PCMS size is about 70nm (Figure 2(b)), less than 1/7 of that in o-CuPc/PVDF. And the size

distribution of o-CuPc-g-PCMS in the later is remarkably improved. In o-CuPc-g-PCMS/PVDF composite, the grafted o-CuPc acts as the nucleation center. On the other side, the PCMS forms a shell to prevent the o-CuPc-g-PCMS particles from growing too big, thus the crystal region of o-CuPc-g-PCMS is reduced to nanometer level. On the contrary, the growing of o-CuPc can hardly be prevented in o-CuPc/PVDF, resulted in much bigger particles.

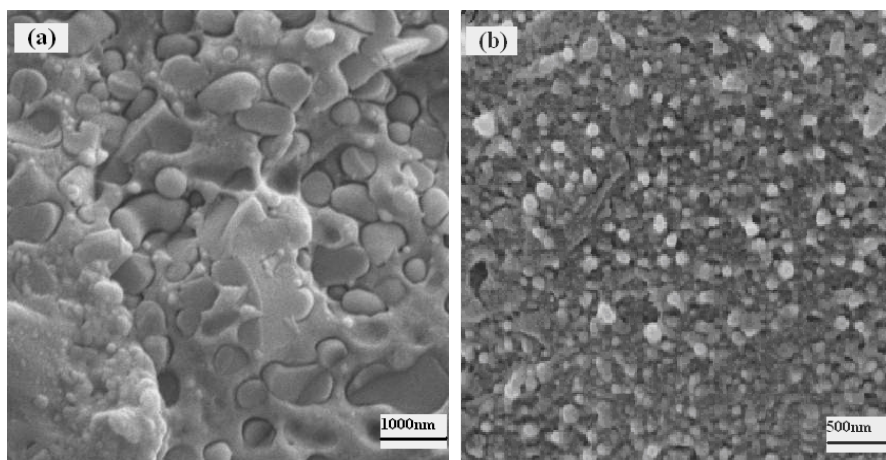


Figure 2. SEM photographs of (a) o-CuPc/PVDF (b) o-CuPc-g-PCMS/PVDF film rupture faces

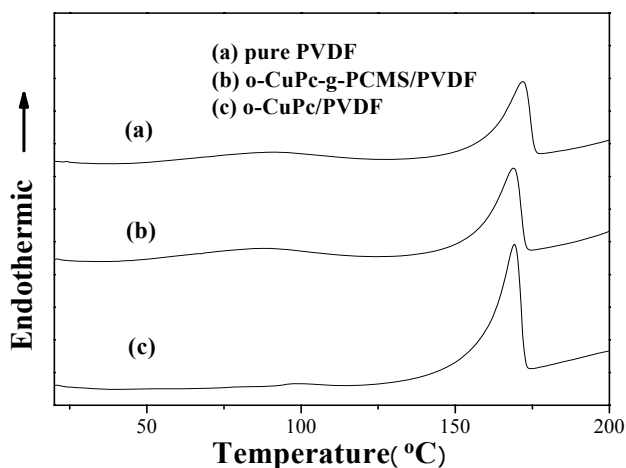


Figure 3. DSC curves of pure PVDF, o-CuPc/PVDF (with 15wt% o-CuPc) and o-CuPc-g-PCMS/PVDF (with 30wt% o-CuPc-g-PCMS)

Figure 3 shows the DSC curves for PVDF and two composites. The melting point of pure PVDF is 172.15°C, for two composites the melting point are lower (169.25°C for o-CuPc/PVDF and 168.92°C for o-CuPc-g-PCMS/PVDF). The decrease of the

melting point of the composites compared with PVDF matrix can be explained by the presence of heterogeneity [12] and the reduced lamellar thickness of PVDF crystallites.

Calculation of the crystallinity degree is also given, according to equation 1 [13].

$$\chi(\%) = (\Delta H_m / W\Delta H_m^0) \quad (1)$$

Here ΔH_m is the experimental heat of fusion, W is the PVDF content in the composite o-CuPc/PVDF and o-CuPc-g-PCMS/PVDF, ΔH_m^0 is the heat of fusion of 100% crystalline PVDF, which is 90.40 J/g. Table 1 shows the results of the melting enthalpy (ΔH_m) and the polymer crystallinity degree (χ) of α -PVDF without phase transformation. It is observed that ΔH_m is 44.68J/g of o-CuPc/PVDF and 34.62J/g of o-CuPc-g-PCMS/PVDF, corresponding to the crystallinity degree of 58.2% and 54.7%, which is higher than that of pure PVDF. The increase of ΔH_m of the two composite is explained by the fact that a certain content of o-CuPc and o-CuPc-g-PCMS can promote nucleation of PVDF crystalline phase [14, 15].

Table 1. Crystallinity degree comparison among the pure PVDF and two composites

Material Type	ΔH_m (J/g)	$\chi(\%)=(\Delta H_m/W\Delta H_m^0)$	Melting temperature (°C)
o-CuPc/PVDF	44.68	58.1	169.25
o-CuPc-g-PCMS/PVDF	34.62	54.7	168.92
Pure PVDF	32.00	35.4	172.15

Figure 4 shows the XRD results of these two kinds of composite film and PVDF matrix. for PVDF the diffraction peaks at 20.2°, 26.8° and 39.3° correspond to (110), (021) and (002) reflections according to *Lovinger's* results [16]. The wider diffraction peak at 27° of o-CuPc/PVDF also indicates that o-CuPc is in the PVDF matrix. The (021) diffraction peak of PVDF at 27° is so weak that it is covered by diffraction peak of o-CuPc at the same position.

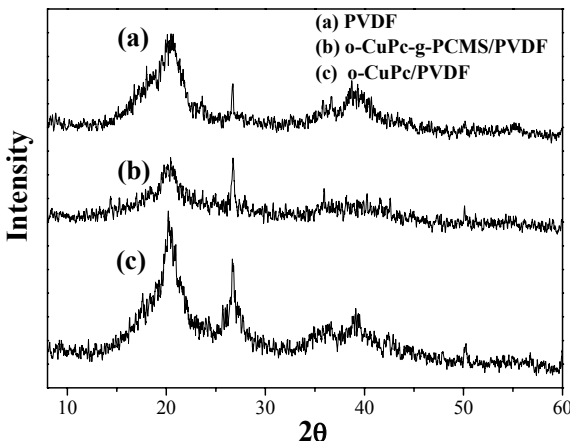


Figure 4. X-ray data of PVDF, o-CuPc (15wt%)/PVDF, o-CuPc-g-PCMS (30wt%)/PVDF

By employing the Scherrer equation [17], the Miller Index L_{hkl} can be estimated according to equation [2].

$$L_{hkl} = 0.9\lambda / (B \cos \theta) \quad (2)$$

Where λ is the X-ray wavelength, B is the full width at half-maximum of the diffraction peak in 2θ , θ is the peak angular position. The Miller Index L in the direction perpendicular to the crystal planes can be deduced. For the o-CuPc/PVDF and o-CuPc-g-PCMS/PVDF sample, L_{110} of PVDF is about 4.8nm and 4.7nm separately. The result shows no evident difference between the composites with two kinds of fillers. In o-CuPc-g-PCMS/PVDF composite, the peak at 39.3° disappears, which can be explained by the much decreased crystallinity region of PVDF caused by the interaction between the filler and the basic matrix [18].

Dielectric Properties of the Composites

Figure 5(a) shows the comparison of dielectric constant (K), dielectric loss (D) of PVDF, o-CuPc/PVDF (with 15wt% o-CuPc) and o-CuPc-g-PCMS/PVDF (with 30wt% o-CuPc-g-PCMS, accordingly the content of o-CuPc is also 15wt%) as a function of frequency from 100Hz to 10MHz at room temperature. It is observed that, the dielectric constant of the two composites is substantially increased compared with the pure PVDF (8.4 at 100Hz), because of the super high dielectric constant of the o-CuPc oligomer. The o-CuPc-g-PCMS/PVDF film shows a dielectric constant of more than 325 at 100Hz, meanwhile, the dielectric constant of o-CuPc/PVDF is just 48 at the same frequency. According to the model in ref [19], logarithm of the dielectric constant of such composites ($K_{\text{composite}}$) is linearly proportional to the volume fraction of the filler (φ_{filler}) with the slope dependent of the dielectric properties of both components (equation [3]). The dielectric constant of o-CuPc (100Hz) was 430,515 showing in Figure 5(b).

$$\log K_{\text{composite}} = \varphi_{\text{filler}} \log\left(\frac{K_{\text{filler}}}{K_{\text{polymer}}}\right) + \log K_{\text{polymer}} \quad (3)$$

It is calculated that, the dielectric constant of composite with 15wt% of o-CuPc is 42.7, which meets the result of the dielectric constant of o-CuPc/PVDF samples. However, the dielectric constant of o-CuPc-g-PCMS/PVDF is more than 7 times higher than that of o-CuPc/PVDF. This could be attributed to the enhanced interface exchange coupling effect between nanosized o-CuPc-g-PCMS and PVDF matrix in o-CuPc-g-PCMS/PVDF [20], as well as the much stronger Maxwell-Wagner-Sillars (MWS) space charge polarization mechanism than in o-CuPc/PVDF [9, 21], which further causes the dielectric dispersion at low frequencies as we can see from the curve in Figure 5(a).

It is surprising to find that at the frequency of 1MHz the dielectric constant still remains 130, 8 times higher than 16 of o-CuPc/PVDF. At even 10MHz, the film has a dielectric constant of 83, which satisfies the properties of current materials used in high frequency applications, such as high frequency capacitor.

From Figure 5(a), the dielectric loss of o-CuPc-g-PCMS/PVDF is less than 0.35, while the o-CuPc/PVDF composite shows a dielectric loss of 0.4 at 1MHz. It is evident that the dielectric absorption of the composite with a maximum near 1MHz is

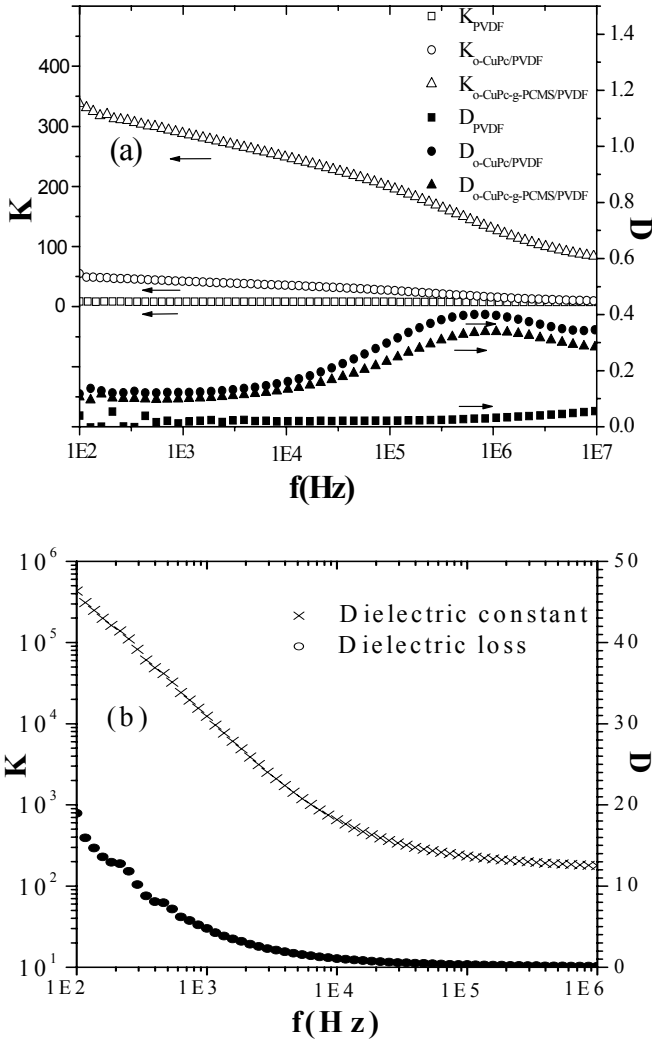


Figure 5. (a) Dielectric properties of the $o-CuPc/PVDF$, $o-CuPc-g-PCMS/PVDF$ composites with 15wt% $o-CuPc$ and 30wt% $o-CuPc-g-PCMS/PVDF$ (accordingly the content of $o-CuPc$ structure is 15wt%) separately as a function of frequency from 100Hz to 10MHz at room temperature. (b) Dielectric properties of $o-CuPc$ powder pressed lamella ($\varphi=5mm$, thickness $d=0.5mm$).

a simple relaxation process [22]. Both composites are much higher than that of pure PVDF (less than 0.1) because of high dielectric loss of $o-CuPc$ blender. The reduced particle size and improved dispersibility of $o-CuPc-g-PCMS$ in PVDF could also explain the decreased dielectric loss of the $o-CuPc-g-PCMS/PVDF$ composite compared with $o-CuPc/PVDF$. Furthermore, the break down field is promoted to 35.1MV/m of $o-CuPc-g-PCMS/PVDF$ compared with 25.6MV/m of $o-CuPc/PVDF$. The higher breakdown field observed in the $o-CuPc-g-PCMS/PVDF$ film is expected due to the notably reduced and more uniformly sized $o-CuPc-g-PCMS$ particulates in PVDF as compared with the $o-CuPc/PVDF$. In the latter, the excessive agglomeration of $o-CuPc$ particulates can easily lead to conductive paths and lower breakdown field.

Conclusions

The size of synthesized o-CuPc-g-PCMS is about 70nm when blended with PVDF, only 1/7 the size of o-CuPc particles in PVDF matrix. Because of the decreased blender size level in PVDF which strongly reinforces the interface coupling effect, the o-CuPc-g-PCMS/PVDF composite exhibits higher dielectric constant (325, 7 times higher than o-CuPc/PVDF composite), smaller dielectric loss (less than 0.35) and higher break down field (35.1MV/m). It certainly will attract more interest in o-CuPc-g-PCMS filler in PVDF and other high quality ferroelectric fluoropolymer matrixes.

Acknowledgements. This research was supported by the Aeronautical Science Foundation of China under Contract No. 2006ZF52060, and the Natural Science Foundation of Jiangsu Province (No. BK2006194). Special thanks are extended to Professor Jinsong Zhu and Kai Chen of National Laboratory of Solid State Microstructures, Nanjing University for providing Impedance Analyzer used in this investigation.

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