Plastic Superconducting Polymer−$NbSe_2$ Nanocomposites

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The rapidly expanding field of organic−inorganic nanocomposites is generating many exciting new materials with novel properties.[1,2] The latter can derive by combining properties from the parent constituents into a single material. There is also the possibility of new properties that are unknown in the parent constituent materials. These innovative, advanced materials promise new applications in many fields such as mechanically reinforced lightweight components,[3,4] nonlinear optics,[5] battery cathodes and ionics,[6] nanowires,[7] and sensors[8] to name but a few.[9−11] It is intriguing to consider this nanocomposite concept for the preparation of plastic-like superconductors. Such materials would combine the superconducting properties of inorganic solids with the processable properties of polymers giving rise to new forms of superconductors such as polymer matrix-based wires and free-standing films, thus enabling new kinds of applications. We have made a first step in this direction by achieving the intercalation of polymers into $NbSe_2$ to produce lamellar polymer/inorganic superconducting solids with plastic-like characteristics. This work is an outgrowth of our studies of intercalative polymer nanocomposites of MoS_2[12] using the exfoliation procedure.[13] In this paper, we report the preparation of flexible metallic polymer/$NbSe_2$ nanocomposites that display bulk superconductivity. $NbSe_2$ was chosen because it has the highest superconducting transition temperature of all the layered dichalcogenide compounds (T_c = 7.2 K).[14]

A mixture of $LiBH_4$ and $NbSe_2$ in the molar ratio 2:1 was loaded into a 5 mL alumina tube, and this alumina tube was loaded into a 100 cm length, 13 mm width Pyrex tube with a gas outlet in a nitrogen atmosphere glovebox. The mixture was heated to 450 °C over 12 h under dynamic vacuum, kept at that temperature for 3 days, and cooled to 50 °C over 12 h. The resulting powder was exfoliated into single layers of $NbSe_2$ by reaction with water. The synthesis of polymer-$NbSe_2$ composites is presented in eqs 1−3.

$$NbSe_2 + xLiBH_4 \rightarrow Li_xNbSe_2 + xBH_3 + x/2H_2 \quad (1)$$

$$Li_xNbSe_2 + xH_2O \rightarrow NbSe_2(\text{monolayer}) + x/2H_2 + xLiOH \quad (2)$$

$$NbSe_2(\text{monolayer}) + \text{polymer} \rightarrow \text{polymer}-NbSe_2 \quad (3)$$

Poly(vinylpyrrolidinone) (PVP), poly(ethylene oxide) (PEO), and poly(ethylene glycol) (PEG) were intercalated by adding polymer solutions in H_2O to an aqueous single-layer suspension of $NbSe_2$. All products were thoroughly washed with the appropriate solvent to remove any extraneous polymer phase. The aqueous colloidal solution of polymer−$NbSe_2$ particles was poured and dried on a glass plate to form stable, well-ordered films. To obtain a single phase of polymer intercalation compound can be potentially difficult, since there are several possible phases with different interlamellar distances. In this work, the most dominant phases (reported here) were maximized by proper adjustment of the reactant ratios. The nanocomposite products appear to contain very little lithium (in the 0.2−0.3 wt

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Table 1. Comparison of Some Properties of the Polymer−$NbSe_2$ Intercalative Nanocomposites

polymer (M_w)	d spacing/Å	expansion of layers/Å	thermal stability under N_2/°C	conductivity (S/cm)	T_c^{onset}/K
PVP (10 000)	24.0	17.7	310[a]	140	7.1
PEO (100 000)	19.6	13.3	224	250	6.5
PEG (10 000)	18.8	12.5	233	240	7.0

[a] By thermal gravimetric analysis (TGA). TGA was performed on a Shimadzu TGA-50. The samples were heated to 800 °C at a rate of 10 °C/min under a steady flow of dry N_2 gas.

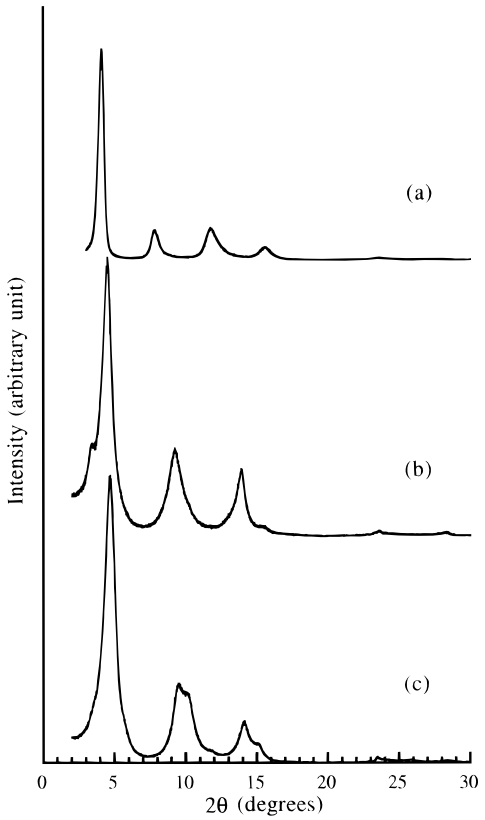
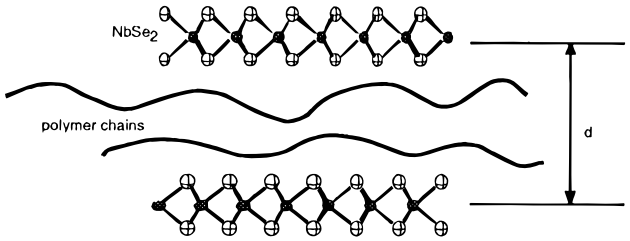


Figure 1. X-ray powder diffraction patterns of films of (a) $(PVP)_yNbSe_2$, (b) $(PEO)_{0.94}NbSe_2$, and (c) $(PEG)_{0.80}NbSe_2$. These patterns were recorded on a Rigaku Denki Rotaflex powder diffractometer equipped with a rotating anode.

% range) which corresponds to <0.1 equiv of Li/Nb.[15] This low level is not significantly above the background levels for lithium and makes a reliable assessment of the importance of lithium in these materials difficult. Because the preparation of these materials was done in air, substantial oxidation of the $[NbSe_2]^{x-}$ layers to less charged or even neutral $NbSe_2$ layers occurred.

X-ray powder diffraction patterns show that all polymer intercalates have layered structure as suggested by the intense *001* reflections and indicate well-defined mono- or bilayers of polymers in the gallery space (see Figure 1). As expected, the incorporation of polymer in $NbSe_2$ leads to an expansion along [001], consistent with the structure in Scheme 1. The interlayer expansions and other properties for the nanocomposites are given in Table 1. The largest layer separation occurs in $(PVP)_{0.14}NbSe_2$.

Scheme 1. The Long Polymer Chains Intercalated in $NbSe_2$[a]



[a] The Nb (black balls) is in a trigonal prismatic coordination environment of Se atoms (crossed balls).

Scanning electron microscopy (SEM) was done with a JEOL-JSM 35 CF microscope at an accelerating voltage of 20 kV. Samples of $(polymer)_yNbSe_2$ films were glued to the microscopic sample holder with conducting graphite paint. The SEM of $(PEG)_{0.80}NbSe_2$ composite films show the best mechanical flexibility. The flexibility of composite films depends on the nature of polymers. For $(PEG)_{0.80}NbSe_2$ and $(PEO)_{0.94}NbSe_2$, the films can be readily bent, rolled, or folded (at room temperature); however, the films of $(PVP)_{0.14}NbSe_2$ are less flexible. The plasticity of the nanocomposites probably derives from the fact that certain polymer chains are intercalated in more than one $NbSe_2$ particles, like threads through beads (see Scheme 2). That these materials can be handled as plastic sheets distinguishes them uniquely from the more classical metal atom or small molecule intercalation compounds of metal dichalcogenides.[14,16]

Charge-transport studies of the polymer nanocomposites and namely four-probe electrical conductivity were carried out on thin-film samples.[17] The room-temperature conductivity values are given in Table 1. Variable-temperature electrical conductivity measurements for $(PEO)_{0.94}NbSe_2$ (MW of polymer 100 000) show remarkably high conductivity and metallic behavior (see Figure 2). A marked feature in the electrical resistivity is an abrupt, well-defined superconducting transition at ~6.1 K (T_c^{mid}), and below 5 K, the electrical resistivity decreases to approach zero. The supercon-

(14) An excellent source of information with many references on the properties of transition-metal dichalcogenide and their intercalation compounds can be found in: *Intercalated Layered Materials*; Levy, F., Ed.; Reidel Publishing: Dordrecht, Holland, 1979.

(15) The Nb-to-Se ratio was consistently found to be very near to 1:2. Quantitative microprobe analyses of the compound were performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energy-dispersive spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 20 kV and a 1 min accumulation time.

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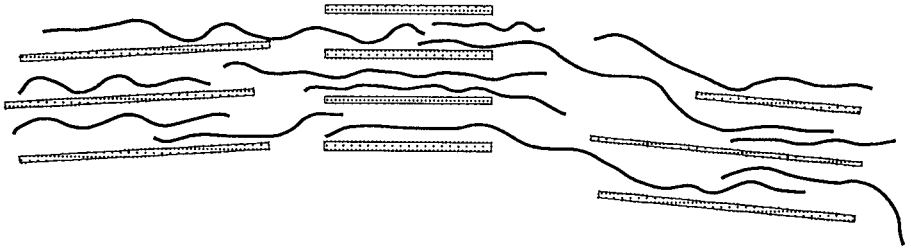
(17) Dc electric conductivity measurements were made on free-standing films. The measurements were performed in the usual four-probe geometry with 60- and 25-μm gold wires used for the current−voltage electrodes, respectively. Conductivity data were obtained with the computer-automated system described elsewhere.[17b] The gold electrodes were held in place on the sample with a conductive Ag paste. Conductivity specimens were mounted on interchangeable sample holders, and thermopower specimens were mounted on a fixed sample holder/differential heater. Mounted samples were placed under vacuum (<10^{-3} Torr) and heated to room temperature for 2−4 h to cure the Ag contacts. The temperature drift rate during an experiment was kept below 1 K/min. Typically, three to four separate variable-temperature runs were carried out for each sample to ensure reproducibility and stability. At a given temperature, reproducibility was within ±5%. (b) Lyding, J. W.; Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. Instrum. Meas.* **1988**, *37*, 76.

Scheme 2. Pictorial Representation of the Relative Arrangement of Polymer-Intercalated Particles in the Film



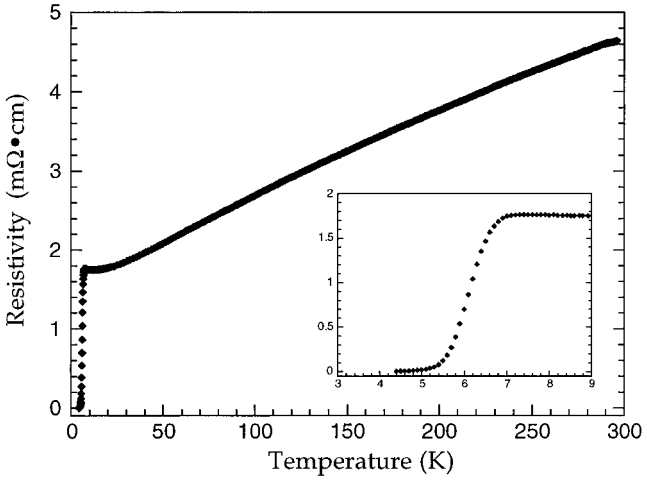


Figure 2. Four-probe variable-temperature electrical conductivity data for thin-film of $(PEO)_{0.94}NbSe_2$.

ducting transition temperature of $(PEO)_{0.94}NbSe_2$ is only slightly lower than the host $NbSe_2$, in contrast to the depressed superconducting transition temperatures reported for layered, metallic $NbSe_2$, phases when intercalated with metal ions.[16] Since in the latter cases additional carriers are injected into the $NbSe_2$ layers depressing T_c, the T_c values observed for the polymer nanocomposites are consistent with very little or no lithium in the samples.

The metal to superconductor transitions of $(polymer)_yNbSe_2$ have also been confirmed by magnetic susceptibility measurements under field-cooling (FC) and zero-field-cooling (ZFC) conditions in an applied field of 5 Oe using a dc SQUID magnetometer (Quantum, Design, MPMS2). The observed susceptibilities include contributions from the core diamagnetism and Pauli paramagnetism. The divergence of the zero-field-cooling (ZFC) and field-cooling (FC) magnetic susceptibility data (see Figure 3) indicates that the $(polymer)_yNbSe_2$ nanocomposites are type-II superconducting materials as is the $NbSe_2$ host. A comparison of the molar susceptibilities and superconductivity onset temperatures in $(PEO)_{0.14}NbSe_2$ and $(PEG)_{0.80}NbSe_2$ phases (Table 1) shows that T_c's are quite similar to that of $NbSe_2$, whereas the T_c of $(PEO)_{0.94}NbSe_2$ is only slightly lower.

Exfoliated layers of $NbSe_2$ have been used for the first time to produce plastic superconducting nanocomposite materials. This preparation method should apply to a large variety of other soluble polymers such as polyethylene, poly(propylene glycol) (PPG), methyl cellulose (MCel), poly(ethylenimine) (PEI),[18] etc., which would

(18) Tsai, H.-L.; Wang, L.; Kanatzidis, M. G., unpublished work

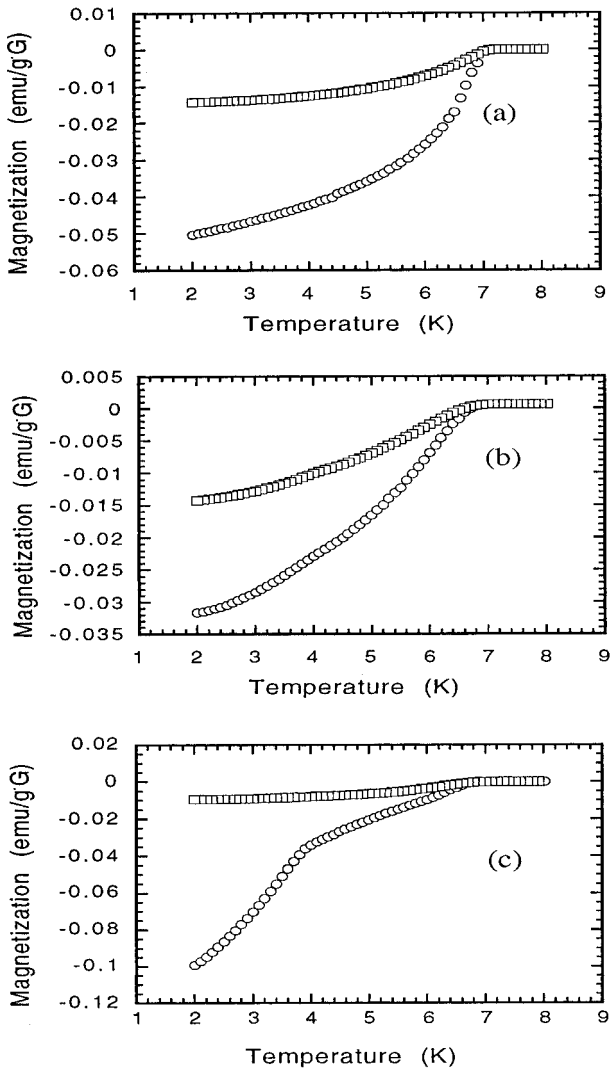


Figure 3. Low-temperature susceptibility of the (a) $(PVP)_{0.14}NbSe_2$, (b) $(PEO)_{0.94}NbSe_2$, and (c) $(PEG)_{0.80}NbSe_2$ phases recorded in a 5.0 Oe field. The circles and squares represent the field-cooling (FC) and zero-field-cooling (ZFC) data, respectively. The magnetic response of the samples was measured over the range of 2−300 K using a MPMS Quantum Design SQUID magnetometer. Samples were ground to a fine powder to minimize possible anisotropic effects and loaded into PVC containers. Corrections for the diamagnetism of the PVC sample containers were made by measuring the magnetic response of the empty container under the same conditions of temperature and field which were measured for the filled container. Core atom diamagnetism was much smaller than the magnitude of the signal measured and so was ignored. Magnetization as a function of field strength (at a constant temperature of 300 K) was first investigated to determine if the samples experienced saturation of their magnetic signal. For all samples, magnetization increased linearly with increasing field over the range investigated (100−55 000 G).

allow tuning of the mechanical properties in these materials. An interesting application of plastic-like superconductors would be in electromagnetic shielding of coils and other components in magnetic resonance imaging (MRI) units. Conducting polymers would be particularly interesting because they might result in new kinds of polymer-assisted superconductivity.[19] One next step would be to devise ways to intercalate polymers in the lamellar, high-T_c cuprate superconductors.

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