Chapter 13

ANISOTROPIC LATTICE DISTORTION OF COMPOSITE MATERIALS OF CHIRAL Cu(II)-Co(III) OR Cu(II) COMPLEXES AND TiO$_2$

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ABSTRACT

In order to control anisotropic lattice distortion for application of solid-state battery materials, composites of chiral complexes $[CuL_2]_3[Co(CN)_6]_2 \cdot nH_2O$ (Cu-Co) or $[CuL_2][(NO_3)_2 \cdot nH_2O$ (Cu) (L = (*1R,2R*)-1,2-diaminocyclohexane) and anatase TiO$_2$ were prepared and measured powder XRD patterns under 100-300 K with a synchrotron radiation (8 keV). Characteristic IR peaks shifted by the ratio of composites (chiral complexes: TiO$_2$ = from 10:0 to 0:10). Based on variable temperature XRD patterns, a linear correlation (lnK = a/T + b) of K (=d(T)-d(0)/d(T)) values, where d(T) and d(0) are spacing of lattice plane (d = $n\lambda/(2\sin\theta)$) at T K and 0 K (extrapolated), respectively, and its deviation from ideal correlation indicates degree of anisotropic lattice distortion of the composite materials. Therefore additional chiral complexes affected on anisotropic lattice distortion of TiO$_2$, which was essentially isotropically distorted crystals.

INTRODUCTION

In recent years, social needs for rechargeable battery such as lithium ion battery and sodium ion battery are increasing in order to solve energy problem [1-5]. However, for solid-state inorganic materials of electrodes in rechargeable battery, it is stated that a regular pattern of crystal structures distort due to affects from charge-discharge and prevent diffusion of ions in solid-state. Especially, developing a sodium ion battery requires large pores more than those for lithium ion battery known and rigidity of crystalline lattice against repeated redox reactions [6].
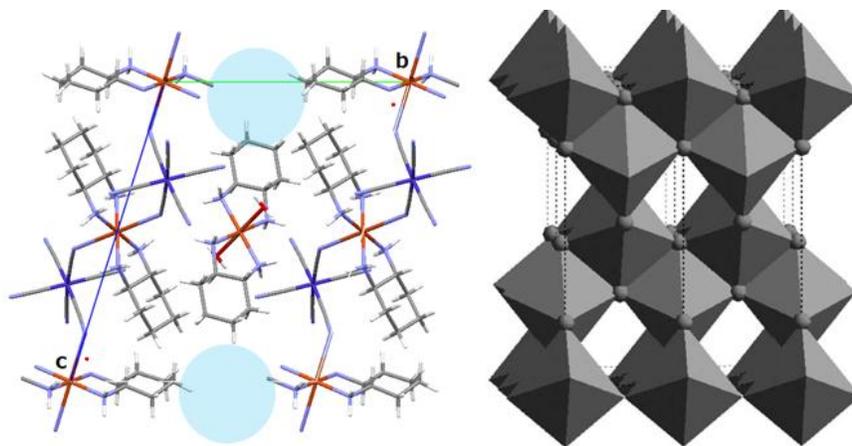
Figure 1. Concept of crystalline surface-modified composite materials of [left] chiral MOF (Cu-Co) and [right] anatase TiO_2.

As the new candidate materials, Prussian Blue Analogues (PBA) including alkali metal ion reported prompt charge-discharge characteristics [7-9]. Still problem raised that deformation in cyanide-bridged bimetallic complex, the part where has nano-scale pores, metal-organic framework (MOF), which ions go in and out, due to structural phase transition causes a decrease in efficiency of battery and characteristics [10]. The merits of PBA-MOF against metal oxide may be (1) large pores bridged by two atoms are appropriate for sodium ion. (2) PBA is essentially electrochemical material with tunable redox potential by replacing metal ions. To solve this problem in view of crystallography of inorganic materials, formation of nano-particles [11], improvement of surface [12], and adsorption of MOF on surface [13] have been proposed as promising strategies by several research groups. We aspire to control undesired crystal structural changes (like phase transition during charge-discharge) by compounding (adsorbing to surface of) chiral coordination polymers (or chiral metal complexes) and giving anisotropy to the deformation in crystal structures of electrode materials used in rechargeable battery. So, we attempt to use anisotropic chial cyanide-bridged metal complexes, which their crystal structures, phase transition, anisotropy of lattice distortion, and responsive to external fields as molecule-based magnetic materials were well researched in the past, to electrode materials [14-20]. For example, thermally-accessible lattice strain and local pseudo Jahn-Teller distortion of chiral mononuclear complex $[Cu((1R,2R)$-diaminocyclohexane$)_2](NO_3)_2$ (Cu) [13] and chiral MOF $[Cu((1R,2R)$-diaminocyclohexane$)_2]_3[M(CN)_6]_2·4H_2O$ (M= Co (Cu-Co) or Cr) [16] and have been reported as systematic studies on molecular crystals of metal complexes. Moreover, $[Cu((1R,2R)$-diaminocyclohexane$)_2][Cr_2O_7]_2$ O-bridged coordination polymer is also reported [21].

Herein, we have prepared and measured composite materials of Cu-Co and anatase TiO_2 (Figure 1) or Cu and anatase TiO_2 micro crystals for improvement of surface to exhibit anisotropic thermally-accessible structural changes.

1) Forming two types of composite materials with the molar ratios of Cu-Co (or Cu) : TiO_2 = 0:10 (pure Cu-Co or pure Cu), 1:9, 2:8, 3:7,4:6, 5:5, 6:4, 7:3, 2:8, 1:9, 10:0

(pure TiO_2). Adsorption of Cu-Co (or Cu) to TiO_2 are confirmed with the shift of IR bands of TiO_2.

2) Observing the anisotropic lattice distortion of TiO_2 affected from large complex and small complex, and which plane indices shows most anisotropy. To argue the anisotropy we used line width for the new challenge in plus to surface separation which we have used before.

EXPERIMENTAL SECTION

Preparations. Cu-Co or Cu incorporating (*1R,2R*)-diaminocyclohexane ligands were prepared according to the literature procedure [16, 19]. Composite materials of Cu-Co and TiO_2 (anatase) and Cu and TiO_2 were prepared by mixing with grinding in the solid states by the molar ratios of Cu-Co (or Cu): TiO_2 = 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 10:0. *Physical measurements.* Infrared spectra (IR) were recorded as KBr pellets on a JASCO FT-IR 4200 plus spectrophotometer at 298 K. Powder XRD patterns were also measured by using synchrotron radiation beamline at KEK PF BL-8B (2012G552) with 8 keV (λ= 1.54184 Å) under variable temperature (100-300 K) apparatus of nitrogen stream equipped with a RIGAKU imaging plate. All the samples were measured for 3 min and constant ring current (440 mA).

RESULTS AND DISCUSSION

Preparations of composite materials. Figure 2 exhibits IR spectra of Cu-Co and their composite materials with the molar ratios of Cu-Co : TiO_2 = 0:10 (pure Cu-Co), 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 2:8, 1:9, 10:0 (pure TiO_2). Low-wave number shift of IR spectra of TiO_2 around 652 cm^{-1} due to increase in ratios of Cu-Co (C≡N bond) around 2118 cm^{-1} due to increase in ratios of TiO_2 are observed. This indicates adsorption of Cu-Co to surface of TiO_2. Figure 3 exhibits IR spectra of Cu and their composite materials with the molar ratios of Cu : TiO_2 = 0:10 (pure Cu), 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 2:8, 1:9, 10:0 (pure TiO_2). High-wave number shifts of IR spectra of TiO_2 around 652 cm^{-1} due to increase in ratios of Cu was observed. This indicates adsorption of Cu to surface of TiO_2. The present study deals with only IR spectra and does not deal with magnetic properties [22] or chiroptical properties [23] of composite materials as well as metal complexes. Our proceeding study suggests that both magnetic interaction and induced CD observation may provide a suitable proof of adsorption on the surface when ferromagnetic metal oxides and chiral coordination polymers are employed [24]. The spectral and diffraction data are good agreement with characteristic features of adsorption and composites containing metal oxides [25].

XRD patterns of various molar ratios. Figure 4 depicts XRD pattern of the composite materials of Cu-Co and TiO_2. We argue (101), (200), (211) planes, the plane which had predominant shift of peak by changing temperature in the range of 100 – 300K. The surface separation erred from line of lnK vs 1/T (see later section [26]), which represents isotropic change. (211) plane showed predominant anisotropic lattice distortion since shift of peaks of TiO_2 by changing temperature was too minim to define lnK vs 1/T.
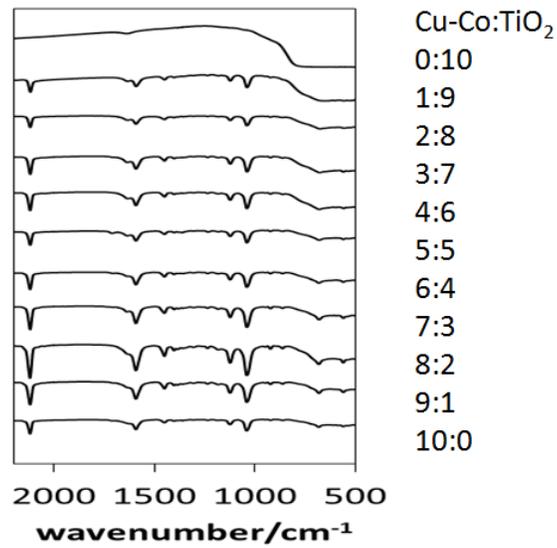
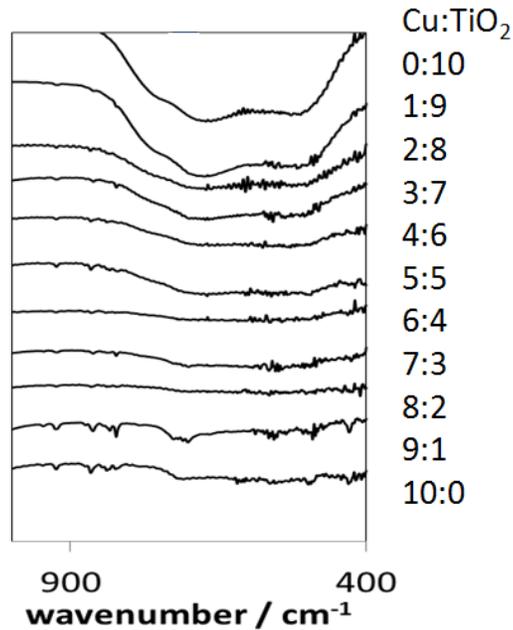Figure 2. IR spectra of the Cu-Co and TiO_2 composite materials of various ratios at 298 K.

Figure 3. IR spectra of the Cu and TiO_2 composite materials of various ratios at 298 K.

Also line width, which enables to argue grain diameter of crystals, of three peaks erred from line of lnK vs 1/T. Just same as the surface separation, (211) plane showed predominant anisotropic lattice distortion. This indicates anisotropic lattice distortion was given in particular plane indices. Figure 5 depicts XRD pattern of the composite materials of Cu and TiO_2. We argue (004), (105), (211) planes, the plane which had predominant shift of peak by

changing temperature in the range of 100K – 300K. The surface separation erred from line of lnK vs 1/T, which represents isotropic change. (211) plane showed predominant anisotropic lattice distortion since shift of peaks of TiO_2 by changing temperature was too minim to define lnK vs 1/T as same as Cu-Co composite. Shift of line width could not define in Cu composite since that of TiO_2 by changing temperature was too minim to define lnK vs 1/T. This indicates MOF complex has large affect then single complex.

   XRD patterns of various temperature. Figures 6 and 7 depict variable temperature XRD patterns at 100 – 300 K for the 5:5 composite materials of Cu-Co and TiO_2 and Cu and TiO_2, respectively. Both composites indicated typical positive thermal expansion, which can be confirmed shift of several XRD peaks by changing temperature.
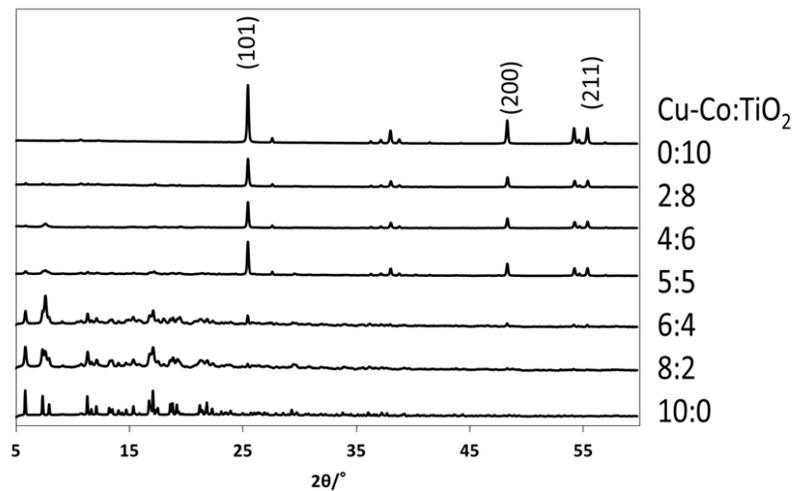

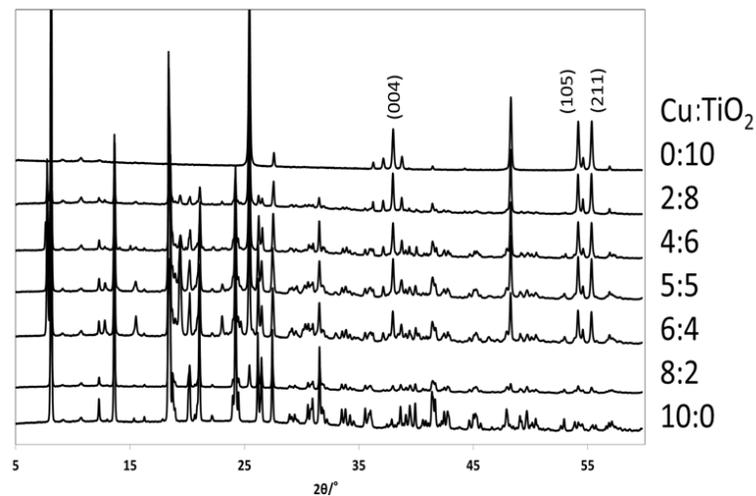Figure 4. XRD patterns of the Cu-Co and TiO_2 composite materials of various ratios at 300 K.

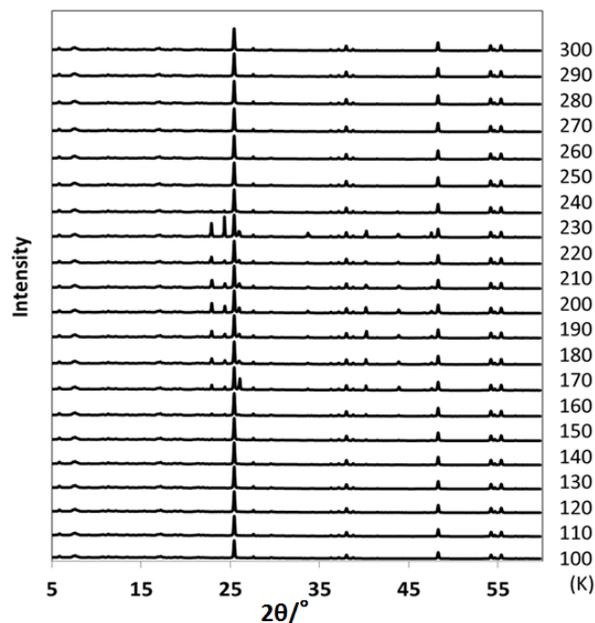Figure 5. XRD patterns of the Cu and TiO_2 composite materials of various ratios at 300 K.

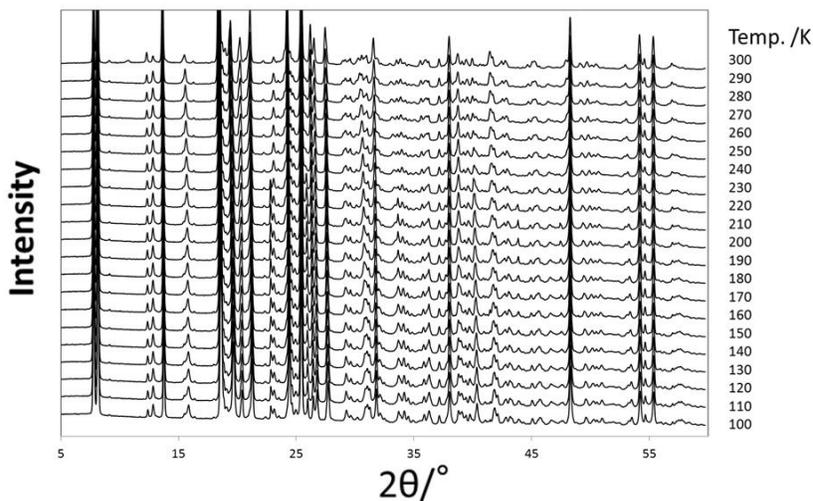Figure 6. XRD patterns of the Cu-Co:TiO$_2$=5:5 composite material under various temperature at 100-300 K.

Figure 7. XRD patterns of the Cu:TiO$_2$=5:5 composite material under various temperature at 100-300 K.

We have reported and discussed some factors and effects on thermally structural changes of lattice for cyanide-bridged bimetallic assemblies of Jahn-Teller Cu(II) units [26]. In the case of molecular crystals of pure metal complexes or pure MOF's, there are several important factors for structural changes derived from this proceeding study: (1) size of metal ions containing in bimetallic assemblies, (2) composition of metal ions, (3) isotope effect for

example H/D substitution (if any), and (3) global lattice constant and local bond distances (namely Jahn-Teller distortion of Cu (II) units). The difference of pure Cu (or Cu-Co) and the 5:5 composites or other ratios may be ascribed to structural effect of surface adsorption on the surface of TiO_2. In this context, we employ sophisticated method to discuss structural changes in view of anisotropy of a certain index in the following paragraph.
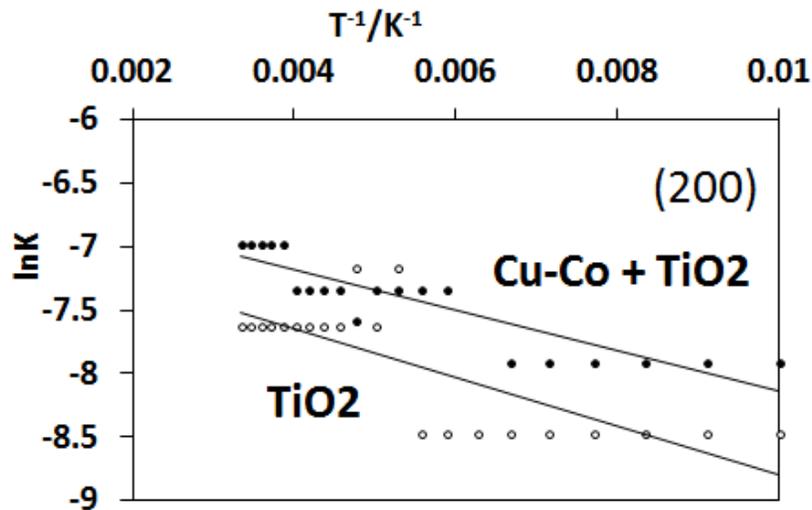

Figure 8. Deviation from isotropic lattice distortion (of TiO_2) about the d-values of (200) plane for the Cu-Co:TiO_2=5:5 composite material at 100-300 K.
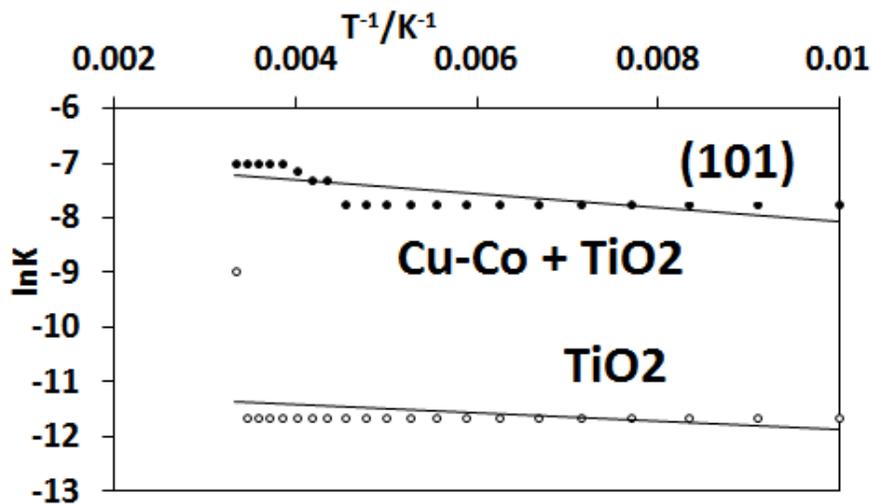

Figure 9. Deviation from isotropic lattice distortion (of TiO2) about the d-values of (101) plane for the Cu-Co:TiO2=5:5 composite material at 100-300 K.
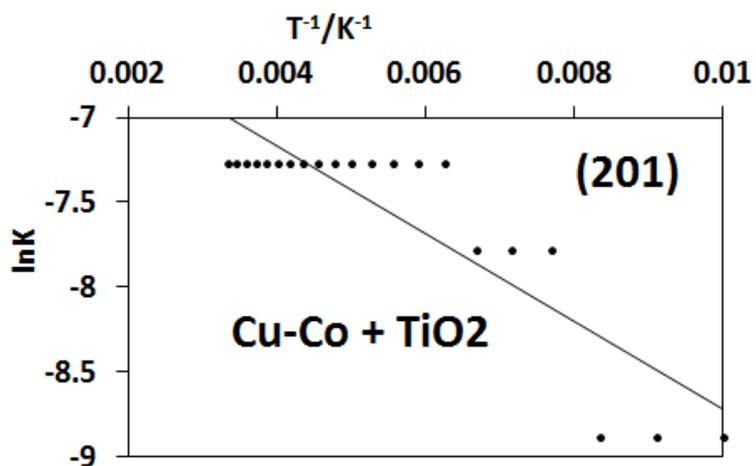
Figure 10. Deviation from isotropic lattice distortion (of TiO_2) about the d-values of (201) plane for the Cu-Co:TiO_2=5:5 composite material at 100-300 K. Little thermal changes for TiO_2 makes impossible to express the linear approximation.
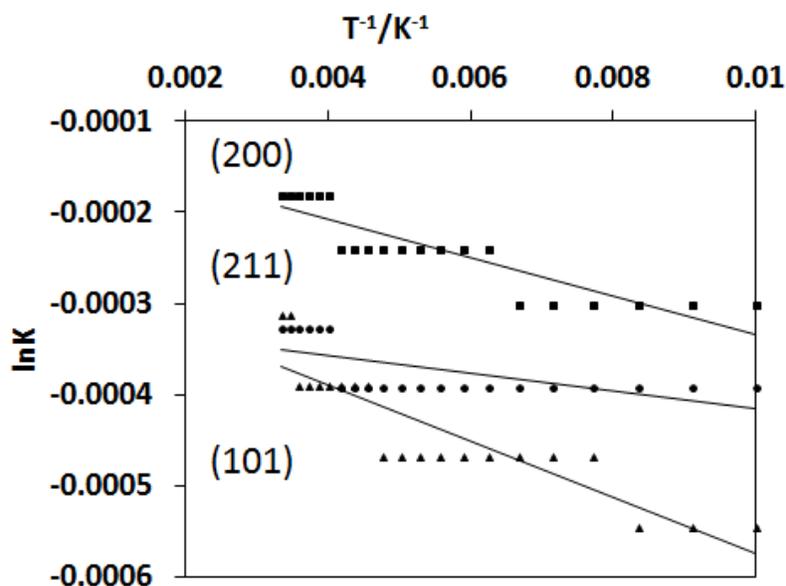

Figure 11. Deviation from isotropic lattice distortion (of TiO_2) about the half width of (200), (211), and (101) peaks for the Cu-Co:TiO2=5:5 composite material at 100-300 K.

The complex bimetallic oxide as the composite exhibited anisotropic thermally-accessible lattice distortion by adsorption of the chiral MOF (Cu-Co is a two-dimensional coordination polymer). Previously, we have reported discussion of variable temperature XRD patterns as follows [26]:

1) Definition of K = [d(T)-d(0)]/d(0) where d(T) and d(0) is spacing at T K and 0 K (extrapolated) for surface separation and K = [w(T)-w(0)]/w(0) where w(T) and w(0)

is spacing at T K and 0K (extrapolated) for line width. Although we have attempted to discuss line widths of XRD peaks in a similar procedure, sufficient precision could not be obtained in contrast to the cases of d-values.

2) Plotting a line of ln K = a/T + b (linear regression).
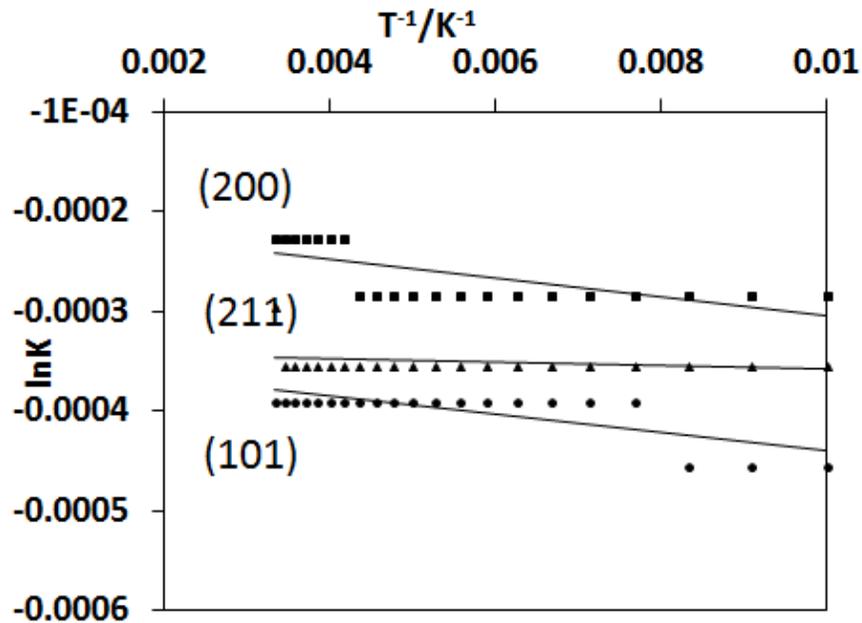3) Estimating of significantly distorted direction (index) of crystal lattices by changing temperature.

Figure 12. Deviation from isotropic lattice distortion about the half width of (200), (211), and (101) peaks for TiO_2 at 100-300 K.
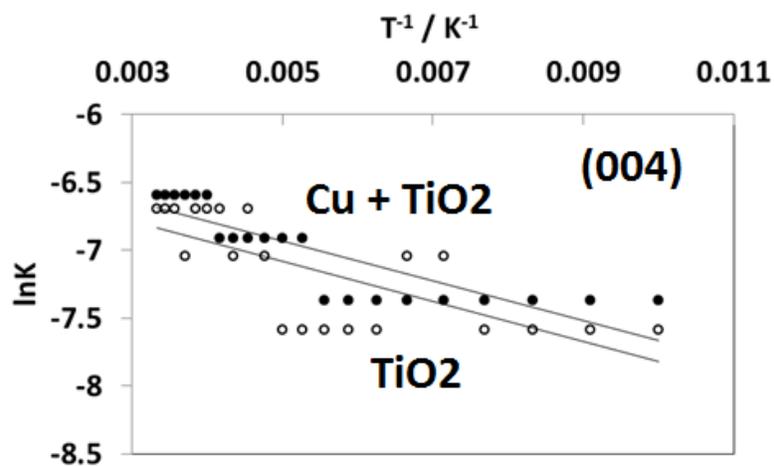
Figure 13. Deviation from isotropic lattice distortion (of TiO_2) about the d-values of (004) plane for the $Cu:TiO_2$=5:5 composite material at 100-300 K.

Figure 14. Deviation from isotropic lattice distortion (of TiO_2) about the d-values of (101) plane for the $Cu:TiO_2$=5:5 composite material at 100-300 K.
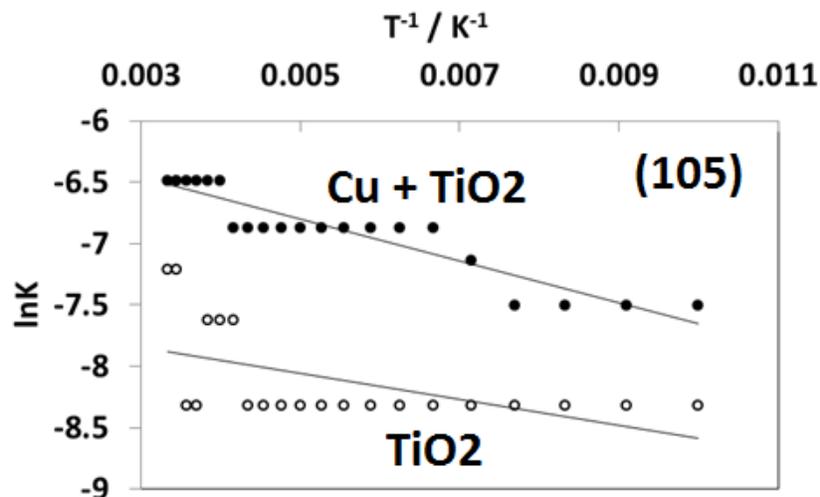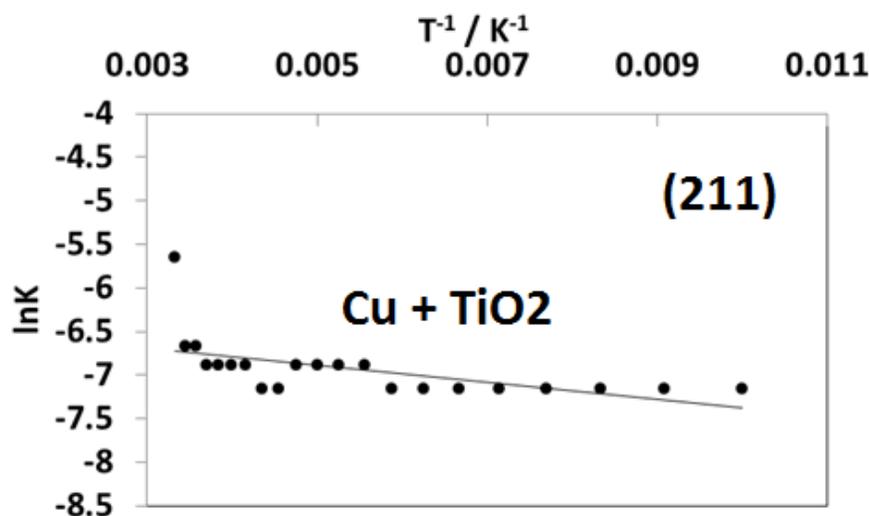

Figure 15. Deviation from isotropic lattice distortion (of TiO_2) about the d-values of (201) plane for the $Cu:TiO_2$=5:5 composite material at 100-300 K. Little thermal changes for TiO_2 makes impossible to express the linear approximation.

Figures 8-15 summarized temperature dependence of lattice strain by predominant peaks of Cu, Cu-Co, and TiO_2. Contrary to a Cu(II)-Cr(VI) bimetallic oxide and one-dimensional coordination polymer, [Cu((*1R,2R*)-diaminocyclohexane)$_2$][Cr$_2$O$_7$]$_2$ [24], the present TiO_2 is more hard and shows little thermally-accessible structural changes even pure materials. However, judging from the d-values, the effect adding anisotropic lattice distortion to TiO_2 of Cu-Co is significantly larger than that of Cu. The result suggests that the area of TiO_2 wrapped by metal complexes is reasonably effective to improvement of surface by this method.

CONCLUSION

In summary, Cu-Co had more affect on giving anisotropy to TiO_2 than Cu. This refers to the size of the complex. Many molecules are connected in Cu-Co to develop large complex and this cause the increase of anisotropic lattice distortion. Larger the complex gets, the surface touching TiO_2 increases and drag in TiO_2 when anisotropic lattice distortion occurs. On the other hand, Cu complex is single molecule and this means the surface touching TiO_2 is small and also anisotropic lattice distortion itself is small therefore the affect decreases compare to Cu-Co. Line width indicates the grain diameter of TiO_2. Rising temperature caused increase in line width, which means the grain diameter increases as temperature rises. We estimated that stretching of Cu-Co, adsorbed to TiO_2, by changing temperature causes the TiO_2 to stretch also.

ACKNOWLEDGMENT

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