Synthesis and Characterization of Alkylammonium/Bi2212 Nanohybrids

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Abstract. Single-phase nanohybrids of Bi₂Sr₂CaCuO₈₊ₓ (Bi2212) with alkylammonium salts have been synthesized for the first time by a stepwise intercalation method. To increase the gallery height between the Bi-O layers of Bi2212 crystal, intercalated precursor was prepared by the chemical vapor transport technique with Bi2212 and HgBr₂ in a sealed quartz ampoule. Then, n-dodecyl trimethylammonium bromide (DTA:Br) or n-hexadecyl trimethylammonium bromide (HTA:Br) was intercalated into HgBr₂/Bi2212 via ion exchange method. Nanohybrids were characterized by powder X-ray diffraction (XRD). There was no trace of the pristine phase in XRD patterns for all nanohybrids, indicating that DTA or HTA ion is incorporated homogeneously into each Bi2212 layer. It is found that the gallery height of Bi2212 host is expanded from 3.08 nm to 8.22 nm (Δc = 5.14 nm) in HTA/Bi2212 nanohybrid. HTA/Bi2212 nanohybrid was exfoliated into single layers in acetone. A transparent colloid is found to be stable for 5 days after ultrasonication.

1. Introduction

Intercalation compounds are formed by inserting guest species between weakly-bound layers of host materials, usually by van der Waals force, without changing the inner crystal structure of the individual layers. Organic-inorganic hybrid materials have advantages in compositional stability and mechanical strength which make them suitable for applications.

It is well known that the high-Tc superconductors have layered structures. As for Bi₂Sr₂CaCuO₈₋ₓ⁺ₓ (Bi2212) superconductor, the crystal structure consists of perovskite blocks separated by weakly-coupled Bi-O layers. Many species were tried to be intercalated into Bi2212 superconductors chemically or electrochemically. Iodine intercalated Bi2212 (I/Bi2212) was first reported [1]. HgX₂ (X = Br and I) intercalated Bi2212 was reported with the basal plane expansion twice larger than that
of I/Bi2212 [2]. Recently, organic molecules, such as bialkyl-pyridinium tetraiodomercurate (Py-CnH2n+1)2HgI4 [3], bistrimethylsulfonium mercuric-tetraiodide (Me3S)HgI4 [4] and diiodobis(pyridine)mercury(II) HgI2Py2 [5], were also intercalated into Bi2212.

In this study, we have first synthesized the alkylammonium/Bi2212 nanohybrids, which contain the primary alkylammonium ions between all individual Bi2212 sheets.

2. Experimental

The chemicals used in this study were of reagent grade or higher purity. n-dodecyl trimethylammonium bromide CH3(CH2)11N(CH3)3Br- (DTA:Br), n-hexadecyl trimethyl ammonium bromide CH3(CH2)15N(CH3)3Br- (HTA:Br), mercury(II) bromide (HgBr2) and acetone were used as received. Distilled and deionized (DI) water was used in all preparations.

Bi2212 hosts were prepared by the solid-state reaction of Bi2O3, SrCO3, CaCO3, Y2O3, and CuO powders (1-2 µm, Soekawa Chemicals) [6-10]. They were mixed in the ratio of Bi:Sr:Ca:Y:Cu = 2:2:0.8:0.2:2. The well-mixed powders were sintered at 800°C for 20 h in air. They were pulverized, mixed, palletized and sintered at 870°C for 24 h with air-flow. This process was repeated twice in order to improve the crystallinity and the superconducting transition temperature TC.

Intercalated precursor was prepared by the chemical vapor transport technique with host and HgBr2 in a vacuum-sealed quartz ampoule. The molar ratio of host and guest was 1:5. HgBr2/Bi2212 precursor was synthesized by heating Bi2212 host and HgBr2 at 230°C for 4 h [2].

Synthesis of DTA/Bi2212 nanohybrid was carried out in aqueous solution or in organic solution. An aqueous solution was prepared from 3.7 mmol of DTA:Br with 200 mL of DI water. 0.8 g of well-ground powder of HgBr2/Bi2212 precursor was dispersed into the DTA solution by ultrasonication for 30 min at ambient temperature. The mixtures were stirred for a controlled time. The nanohybrids were then collected by filtration, washed several times with small amounts of DI water, and air-dried overnight. Alkylammonium/Bi2212 nanohybrids were also synthesized in organic solution. The molar ratio of HgBr2/Bi2212 precursor and alkylammonium salt was 1:3. They were mixed with 15 ml of acetone in a flask. The mixture was vigorously stirred at 60°C for 6 h. The black solid was filtered and washed with acetone and diethyl ether to remove the excess reactant, and then air-dried.

X-ray powder diffraction (XRD) data were collected on a Rigaku RINT Ultima+ diffractometer using Ni-filtered CuKα radiation.

3. Results and discussion

3.1. Alkylammonium/Bi2212 nanohybrids

It is well known that the superconducting properties of the oxide high-Tc superconductors are very sensitive to the hole concentration. In the Bi2212 system, the hole concentration can be easily varied by substituting the divalent Ca ion by trivalent rare-earth ions, e. g. Y [6-7, 11]. In this study, host Bi2212 single crystals were prepared at Y content x = 0.2, where the highest TC can be obtained at the optimum hole concentration in the Bi2Sr2Ca1-xYxCu2O8+d system [6-7].

| Table 1. XRD data for Bi2212 nanohybrids. |
|------------------------------------------|
| Sample | a (nm) | b (nm) | c (nm) | Δc (nm) |
|--------|--------|--------|--------|---------|
| Bi2212 | 0.539  | 0.543  | 3.074  | —       |
| HgBr2/Bi2212 | 0.540  | 0.544  | 4.332  | 1.258   |
| DTA/Bi2212a | 0.539  | 0.541  | 5.121  | 2.047   |
| Bi2212 | 0.541  | 0.543  | 3.078  | —       |
| HgBr2/Bi2212 | 0.540  | 0.540  | 4.335  | 1.257   |
| DTA/Bi2212b | 0.540  | 0.542  | 4.197  | 1.119   |
| Bi2212 | 0.541  | 0.543  | 3.078  | —       |
| HgBr2/Bi2212 | 0.540  | 0.540  | 4.335  | 1.257   |
| HTA/Bi2212 | 0.540  | 0.546  | 8.223  | 5.145   |

* Prepared in aqueous solution.  b Prepared in organic solution.
A large molecule, such as alkylammonium ion, cannot be intercalated directly into the narrow Bi-O layers of Bi2212 host. To increase the gallery height between the Bi-O layers, we prepare the HgBr2/Bi2212 precursors prior to the alkylammonium 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 HgBr2 intercalation. The observed lattice expansion along the \(c\)-axis for HgBr2/Bi2212 precursor, \(\Delta c = 1.258\) nm, is in good agreement with 1.26 nm of the reported value [2-3]. This suggests that the HgBr2 monolayer is intercalated between the Bi-O double layers of Bi2212 host crystal.

Arrangement of alkylammonium ions in the interlayer space have been studied and shown to depend on the layer charge of host materials. In the host gallery with a small layer charge, alkylammonium ions are placed with their long axis parallel to layers. On the other hand, in the host layers with a large layer charge, the molecular axes in alkylammonium ions are tilted to the layers with certain angles.

Figure 1 shows the XRD patterns of the sample during synthesis of DTA/Bi2212 nanohybrid in aqueous solution. Here, the solid triangle denotes the diffraction from the stage-2 compound of Bi2212 with H2O monolayer, and the cross means that from unknown phase. Peaks at 3.5° \((d = 2.56\) nm) in figures 1(b)-(d) correspond to the (002) diffraction from DTA/Bi2212 nanohybrid. The size of DTA ion can be estimated as 0.477 nm × 1.86 nm [12-13]. From the deference in the interlayer spacing, alkylammonium ions are considered to lie tilted at an angle of 33°. The tilting angles of the alkylammonium ions are retorted to be 56-90° in TaS2 [12] and 0-65° in MnPS3 [13]. This difference may be resulted from the different layer charges of the host materials.

DTA/Bi2212 nanohybrid synthesized in acetone, however, shows a different basal expansion, as shown in figure 2. Broad beak at 4.2° \((d = 2.10\) nm) in figure 2(b) suggests the lattice expansion of \(\Delta c = 1.119\) nm, indicating a tilt of DTA ions by 18° to Bi2212 layers.

**Figure 1.** XRD patterns of the sample during DTA/Bi2212 nanohybrid synthesis in DI water; (a) pristine Bi2212 host, (b) 24 h, (c) 48 h, (d) 72 h.

**Figure 2.** XRD patterns of DTA/Bi2212 nanohybrid prepared in acetone; (a) pristine Bi2212 host and (b) DTA/Bi2212.

**Figure 3.** XRD patterns of HTA/Bi2212 nanohybrid prepared in acetone; (a) pristine Bi2212 host and (b) HTA/Bi2212.
Figure 3 shows the XRD pattern of HTA/Bi2212 nanohybrid synthesized in acetone. The basal expansion of $\Delta c/2 = 2.573$ nm is longer than the HTA long axis (1.86 nm). This indicates that the HTA bilayer is incorporated into Bi2212 gallery tilting at 33° to Bi2212 layers.

3.2. Bi2212 colloids
Various layered compounds have been delaminated into their colloidal single-sheets via the so-called soft chemical techniques, which require neither high temperature nor ultrahigh vacuum for preparations. The resulting nanosheets exhibit novel physical and chemical properties due to an extremely small thickness of around 1 nm.

Treatment of 0.05 g of alkylammonium/Bi2212 nanohybrid with acetone of 100 mL after ultrasonication for 200 min in the ice bath yields a transparent colloidal solution. A clear Tyndall light scattering can be observed, indicating the presence of exfoliated Bi2212 nanosheets dispersed in acetone. The resulting colloidal suspension is stable for 1 day in the case of DTA/Bi2212 and for 5 days in the case of HTA/Bi2212 nanohybrid.

Further study will be needed to prepare the more stable colloidal suspension of Bi2212 nanosheets, which are useful as a building block for the fabrication of a wide variety of functional nanomaterials.

4. Conclusion
The single-phase stage-1 intercalation nanohybrids of Bi2212 with alkylammonium ions have been synthesized for the first time via HgBr$_2$/Bi2212 precursors. DTA:Br and HTA:Br are adopted as guest intercalants. It is found that the gallery height of Bi2212 host is expanded by 5.145 nm in HTA/Bi2212 nanohybrid. HTA/Bi2212 nanohybrid is exfoliated into single layers in acetone, which is found to be stable for 5 days after ultrasonication.

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