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Structural and electrical properties of gold nanowires/ P(VDF-TrFE) nanocomposites

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Abstract

High aspect ratio gold nanowires were uniformly dispersed into a P(VDF-TrFE) matrix. The nanowires were synthesized by electrodeposition using nanoporous anodic alumina oxide templates. Intrinsic optical conductivity of gold nanowires was determined by Valence Electron Energy Loss Spectroscopy. The effect of increasing volume fraction of Au nanowires on the morphology and crystallization of P(VDF-TrFE) matrix was investigated by Differential Scanning Calorimetry. The crystallinity of P(VDF-TrFE) is strongly depressed by the randomly dispersed nanowires. Above 30 vol % the crystallisation of P(VDF-TrFE) is suppressed. The bulk electrical conductivity of nanocomposite films, at room temperature, obeys a percolation behaviour at a low threshold of 2.2 vol. % and confirmed using surface resistivity value. An electrical conductivity of 100 S.m^{-1} is achieved for a 3 vol. % filler content.

1. Introduction

The polymer composites reinforced with a low content of strong fillers can significantly improve the mechanical, thermal and electrical properties of the pure polymer matrix. Moreover, these improvements are achieved through conventional processing techniques without any detrimental effects on process ability of the matrix. Typical mixed fillers into polymer matrix are carbon black [1-3], CNTs [4,5] and metal nanoparticles [6,7]. These studies showed that electrical and mechanical properties of reinforced polymer composites depend on many factors, such as inherent properties, degree of dispersion, orientation [8], interfacial adhesion, aspect ratio and content of filler. The degree of dispersion was especially well-known as one of the most important factors in electrical properties and difficult to control in nanocomposites. Experimentally observed percolation threshold was known to be strongly dependent on the aspect ratio of the filler and not on their nanometric size. Very low percolation threshold were obtained with aspect ratio ζ (ratio length to width) higher than 100 and even 1000. Metal nanowires have attracted much attention because of their specific properties such as electrical conductivity [9] and magnetic susceptibility [10-12]. Nickel nanowires (Ni NWs) have a great surface reactivity due to the nanometric dimension. This reactivity of nickel nanowire induces a surface oxidation. To elaborate conductive nanocomposites, the nickel nanowires required removal oxide layer onto their surface prior their introduction in Poly(vinylidene difluoride–trifluoroethylene) [P(VDF-TrFE)] copolymer matrix in order to reach high conductivity at low filler content [13]. P(VDF-TrFE) is a semi-crystalline thermoplastic polymer with excellent process ability, high mechanical strength, high dielectric permittivity and thermal stability. But its degree of crystallinity was affected by filling it with nanoparticles like carbon nanofiber (CF) [14], carbon nanotubes (CNTs) [15] or nanoclays [16,17]. The mechanical properties are directly linked to the crystallinity ratio.

In this study, Au nanowires were prepared in order to elaborate high conductive nanocomposites at low Au NWs volume fraction to preserve the mechanical properties of P(VDF-TrFE) matrix. The optical conductivity of Au NWs was extracted from Valence Electron Energy Loss Spectroscopy (VEELS) spectra in combination with transmission electron microscopy (TEM). The influence of the Au NWs content and their aspect ratio on crystallization of P(VDF-TrFE) and on the Au NW/ P(VDF-TrFE) nanocomposites electrical properties was investigated. Structural analysis and physical performances of the resulting nanocomposites materials were examined using scanning electron

microscopy (SEM), differential scanning calorimetry (DSC) and dc and ac conductivity measurements. The influence of preparation and processing conditions on the percolation threshold was discussed.

2. Experimental Section

2.1 Materials and sample preparation

2.1.1. Au nanowire synthesis

Gold nanowires (Au NWs) were synthesized by electrochemical deposition in an anodic aluminium oxide (AAO) porous template using free cyanide electrolyte. Direct current (DC) electrodeposition was carried out at 50°C using a gold wire of 1.0 mm in diameter as anode. A porous AAO membrane of 200 nm in diameter and 50 µm thickness was supplied by Whatman. One side of the AAO membrane was coated with a 35 nm thickness silver layer by using sputtering technique as cathode for electrodeposition. Gold NWs growing was controlled by the time deposition and the direct current intensity using a Keithley 2420 source meter. The AAO membrane was dissolved in NaOH 6M for 30 min, releasing Au NWs from the template.

High purity of Au nanowires as fillers has a great interest in order to achieve high dc conductivity in nanocomposites. Filling AAO membrane pores with Au was performed using a direct current intensity of 3 mA under a voltage of 0.7 V. The Au NWs morphology was characterized by SEM to determine the aspect ratio ζ . Au NWs exhibit an uniform length of 45 µm and a regular diameter of 200 nm. The silver coated layer backside and the AAO membrane have been dissolved in HNO₃ and NaOH solution, respectively. The nanowire suspension was then filtered through a polyamide (200 nm pore size) membrane. Filtered nanowires were stored in acetone and dispersed using an ultrasonic bath. A droplet of this solution was deposited onto a SEM pin.

For comparison, bulk Au powder with particle size in the range 0.5 to 10 µm, supplied by Aldrich, were chosen.

2.1.2. Nanocomposite preparation

Poly(vinylidene fluoride–trifluoroethylene) P(VDF-TrFE) (70/30) mol% copolymer was supplied by Piezotech S.A. (Saint Louis, France). Melting temperature of 150°C was determined by differential scanning calorimetry and the density was about 1.8 g.cm⁻³.

The nanocomposites were prepared by using solvent casting method. P(VDF-TrFE) was dissolved into acetone. Nanoparticles were poured into the polymer solution and the mixture was submitted to 5 s short pulse of sonication, corresponding to a dissipated power of 25 W. A slight curvature of Au NWs is observed after sonication because of the Au NWs ductility and high aspect ratio. Sonication parameters were optimized by the observation of Au NWs dispersion using Scanning Electron Microscopy (SEM). The solvent was evaporated using a magnetic stirrer at 80°C for 1h. Pellets of randomly dispersed Au NWs in P(VDF-TrFE) matrix were obtained. Films with 200 µm in thickness were moulded in a hot press at 200°C under a pressure of about 0.3 MPa. The coating samples were elaborated by spray coating. The matrix was dissolved in acetone and nanowires were poured into the polymer solution. This mixing suspension was sprayed as coating on a glass substrate of 120 mm × 120 mm. The coating is about 20 µm in thickness. It was heated at 80°C for 1h to evaporate the solvent. No residue of solvent was found in the thermogravimetric analysis, indicating a complete removal of acetone from films and coatings.

Au NWs/P(VDF-TrFE) nanocomposites were elaborated with a volume fraction varying from 0 to 30 vol%.

2.2. Differential scanning calorimetry

The crystallization and melting of the nanocomposites were investigated using a TA Instruments 2920 differential scanning calorimeter. The temperature of calorimeter was calibrated using the onset of melting of Tin ($T_m = 231.88$ °C), Indium ($T_m = 156.6$ °C) and cyclohexane ($T_m = 6$ °C) at a heating rate of 10 °C min⁻¹. The heat-flow rate was calibrated with heat of fusion of Indium (28.45 J.g⁻¹), then refined with a baseline run of two empty Al pans and a calibration run with sapphire as a standard. Before the heating and cooling runs, the samples were melted at 200°C and maintained at this temperature for 5 min in order to erase the thermal history. Samples were then cooled from 200 to 20°C at a rate of 10°C.min⁻¹ and then heated from 20 to 200°C at 10°C.min⁻¹. All the DSC measurements were performed under N₂ atmosphere.

The transition temperatures were taken as the peak maximum or minimum in the DSC curves. The degree of crystallinity of P(VDF-TrFE) composites was calculated according to the following

equation: $\chi_c = \frac{\Delta H_m}{(\Delta H_{m,P(VDF-TrFE)}^0) \text{wt}\%_{P(VDF-TrFE)}}$ where ΔH_m and $\text{wt}\%_{P(VDF-TrFE)}$ are respectively

the apparent melting enthalpy and the weight fraction of P(VDF-TrFE) in the composites and $\Delta H_{m,P(VDF-TrFE)}^0$ the value of the enthalpy corresponding to a 100% crystalline P(VDF-TrFE) (70/30) copolymer, taken as 91.45 J.g^{-1} [18].

2.3. Optical conductivity of Au nanowires

Intrinsic optical conductivity of Au NWs was performed using Valence Electron Energy Loss Spectroscopy (VEELS). VEELS experiments were carried out using a high resolution Gatan Imaging Filtering (HRGIF) system in a Tecnai F20 transmission electron microscope equipped with a Wien-filter type monochromator at the National centre for High Resolution Electron Microscopy (HREM) of Delft University of Technology. A 100 kV operation voltage allowed an energy resolution of 0.50 eV as determined from the full width at half maximum of the zero-loss peak. The VEELS spectra were collected with an energy dispersion of 0.1 eV/channel, an illumination semi-angle α of 2.5 mrad and a collection semi-angle β of 6.5 mrad. The dielectric function was calculated using 'Epsilon' software performing deconvolution, angular correction, normalisation and Kramers-Krönig (KK) transformation successively [19]. Prior any quantitative analysis of the VEELS data, the spectrum was corrected for the point-spread function (PSF) of the instrumentation by a Fourier-ratio deconvolution and followed by a Fourier-log deconvolution to eliminate contributions from the plural scattering. The material loss function $\text{Im}(-1/\epsilon(E))$ is extracted after angular correction and normalisation of the signal. The real part $\text{Re}(1/\epsilon)$ is calculated using a KK transformation. $\text{Re}(\epsilon)$ and $\text{Im}(\epsilon)$ are then deduced. So the optical conductivity $\sigma(E)$ can be deduced [20,21] using the following relation implanted in the

$$\text{Epsilon software [19]: } \sigma(E) = \frac{E \text{Re}(\epsilon)\text{Im}(\epsilon)}{\hbar} \quad (1)$$

2.4. Electrical conductivity

Bulk electrical conductivity of nanocomposites was measured by recording the complex conductivity $\sigma^*(\omega)$ using a Novocontrol broadband spectrometer. The measurements were carried out in the frequency range from 10^{-2} Hz to 10^6 Hz at room temperature. The real part $\sigma'(\omega)$, of the complex

conductivity $\sigma^*(\omega)$ was investigated. For all the nanocomposite samples considered in this study, the phase lag between the measured impedance and the applied ac voltage was negligible at low frequencies, so that the reported impedance at 0.01 Hz is equivalent to the dc resistance. The dc conductivity σ_{dc} of samples was determined from the independent frequency part of $\sigma'(\omega)$ [4]; i.e. the low frequency plateau. Films of 200 μm thickness were introduced between two circular gold plated electrodes (20 mm in diameter). To reduce contact resistivity with the cell electrodes, a thin layer of gold (100nm) was sputtered onto both sides of the films using a BOC Edwards scancoat six sputter coater.

The surface resistivity ρ_s of nanocomposites films was performed using a concentric ring-probe technique. Surface resistance R_s was measured using a Keithley 2420 source-meter in a four probe configuration and converted to surface resistivity.

3. Results and discussion

The Au nanowires, released from the membrane, are well dispersed in acetone suspension, as shown in the SEM image in figure 1. The EDX spectrum was recorded to prove the chemical nature of the gold nanowires. The Au peak shows the most prominent intensity indicating that the nanowires were made up of metallic gold. The weak peaks at low energy reveal the presence of oxygen and aluminium coming from the AAO template. Au NWs occur individually, no bundles and no sonication induced damage are observed except for a slight curvature. Figure 2 shows the SEM image of a matrix filled by 7.7 vol% of Au NWs. As in acetone suspension, Au NWs occur also individually in P(VDF-TrFE) matrix. The SEM image shows a slight orientation of the nanowires resulting from the compression molding processing of the nanocomposites.

3.1 Intrinsic conductivity of a single Au NW

High Angle Annular Dark Field (HAADF) image of Au nanowires associated with the VEEL spectrum is presented in figure 3. A small probe (0.5 nm) was used to acquire all the VEEL spectra which the shape remains identical along a NW and for different NWs. The dielectric function and the optical conductivity were calculated using the “Epsilon” software. Since the intensive zero-loss peak

hides fine structure below 1eV, $\sigma(E)$ is significant only above 1eV. Thus, to determine the electrical conductivity at $E = 0$ eV, the electrical conductivity is extrapolated linearly in the range between 1 and 0 eV starting from 1 eV [20]. Assuming that this extrapolation is correct, the electrical conductivity of Au nanowire is 72.10^6 S.m⁻¹. This value is consistent with other observations for bulk (45.10^6 S.m⁻¹) and with four-probe measurements on Au nanowires [22].

3.2 P(VDF-TrFE) crystallization inhibition

Figure 4 shows DSC curves of Au NW/P(VDF-TrFE) nanocomposites recorded during cooling scans. These curves exhibit a crystallization and para-ferroelectric (p-f) transition at 140 and 60°C respectively. These two exothermic events were used to calculate the degree of crystallinity χ_c of P(VDF-TrFE). The glass transition T_g of the matrix, generally observed around -30°C, is ill-defined. The insert of figure 4 shows a magnification of the Curie transition temperature range. The two exothermic peaks, reported by Tanaka *et al* (1988) [23] and discussed by Moreira *et al* (1989) [24] and Gregorio *et al* (1998) [25] in terms of a mixture of two crystalline phases, are well observed. The low-temperature peak T_{c1} was assigned to the Curie transition in a less ordered crystalline phase. The high temperature peak T_{c2} is attributed to well-formed crystallites. For all Au NWs volume fractions, no significant change in the p-f temperature transition and crystallization were observed.

The influence of Au particles on the crystallization of P(VDF-TrFE) is illustrated in figure 5. The degree of crystallinity χ_c decreases linearly as a function of the Au volume fraction. As shown previously, the presence of the dispersed NWs induces a slight decrease in the shape and temperature of transition peaks. The crystallinity of P(VDF-TrFE) matrix is inhibited gradually by the decrease of the number of crystallites. A linear extrapolation of the experimental points until zero crystallinity (solid line) gives a critical Au NWs volume fraction of 35 vol%. The effect of a dispersion of nano-clays on the crystallinity behaviour of PVDF and its copolymer was largely described by Cebe *et al* (2004) [16] and Dillon *et al* (2006) [17]. The presence of nano-clays induced a weak decrease of the crystallinity and a shift of the melting peak towards lower temperatures. Up to 25 wt% of nano-clays, this concomitant decrease becomes drastic [16]. Carbon fibers (CF) filled PVDF nanocomposites exhibited only a decrease in crystallinity at 4 wt% loading [14]. Similar results were obtained by

Wang *et al* (2004) with 25 wt% of chemically modified copper phthalocyanine (CuPc) oligomers in P(VDF-TrFE) 70-30 copolymer [26].

The geometry of particles and the aspect ratio particularly are the factor providing the higher decrease in crystallinity, except for carbon nanotubes [15] which have a nucleating effect and induce a polymer transcristallinity. To identify precisely the parameter responsible for crystallinity decrease, effects of Au NWs and spherical particles were compared. Others composites were elaborated with Au particles of 500 nm and 10 μ m in diameter. The corresponding experimental data points are reported in figure 5. The same linear decrease in crystallinity is observed for each diameter, but the rate of decrease is higher for Au NWs.

The para-ferroelectric transition temperature is Au NWs volume fraction independent, which indicates that the fillers are not confined in the P(VDF-TrFE) crystalline phase as expected. The crystallization enthalpy related with T_{c1} and T_{c2} were calculated from the DSC curves reported on figure 6(a). The decrease in enthalpy is found to be drastically different between the two crystalline phases. A peak deconvolution procedure was used to investigate the Curie transition in terms of coexistence two crystalline phases. The enthalpy ΔH_{C1} and ΔH_{C2} of the deconvoluted exothermic peak were determined and the ratio $\Delta H_{C1}/\Delta H_{C2}$ was reported as a function of Au NWs volume fraction in figure 6(b). Above 20 vol%, the ratio $\Delta H_{C1}/\Delta H_{C2}$ increases drastically which is characteristic of a strong modification in the P(VDF-TrFE) crystalline phase structure. Above this critical volume fraction, the low temperature exothermic peak becomes largely dominant which suggests the presence of a imperfect P(VDF-TrFE) crystalline phase in nanocomposites at high Au NWs content.

3.3 Nanocomposites bulk conductivity

The electrical conductivity of the insulating P(VDF-TrFE) copolymer is 10^{-12} S.m⁻¹ at room temperature. The dc electrical conductivity σ_{dc} of the Au NW/P(VDF-TrFE) samples at room temperature is plotted as function of the Au NWs volume fraction (see figure 7). The electrical conductivity increases drastically by 13 orders of magnitudes at a very low percolation threshold of 2 vol%. As expected, this value is very low in comparison with the value of 20 vol % obtained for spherical particles [27]. The data points are best fitted by a scaling law according to (2):

$$\sigma = \sigma_0 (p - p_c)^t \quad (2)$$

with $p_c = 2.2$ vol%, $\sigma_0 = 0.6 \times 10^4 \text{ S.m}^{-1}$, and $t = 1.21 \pm 0.27$. The critical exponent value t is smaller than the universal value for three-dimensional percolation systems which is equal to 1.94. From the scaling law, σ_0 is an extrapolation at 100 vol% of Au NWs, which corresponds to the electrical conductivity of Au NWs. The dc conductivity of Au nanowires pressed in a sheet form was measured at $1.6 \times 10^4 \text{ S.m}^{-1}$. Hence, σ_0 value is in a good agreement with the conductivity of pressed Au NWs.

The Au NWs display a narrow distribution of their aspect ratio centred on an average aspect ratio of $\zeta \approx 225$. According to Balberg *et al* (1984) [28], the excluded volume V_{ex} was given in an insulating three dimensional system containing conductive sticks randomly oriented. This model expresses the critical volume fraction necessary to reach the percolation for a given value of the aspect ratio.

$$V_{ex}^{cr} = \frac{L}{r} f_c = 1.6 \pm 0.2 \quad (3)$$

Assuming the stick is a Au nanowire, we find a critical volume fraction (f_c) of 0.71 ± 0.08 vol% using (3), a value lower than the experimental one of 2.2 vol%. This difference can not be explained by the nanowires re-aggregation in P(VDF-TrFE) matrix or the presence of some NWs bundles. Figure 2 showed that Au NW/P(VDF-TrFE) nanocomposites displayed an acceptable dispersion of NWs, and ruling out re-agglomeration. These observations confirm the ability of the metal nanowires to be easily dispersed in P(VDF-TrFE) [13]. The curvature of Au NWs after sonication results in a decrease of their apparent aspect ratio, as shown in SEM image in figure 1. It is well-known in CNTs filled conductive polymer composites that alignment of the filler changes the initial three-dimensional conductive network in into a two-dimensional network [29]. A such decrease in dimensionality could be suggested in Au NW/P(VDF-TrFE) nanocomposites upon an orientation of Au NWs in P(VDF-TrFE) matrix resulting from the film sample melting processing.

Contrary to Ni NWs in P(VDF-TrFE) matrix, Au nanowires display the same electrical conductivity than the bulk material [13]. Hence Au NWs don't require the prior surface treatment applied to Nickel NWs [13]. Above the percolation threshold p_c , the electrical conductivity of Au NW/P(VDF-TrFE) nanocomposites is the same than that of Ni NW/P(VDF-TrFE) nanocomposites: 10^2 S.m^{-1} [13]. According to the nanocomposites preparation, this value seems to be the high limit of electrical conductivity using filled metal nanowires in P(VDF-TrFE) matrix. This observed conductivity

limitation is in a good agreement with the values reported for spherical metal nanofillers in homogeneous nanocomposites [27,30].

3.4 Nanocomposites surface resistivity

The surface resistivity ρ_s was measured on nanocomposite coatings. Figure 8 shows the surface resistivity as a function of Au NWs volume fraction. The resistivity exhibits a percolation threshold around 2 vol%. This result is consistent with the electrical behaviour of the melt-pressed films and rules out the presence of large Au NWs aggregates or bundles. At the percolation threshold, the surface resistivity is about $10^4 \Omega/\square$. Above 3 vol %, ρ_s is constant and equals to $4 \Omega/\square$. ρ_s is independent of Au NWs volume fraction. This value is more than 1000 time lower than that of sprayed carbon nanotubes layer as coating developed by Kaempgen *et al* (2005) [31] and 10^6 time lower than that of commercial conductive coatings. Electrically conductive nanocomposites thin films are required for various applications as electrostatic dissipation or electromagnetic interference shielding.

4. Conclusion

High aspect ratio ($\zeta \sim 225$) Au nanowires were successfully prepared by free cyanide electrodeposition into pores of an AAO template. The aspect ratio is preserved after dispersion in a solvent. The intrinsic optical conductivity of Au nanowires obtained from valence EELS spectra is in a good agreement with their bulk electrical conductivity.

The addition of Au NWs in P(VDF-TrFE) impedes the crystallization process of P(VDF-TrFE) with increasing Au NWs volume fraction. The presence of metal filler promotes, in nanocomposites, a less ordered crystalline phase than in pure P(VDF-TrFE) copolymer. The influence of NWs aspect ratio on the crystallinity decrease was demonstrated.

Au NW/ P(VDF-TrFE) nanocomposites exhibit an electrical percolation threshold at 2.2 vol%. Such low nanowires loading results from a homogeneously dispersion of Au NWs in the P(VDF-TrFE) matrix as supported by SEM. A high level of electrical conductivity of 10^2 S.m^{-1} is reached and is consistent with that of nickel NW/P(VDF-TrFE) nanocomposites. This value is founded to be an upper limit for metal nanowire or powder as filler in P(VDF-TrFE). Melt-pressed samples and spray coating

samples exhibit the same low percolation threshold. The surface resistivity is about $4 \Omega / \square$ above the percolation threshold for the conductive coatings.

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References

- [1] Medalia A I 1986 *Rubber. Chem. Tech.* **59** 432
- [2] Tang H, Chen X, Tang A and Luo Y 1996 *J. Appl. Polym. Sci.* **59** 383
- [3] Untereker D, Lyu S, Schley J, Martinez G and Lohstreter L 2009 *Appl. Mater. Interfaces* **1** 97
- [4] Barrau S, Demont P, Peigney A, Laurent C and Lacabanne C 2003 *Macromolecules* **36** 5187
- [5] Sandler J K W, Kirk J E, Kinloch I A, Shaffer M S P and Windle A H 2003 *Polymer* **44** 5893
- [6] Karttunen M, Ruuskanen P, Pitkanen V and Albers W M 2008 *J. Electron. Mater.* 2008 **37** 951
- [7] Lee H S, Chou K S and Shih Z W 2005 *Int. J. Adhes. Adhes.* **25** 437
- [8] Keshoju K and Sun L 2009 *J. Appl. Phys.* **105** 023515
- [9] Miura S, Kiguchi M and Murakoshi K 2007 *Surf. Sci.* **601** 287
- [10] Denver H, Heiman T, Martin E, Gupta A and Borca-Tasciuc D A 2009 *J. Appl. Phys.* **106** 064909
- [11] Su H L, Ji G B, Tang S L, Chen W, Li Z, Gu B X and Du Y W 2005 *J. Appl. Phys.* **97** 116104
- [12] Xu J X, Huang X M, Xie G Z, Fang Y H and Liu D Z 2005 *Mater. Lett.* **59** 981
- [13] Lonjon A, Laffont L, Demont P, Dantras and Lacabanne C 2009 *J. Phys. Chem. C* **113**, 12002
- [14] Vidhate S, Shaito A, Chung J and D'Souza N A 2008 *J. Appl. Polym. Sci.* **112** 254
- [15] Wang M, Shi J H, Pramoda K P and Goh S H 2007 *Nanotechnology* **18** 235701
- [16] Cebe P and Runt J 2004 *Polymer* **45** 1923
- [17] Dillon D, Tenneti, Li K, Ko F, Sics I and Hsiao B 2006 *Polymer* **47** 1678
- [18] Clements J, Davies G R, Ward I M 1992 *Polymer* **33** 1623
- [19] Schamm S and Zanchi G 2003 *Ultramicroscopy* **96** 559
- [20] Cheynet M C and Pantel R 2006 *Micron* **37** 377
- [21] Wang Y Y, Zhang H and Dravid V P 1993 *Ultramicroscopy* **52** 523
- [22] Walton A S, Allen C S, Critchley K, Gorzny M L, McKendry J E, Brydson R M D, Hickey B J and Evans S D 2007 *Nanotechnology* **18** 065204
- [23] Tanaka H, Yukawa H and Nishi T 1988 *Macromolecules* **21** 2463
- [24] Moreira R L, Saint-Gregoire P and Latour M 1989 *Phase Transitions* **14** 243
- [25] Gregorio R J and Botta M M 1998 *J. Polym. Sci.: Part B: Polym. Physics.* **36** 403
- [26] Wang J W, Shen Q D and Yang C Z 2004 *Macromolecules* **37** 2294
- [27] Forster R J and Keane L 2003 *J. Electroanal. Chem.* **554** 345
- [28] Balberg I and Binenbaum N 1984 *Phys. Rev. Lett.* **52** 1465
- [29] Deng H, Zhang R, Bilotti E, Loos J and Peijs T 2009 *J. Appl. Polym. Sci.* **113** 742
- [30] Alvarez M P, Poblete V H, Pilleux M E and Fuenzalida V M 2006 *J. Appl. Polym. Sci.* **99** 3005
- [31] Kaempgen M, Duesberg G S and Roth S 2005 *Appl. Surf. Sci.* **252** 425

Figures captions

Figure 1. SEM Image and EDX spectrum of Au NWs after complete removal of AAO membrane and dispersion in acetone.

Figure 2. SEM image of the cryofractured surface of Au NW/P(VDF-TrFE) nanocomposites with 7.7 vol% Au content.

Figure 3. (a) HAADF image of Au NWs. (b) VEEL spectrum Au NWs.

Figure 4. DSC thermograms upon cooling of: P(VDF-TrFE) (\times) and Au NWs filled P(VDF-TrFE) nanocomposites with 15 vol% (\square), 25 vol% (\circ) and 30 vol% (Δ).

Figure 5. Degree of crystallinity χ_c of P(VDF-TrFE) matrix as a function of Au volume fraction and particle size: (\blacksquare) Au NWs, (\circ) 500 nm, (Δ) 10 μm . Lines correspond to the best-fitting.

Figure 6. (a) Deconvoluted exothermic peaks T_{c1} and T_{c2} associated with the ferro-para electric transition. (b) Enthalpy ratio of ΔH_{C1} to ΔH_{C2} plotted versus Au NWs volume fraction.

Figure 7. Dependence of the dc conductivity σ_{dc} versus Au NWs volume fraction at 25°C. The solid line connecting symbols is a guide for the eyes. The inset shows the log-log plot of σ_{dc} versus $(p-p_c)$ with $p_c=2.2$ vol% and $t=1.21$. The solid line corresponds to the best-fitted line.

Figure 8. Surface resistivity ρ_s dependence of Au NWs volume fraction at 25°C of sprayed Au NW/P(VDF-TrFE) nanocomposites onto glass substrate.

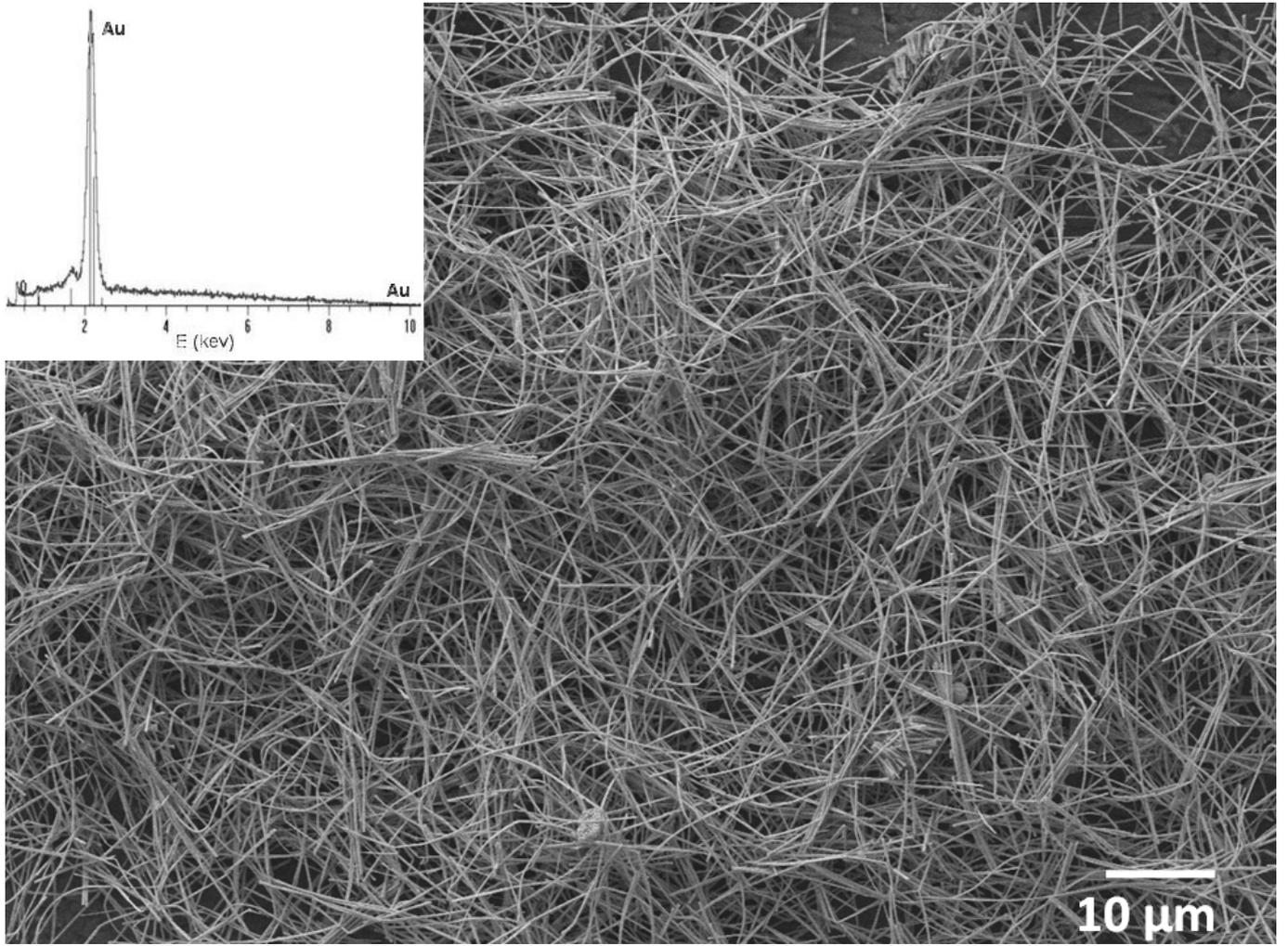


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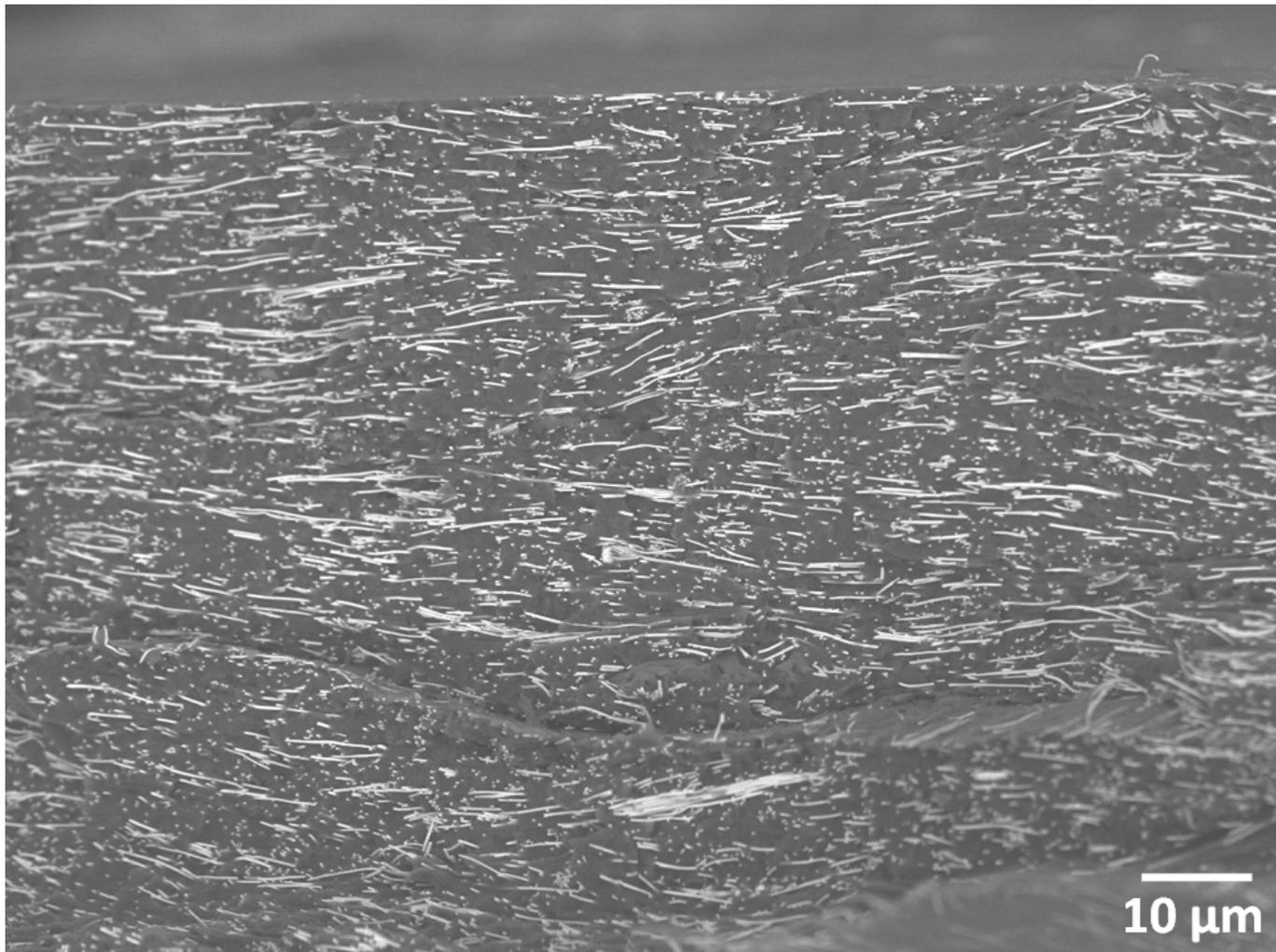


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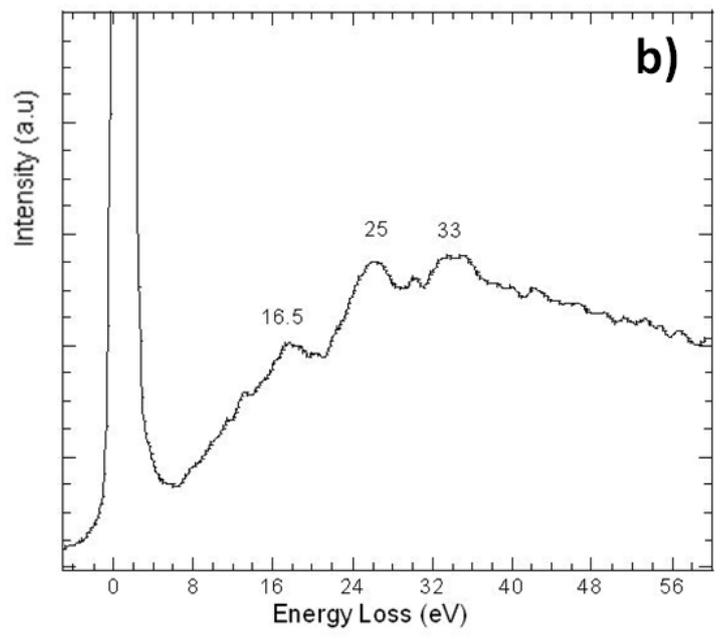
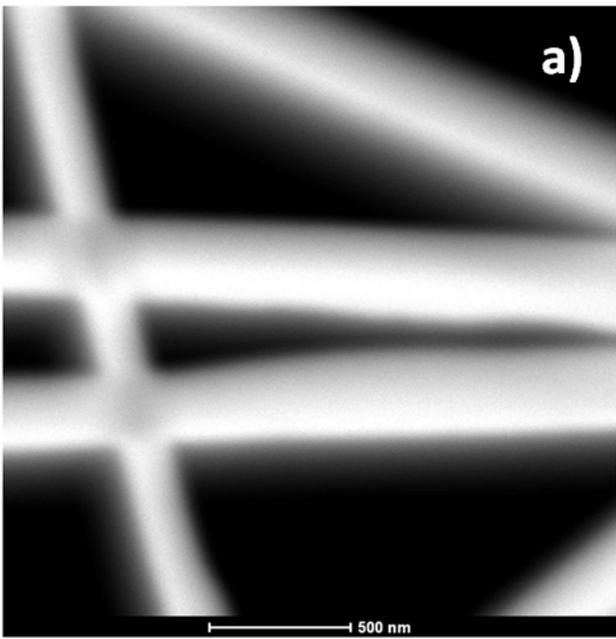


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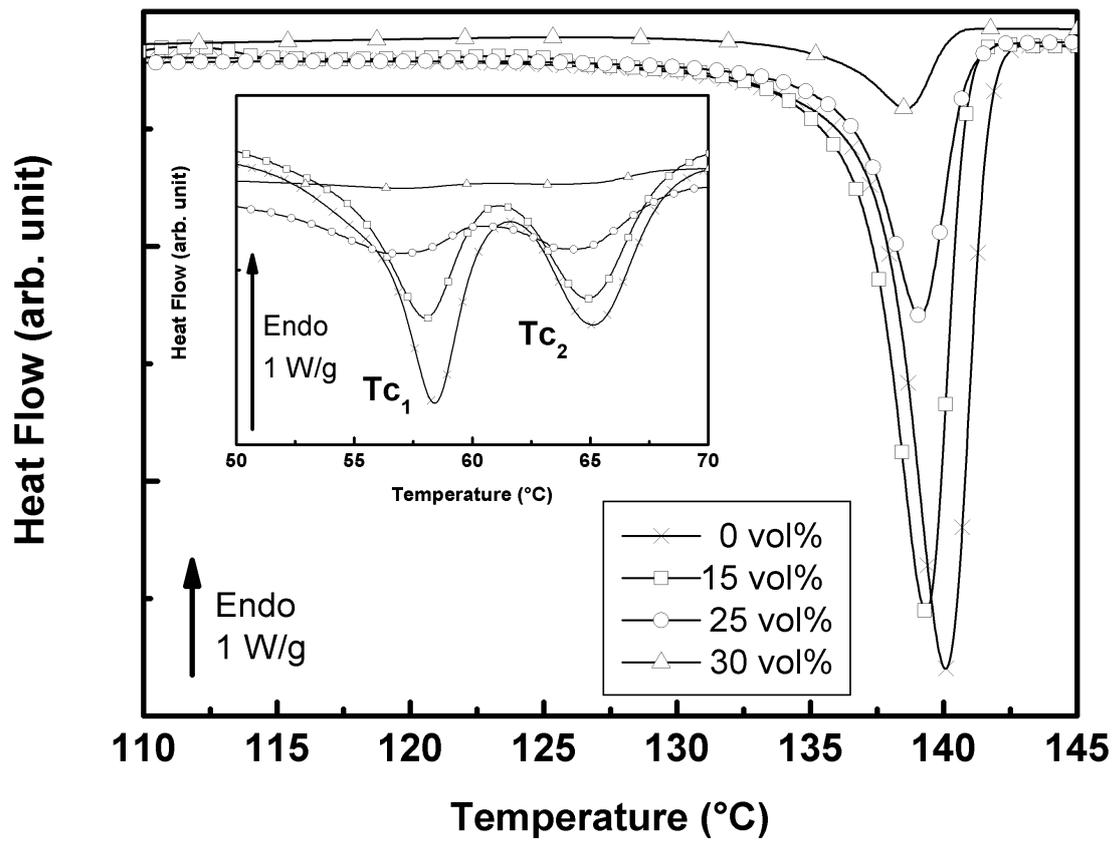


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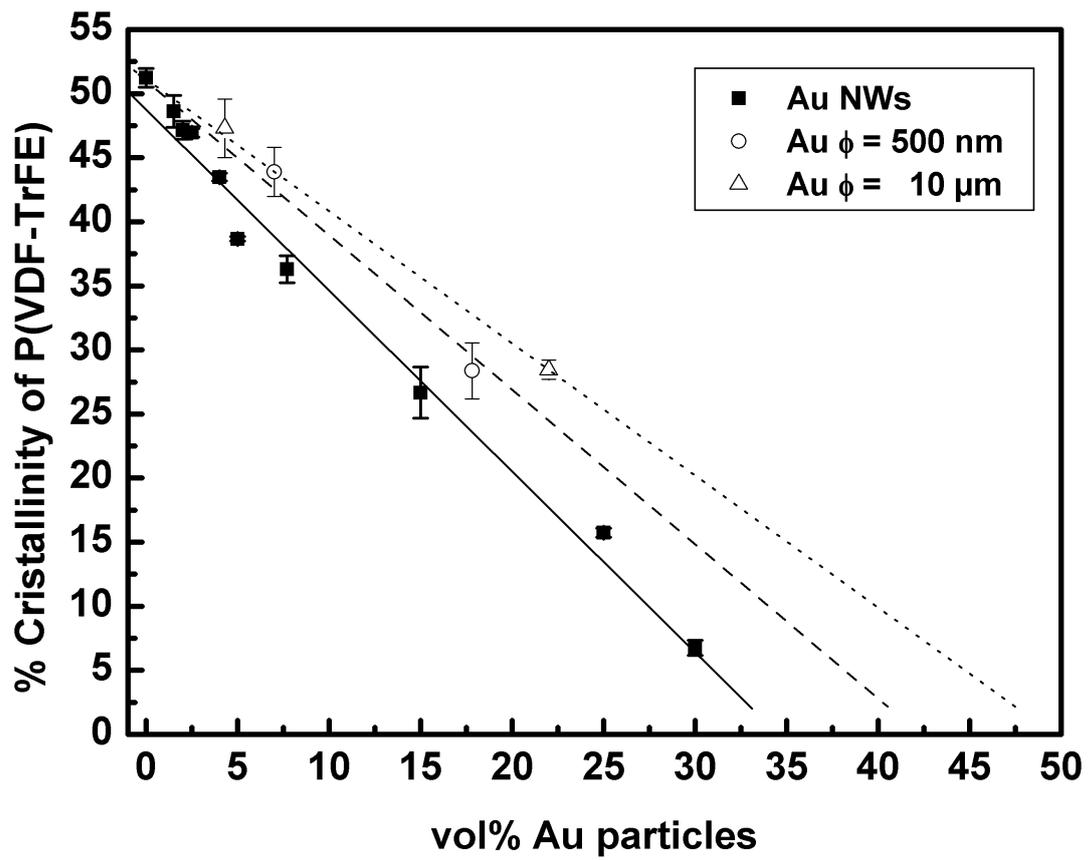


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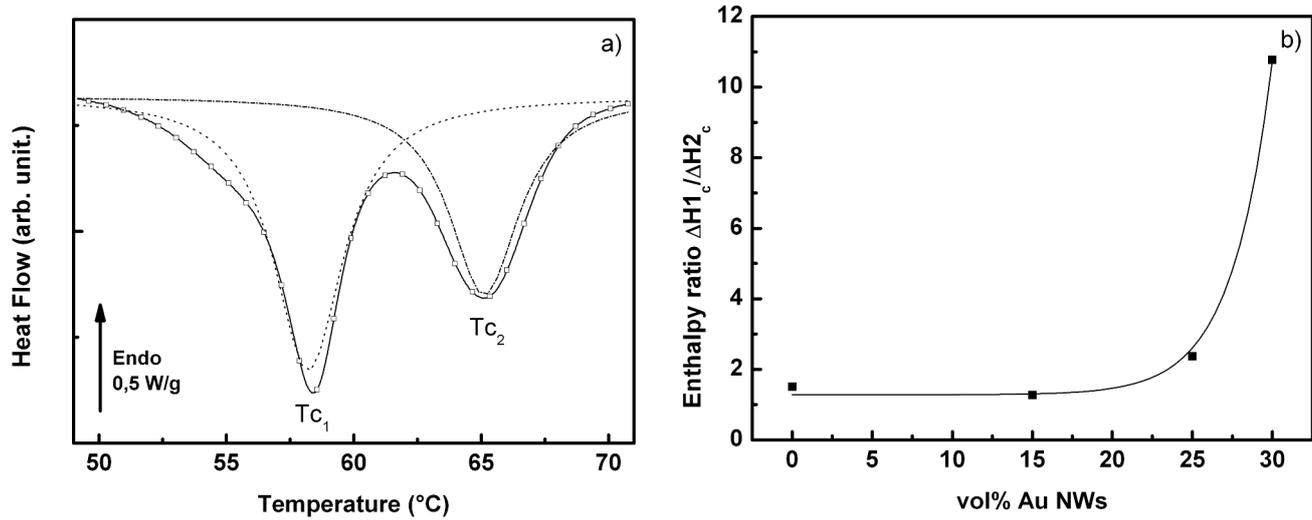


Figure 6 (figure6.tif.tif)

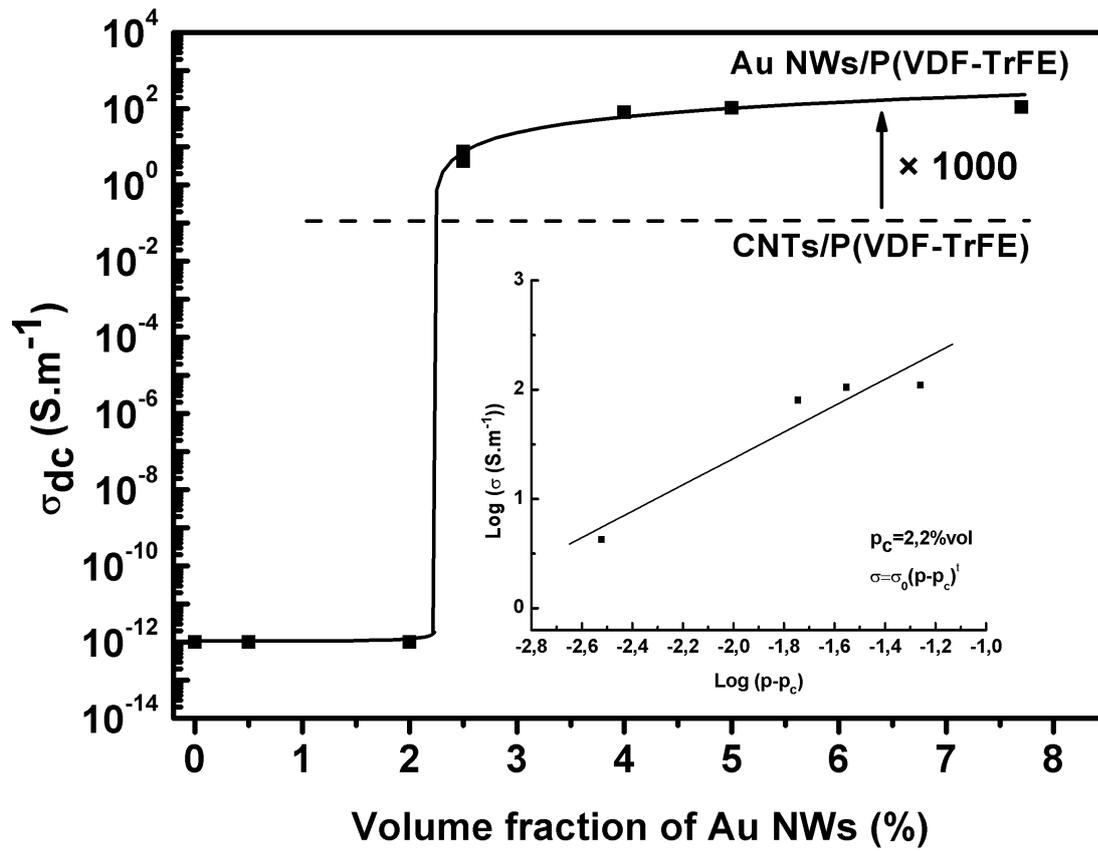


Figure 7 (figure7.tif.TIF)

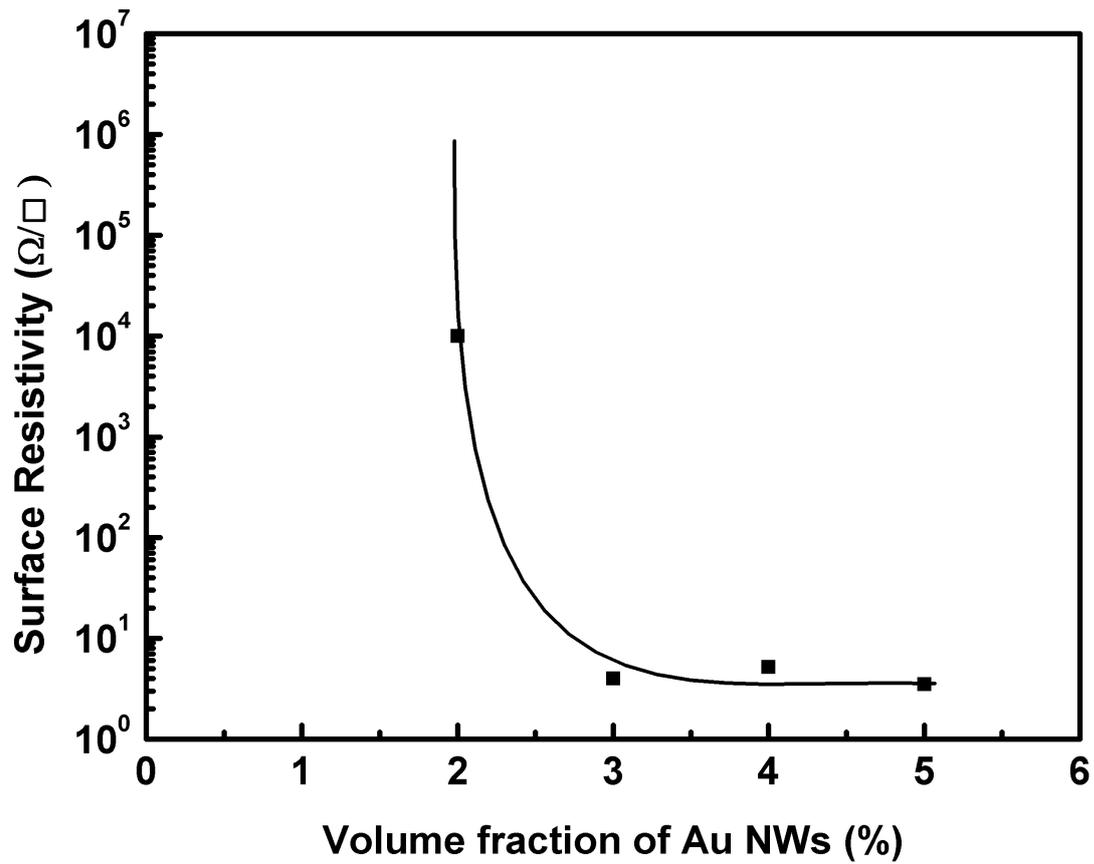


Figure 8 (figure8.tif.TIF)