Synthesis and Exfoliation of Alkyl-pyridinium/Bi2212 Nanohybrids

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Abstract. Nanohybrids of superconducting Bi2Sr2CaCu2O8+δ (Bi2212) with alkyl-pyridinium salts were synthesized by a stepwise intercalation method. HgBr2 was intercalated into Bi2212 crystal to prepare a precursor before intercalation of alkyl-pyridinium ions. Alkyl-pyridinium (Py-CnH2n+1, where Py = pyridine and n = 4, 12 and 16) was adopted as guest intercalants. Nanohybrids were characterized by X-ray powder diffraction. It is found that the gallery height of Bi2212 host is expanded from 3.07 nm to 8.69 nm (Δc = 5.61 nm) in Py-C16H33/Bi2212. We were successful in preparing transparent colloidal suspension of Py-C16H33/Bi2212 nanohybrid in organic solvent. This colloid is found to be stable for 6 days. Ultrathin films assembled by the layer-by-layer technique from Bi2212 colloids with a cationic polymer were fabricated.

1. Introduction

A systematic application of intercalation techniques to layered superconducting oxides enables us to open a new chapter in the development of nanohybrids with various functions. Many species were tried to be intercalated into Bi2Sr2CaCu2O8+δ (Bi2212) superconductors chemically or electrochemically. HgX2(X = Br and I) intercalated Bi2212 was reported with a large expansion of the basal plane [1-2]. Recently, organic molecules, such as bialkyl-pyridinium tetrabromomercurate (Py-CnH2n+1)2HgBr4 (n = 1~12) [3] and di-iodobis(pyridine)mercury(II) HgI2Py2 [4], were also intercalated into Bi2212.

The layered bulk materials are exfoliated into individual sheets, so-called nanosheets, in solution to form colloidal suspensions, being expected to open a new route to synthesize nanoparticles and thin films. One of the most important and attractive aspects of the exfoliated nanosheets is that various nanostructures can be fabricated using them as two-dimensional building blocks. It is even possible to tailor superlattice-like assemblies, incorporating a wide range of materials, such as polymers, into the nanosheets [5-6]. From a viewpoint of application, the intercalation of large organic molecules provides a new synthetic route to high-Tc superconducting thin-film and nanoparticles by separating superconducting blocks into isolated single sheets.

It this study, we have fabricated the PDDA/Bi2212 multilayer films for the first time via layer-by-layer technique from Bi2212 colloids.
2. Experimental

The chemicals used in this study were of reagent grade or higher purity. 1-butylpyridinium bromide \( \text{CH}_3(\text{CH}_2)_3\text{NC}_5\text{H}_5^{+}\text{Br}^- \) (Py-C \( _4\text{H}_9 \)), dodecylpyridinium bromide monohydrate \( \text{CH}_3(\text{CH}_2)_11\text{NC}_5\text{H}_5^{+}\text{Br}^--\text{H}_2\text{O} \) (Py-C \( _{12}\text{H}_{25} \)), hexadecylpyridinium bromide monohydrate \( \text{CH}_3(\text{CH}_2)_15\text{NC}_5\text{H}_5^{+}\text{Br}^--\text{H}_2\text{O} \) (Py-C \( _{16}\text{H}_{33} \)), mercury(II) bromide (HgBr \( _2 \)), acetone and polydiallyldimethylammonium (PDDA, \( M_w = 1\sim2 \times 10^5 \)) were used as received.

Bi\(_{2212}\) hosts were prepared by the conventional solid-state reaction. Powders of Bi\(_2\)O\(_3\), SrCO\(_3\), CaCO\(_3\), Y\(_2\)O\(_3\) and CuO were mixed with molar ratios of Bi:Sr:Ca:Y:Cu = 2.0:2.0:0.8:0.2:2.0, and calcined at 800 °C for 20 h in air. Then the calcined powder was pressed into pellets and sintered at 870 °C for 24 h in air with some intermittent grindings.

The organic-inorganic hybrids Py-C\(_n\)H\(_{2n+1}\)/Bi\(_{2212}\) (Py = pyridine and \( n = 4, 12, \text{ or } 16 \)) were synthesized by the stepwise intercalation route. The HgBr\(_2\) intercalated Bi\(_{2212}\) was first synthesized by vapor transport reaction between Bi\(_{2212}\) and HgBr\(_2\) in a vacuum-sealed quartz tube. The HgBr\(_2\) intercalated Bi\(_{2212}\) was easily obtained by heating the pure compounds with excess HgBr\(_2\) at 230 °C for 4 h.

Then, the intercalation of the organic molecule was carried out by the solvent-mediated reaction between the HgBr\(_2\) intercalated Bi\(_{2212}\) and alkyl-pyridinium. The HgBr\(_2\) intercalated Bi\(_{2212}\) was easily obtained by heating the pure compounds with excess HgBr\(_2\) at 230 °C for 4 h.

Exfoliation of Bi\(_{2212}\) was carried out by sonicating the alkyl-pyridinium intercalated Bi\(_{2212}\) in acetone solvent for 200 min, which was kept in an ice bath to prevent overheating of the suspension.

Multilayer ultrathin films of the Bi\(_{2212}\) nanosheets were fabricated by applying the layer-by-layer assembly procedure [6]. The diffraction-free Si substrates were cleaned by treatment in a bath of methanol/HCl (1/1 v/v) and then concentrated H\(_2\)SO\(_4\) for 20 min each. The substrate was immersed in an aqueous solution of PDDA (20 g dm\(^{-3}\)) for 20 min, followed by rinsing with a copious amount of water. The substrate was then dipped in a colloidal suspension (1 g dm\(^{-3}\)) of Bi\(_{2212}\) nanosheets for 20 min and washed with acetone. A series of deposition operations for the PDDA and Bi\(_{2212}\) nanosheets was repeated by \( n \) times to produce multilayer films of (PDDA/Bi\(_{2212}\))\(_n\). The resulting films were dried under vacuum.

The formation of hosts and intercalation compounds was checked by X-ray diffraction (XRD) using Rigaku RINT Ultima equipped with Ni-filtered CuK\(\alpha\) radiation.

3. Results and discussion

3.1. Alkyl-pyridinium/Bi\(_{2212}\) nanohybrids

It is well known that the superconducting properties of the oxide high-\(T_C\) superconductors are very sensitive to the hole concentration. The hole concentration can be easily varied by substituting the divalent Ca ion by trivalent Y. The highest \(T_C\) can be obtained at the optimum hole concentration of \( x = 0.2 \) in Bi\(_2\)Sr\(_2\)Ca\(_{1-x}\)Y\(_x\)Cu\(_2\)O\(_{8+d}\).

A large molecule, such as alkyl-pyridinium ion, cannot be intercalated directly into the narrow Bi-O layers of Bi\(_{2212}\) host. To increase the gallery height between the Bi-O layers, we prepare the HgBr\(_2\)/Bi\(_{2212}\) precursors prior to the alkyl-pyridinium ion intercalation. The XRD data obtained are summarized in Table 1. In this study, all XRD peaks are assigned by the basic double-block model, although the \((a + b)/2\) shift of the cuprate block may not occur upon HgBr\(_2\) intercalation. The observed lattice expansion along the \(c\)-axis \( \Delta c = 1.266 \text{ nm for HgBr}\(_2\)/Bi\(_{2212}\) precursor is in good agreement with 1.26 nm of the reported value [1-2].

Figure 1 shows the XRD pattern of Py-C\(_4\)H\(_8\)/Bi\(_{2212}\) nanohybrid. Here, the open triangle denotes the diffraction from unreacted HgBr\(_2\)/Bi\(_{2212}\) precursor, and the cross means unknown phase. As the
basal expansion of $\Delta c/2 = 1.076$ nm is shorter than the Py-C$_4$H$_9$ long axis (1.092 nm), Py-C$_4$H$_9$ monolayer is considered to lie tilted at an angle of 80º to Bi2212 layers.

Table 1. XRD data for Bi2212 nanohybrids.

| Sample          | $a$ (nm) | $b$ (nm) | $c$ (nm) | $\Delta c$ (nm) |
|-----------------|----------|----------|----------|-----------------|
| Bi2212          | 0.540    | 0.540    | 3.069    | —               |
| HgBr$_2$/Bi2212 | 0.540    | 0.540    | 4.335    | 1.266           |
| Bi2212          | 0.540    | 0.541    | 3.068    | —               |
| Py-C$_4$H$_9$/Bi2212 | 0.544  | 0.542    | 5.220    | 2.152           |
| Bi2212          | 0.541    | 0.543    | 3.078    | —               |
| Py-C$_{12}$H$_{25}$/Bi2212 | 0.543 | 0.544    | 8.666    | 5.588           |
| Bi2212          | 0.543    | 0.544    | 3.078    | —               |
| Py-C$_{16}$H$_{33}$/Bi2212 | 0.543 | 0.544    | 8.685    | 5.606           |

Figure 2 shows the XRD pattern of Py-C$_{12}$H$_{25}$/Bi2212 nanohybrid. The basal expansion of $\Delta c/2 = 2.794$ nm is narrowed compared with 3.16 nm of the reported value [3]. As Py-C$_{12}$H$_{25}$/Bi2212 nanohybrid of $\Delta c/2$ is longer than the Py-C$_{12}$H$_{25}$ long axis (2.100 nm), Py-C$_{12}$H$_{25}$ bilayer is incorporated into the host gallery and is considered to lie tilted at an angle of 42º to Bi2212 layers.

Figure 3 shows the XRD pattern of Py-C$_{16}$H$_{33}$/Bi2212 nanohybrid. As all the detectable XRD peaks can be assigned into the Py-C$_{16}$H$_{33}$/Bi2212 nanohybrid, the single-phase nanohybrid is obtained, which contains Py-C$_{16}$H$_{33}$ between each Bi2212 layer. As the basal expansion of $\Delta c/2 = 2.803$ nm is longer than the Py-C$_{16}$H$_{33}$ long axis (2.604 nm), Py-C$_{16}$H$_{25}$ bilayer are considered to lie tilted at an angle of 33º to Bi2212 layers.
3.2. Bi2212 colloids
Various layered compounds have been delaminated into their colloid. A clear Tyndall light scattering can be observed, indicating the presence of exfoliated Bi2212 nanosheets dispersed in acetone. The resulting colloidal suspension is found to be stable for 1 day in the case of Py-C4H9/Bi2212, for 6 day in Py-C12H25/Bi2212 and for 6 day in Py-C16H33/Bi2212 nanohyrid.

3.3. PDDA/Bi2212 multilayer films
We are successful in fabricating the PDDA/Bi2212 multilayer films by the layer-by-layer technique from Py-C12H25/Bi2212 colloids. Figure 4 shows the XRD pattern of (PDDA/Bi2212)n films. The XRD data obtained are summarized in Table 2. The observed lattice expansion along the c-axis ∆c/2 = 1.089 nm for PDDA/Bi2212 is in good agreement with 1.09 nm of the reported value in manganese oxide [7]. This diffraction feature is attributable to a repeating periodicity of bilayers of inorganic Bi2212 nanosheet and PDDA polymer, and its enhancement with increasing numbers of deposition cycles indicates the progressive growth of its nanostructured assemblies.

Further spectroscopic studies on the electronic structures of the PDDA/Bi2212 multilayer films will accelerate their application to the superconducting devices.

Table 2. XRD data for (PDDA/Bi2212)10 multilayer film.

| Sample            | a (nm) | b (nm) | c (nm) | ∆c (nm) |
|-------------------|--------|--------|--------|---------|
| Bi2212            | 0.541  | 0.543  | 3.078  | —       |
| HgBr2/Bi2212      | 0.543  | 0.542  | 4.298  | 1.220   |
| Py-C12H25/Bi2212  | 0.543  | 0.544  | 8.666  | 5.588   |
| PDDA/Bi2212       | 0.545  | 0.546  | 5.255  | 2.177   |

4. Conclusion
Nanohybrids of superconducting Bi2212 with alkyl-pyridinium ion are synthesized by a stepwise method. HgBr2 is intercalated into Bi2212 crystal to prepare the precursors before intercalation of alkyl-pyridinium ions. Py-C4H9, Py-C12H25 and Py-C16H33 are adopted as guest intercalants. It is found that the gallery height of Bi2212 host is expanded by 5.606 nm in Py-C16H33/Bi2212 nanohybrid. Py-C16H33/Bi2212 nanohybrid is exfoliated into single layers in acetone, which is found to be stable for 6 days after ultrasonication. PDDA/Bi2212 multilayer films have been fabrication for the first time via layer-by-layer self-assembly and spontaneous flocculation.

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