Plastic Superconducting Polymer $\text{NbSe}_2$ Nanocomposites

Hui-Lien Tsai,† J. O. Schindler,‡ Carl R. Kannewurf,‡ and Mercouri G. Kanatzidis*,†

Department of Chemistry and Center for Fundamental Materials Research Michigan State University East Lansing, Michigan 48824 Department of Electrical and Computer Engineering Northwestern University, Evanston, Illinois 60208

Received October 1, 1996

The rapidly expanding field of organic–inorganic nanocomposites is generating many exciting new materials with novel properties. The latter can derive from combining polymer and inorganics to produce lamellar polymer/inorganic superconducting solids with plastic-like characteristics. This work is an outgrowth of studies of intercalative polymer nanocomposites of $\text{MoS}_2$-using the exfoliation procedure. In this paper, we report the preparation of flexible metallic polymer/$\text{NbSe}_2$ nanocomposites that display bulk superconductivity. $\text{NbSe}_2$ was chosen because it has the highest superconducting transition temperature of all the layered dichalcogenide compounds ($T_c = 7.2$ K).

A mixture of LiBH$_4$ and $\text{NbSe}_2$ 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 $\text{NbSe}_2$ by reaction with water. The synthesis of polymer-$\text{NbSe}_2$ composites is presented in eqs 1–3.

$$\text{NbSe}_2 + x\text{LiBH}_4 \rightarrow \text{Li}_x\text{NbSe}_2 + x\text{BH}_3 + x/2\text{H}_2$$ (1)

$$\text{Li}_x\text{NbSe}_2 + x\text{H}_2\text{O} \rightarrow \text{NbSe}_2(\text{monolayer}) + x/2\text{H}_2 + x\text{LiOH}$$ (2)

$$\text{NbSe}_2(\text{monolayer}) + \text{polymer} \rightarrow \text{polymer}–\text{NbSe}_2$$ (3)

Poly(vinylpyrrolidone) (PVP), poly(ethylene oxide) (PEO), and poly(ethylene glycol) (PEG) were intercalated by adding polymer solutions in H$_2$O to an aqueous single-layer suspension of $\text{NbSe}_2$. All products were thoroughly washed with the appropriate solvent to remove any extraneous polymer phase. The aqueous colloidal solution of polymer–$\text{NbSe}_2$ 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% range).

1 Michigan State University.
2 Northwestern University.
3 To whom correspondence should be addressed. E-mail: kanatzidis@cemvax.cem.msu.edu.


Table 1. Comparison of Some Properties of the Polymer–NbSe₂ Intercalative Nanocomposites

<table>
<thead>
<tr>
<th>Polymer (Mₙ)</th>
<th>d spacing/Å</th>
<th>expansion of layers/Å</th>
<th>thermal stability under N₂/°C</th>
<th>Conductivity (S/cm)</th>
<th>T_{onset}/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVP (10000)</td>
<td>24.0</td>
<td>17.7</td>
<td>310*</td>
<td>140</td>
<td>7.1</td>
</tr>
<tr>
<td>PEO (100000)</td>
<td>19.6</td>
<td>13.3</td>
<td>224</td>
<td>250</td>
<td>6.5</td>
</tr>
<tr>
<td>PEG (10000)</td>
<td>18.8</td>
<td></td>
<td>233</td>
<td>240</td>
<td>7.0</td>
</tr>
</tbody>
</table>

* 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 N₂ gas.

Figure 1. X-ray powder diffraction patterns of films of (a) (PVP)₀.₁₄NbSe₂, (b) (PEO)₀.₉₄NbSe₂, and (c) (PEG)₀.₈₀NbSe₂. 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. 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 NbSe₂ layers to less charged or even neutral NbSe₂ layers occurred.

Scheme 1. The Long Polymer Chains Intercalated in NbSe₂

% range) which corresponds to <0.1 equiv of Li/Nb. 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 NbSe₂ layers to less charged or even neutral NbSe₂ 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 NbSe₂ 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)₀.₁₄NbSe₂.

Scanning electron microscopy (SEM) was done with a JEOL-JSM 35 CF microscope at an accelerating voltage of 20 kV. Samples of (polymer)₀.₇₄NbSe₂ films were glued to the microscopic sample holder with conducting graphite paint. The SEM of (PEG)₀.₈₀NbSe₂ composite films show the best mechanical flexibility. The flexibility of composite films depends on the nature of polymers. For (PEG)₀.₈₀NbSe₂ and (PEO)₀.₉₄NbSe₂, the films can be readily bent, rolled, or folded (at room temperature); however, the films of (PVP)₀.₁₄NbSe₂ are less flexible. The plasticity of the nanocomposites probably derives from the fact that certain polymer chains are intercalated in more than one NbSe₂ 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 or small molecule intercalation compounds of metal dichalcogenides.

Charge-transport studies of the polymer nanocomposites and namely four-probe electrical conductivity were carried out on thin-film samples. The room-temperature conductivity values are given in Table 1. Variable-temperature electrical conductivity measurements for (PEO)₀.₉₄NbSe₂ (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_{onset}), and below 5 K, the electrical resistivity decreases to approach zero. The supercon-
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)\( NbSe_2 \) 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)\( NbSe_2 \) 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 also 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 (MCe), poly(ethyleneimine) (PEI),\(^{18} \) etc., which would

---

\(^{18} \) Tsai, H.-L.; Wang, L.; Kanatzidis, M. G., unpublished work
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. One next step would be to devise ways to intercalate polymers in the lamellar, high-$T_c$ cuprate superconductors.

Acknowledgment. Financial support from the National Science Foundation (DMR-93-06385) is gratefully acknowledged. This work made use of the SEM facilities of the Center for Electron Optics at Michigan State University. At Northwestern University this work made use of Central Facilities supported by the NSF through the Materials Research Center.