Supplementary Information

Synthesis of Chiral Metal Oxide Complexes with Tunable Electron Transition-Based Optical Activity

Liguo Ma[1], Yingying Duan[1], Yuanyuan Cao[1], Shunsuke Asahina[2], Zheng Liu[3] and Shunai Che[1,*]

Experimental section

Materials

Zirconium oxychloride, ferric chloride, manganese acetate (SCRC, China) and TDA (TCI, Japan) were purchased. All N-acylamino acids (N-AAA) were synthesized according to the previous report. All chemicals were used as received without further purification.

Methods

The helical metal oxides complex nanofibres can be synthesised over a wide range of molar compositions of C_{18}-D-Glu:TDA:Metal precursor:MeOH:H_2O =1:7.5:x:5312:55962, where x can be adjusted in the range of 2~10. A temperature of 50~65 °C is favourable for the formation of helical fibres. In a typical synthesis, C_{18}-D-Glu (0.03 g, 0.08 mmol) was dissolved in a mixture of methanol (13.6 g) and deionised water (80 ml) while stirring at room temperature. After the mixture was stirred for 10 min, TDA (0.29 g, 75% in isopropanol) and zirconium oxychloride (0.4606g, 33% in methanol) were added to the mixture with stirring at 60 °C, respectively. The mixture was allowed to react at 60 °C with stirring for 2 h. The products were collected by centrifugal separation and dried by freeze drying at -60 °C, which resulted in a pale yellow powder. All organics in this product were removed by calcination at 550 °C, and inorganic oxides complex crystalline were obtained. The method for the synthesis of other helical metal oxides complex nanofibres using C_{18}-L-Glu or C_{18}-D-Glu are the same as the above and other inorganic precursors are ferric chloride and manganese acetate, respectively.

Characterization

The morphology of the chiral metal oxide complex nanofibres were observed with SEM (JEOL JSM-7401F) with an accelerating voltage of 1.0 kV. HRTEM images were taken with a JEOL JEM-2100 microscope operating at 200 kV. Powder X-ray diffraction patterns were recorded on a Rigaku X-raydiffractometer D/MAX–2200/PC equipped with Cu K a radiation (40 kV, 20 mA). Ultraviolet and DRUV spectra were taken by using a Shimadzu UV-2450 spectropolarimeter fitted with DRUV apparatus. CD and DRCD spectra were taken by using a JASCO J-815 spectropolarimeter fitted with DRCD apparatus.

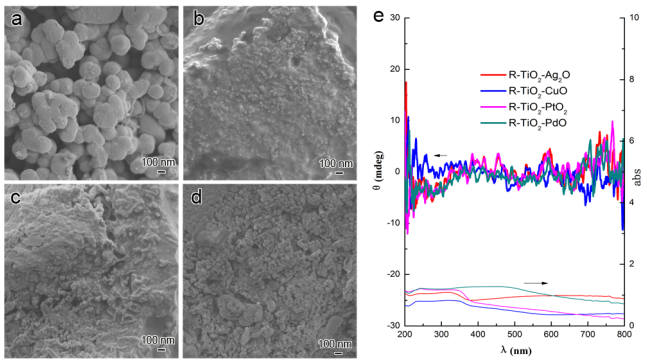

Figure S1. SEM images, DRUV-Vis and DRCD spectra of R-TiO_2-Ag_2O, R-TiO_2-CuO, R-TiO_2-PtO_2, and R-TiO_2-PdO.The molar composition for the synthesis was C_{18}-D-Glu:TDA:Metal: MeOH:H_2O=1:7.5:5:5312: 55962, the metal sources are $AgNO_3$, $Cu(NO_3)_2$•$3H_2O$, K_2PtCl_6, and K_2PdCl_6, respectively.

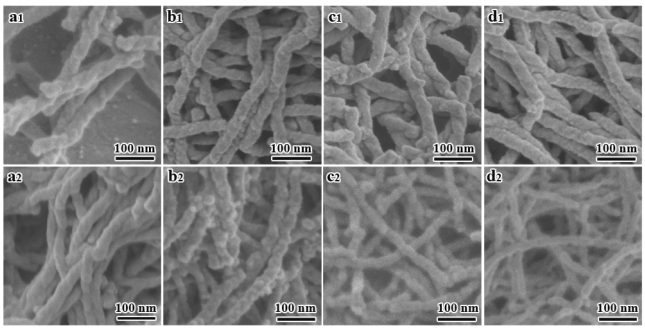

Figure S2. SEM images of the as-made (a_1-d_1) and calcined chiral metal oxides (a_2-d_2); L-ZrO_2 (a_1 and a_2), L-TiO_2-ZrO_2 ($b_1$and b_2), L-TiO_2-Fe_2O_3 (c_1 and c_2), and L-TiO_2-Mn_2O_3 (d_1 and d_2). The synthesis compositions were: (a_1) C_{18}-L-Glu:$ZrOCl_2$•$8H_2O$:MeOH:H_2O=1:7.5:5312:55962.(b_1-d_1) C_{18}-L-Glu:TDA:Metal:MeOH:H_2O=1:7.5:5:5312:55962, the metal sources are $ZrOCl_2$•$8H_2O$, $FeCl_3$•$6H_2O$ and $C_4H_6MnO_4$•$4H_2O$, respectively.

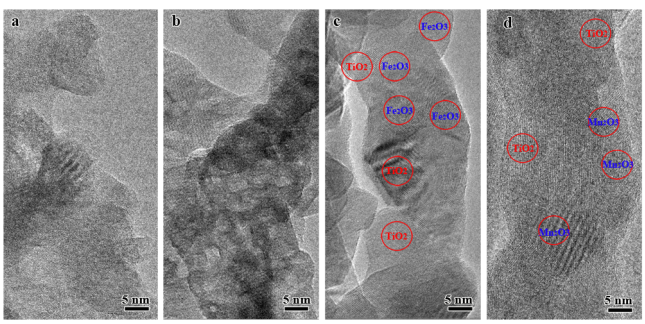

Figure S3. TEM images of calcined chiral metal oxides and complexes shown in Fig.1. R-ZrO_2 (**a**), R-TiO_2-ZrO_2 (**b**), R-TiO_2-Fe_2O_3 (**c**), and R-TiO_2-Mn_2O_3 (**d**). The lattice fringes of *d*=1.4 Å match that of the (215) crystallographic planes of anatase-TiO_2; the lattice fringes of *d*=1.6, 1.8, and 2.2 Å match that of the (116), (024), and (113) crystallographic planes of hematite α-Fe_2O_3. The lattice fringes of *d*=1.7 Å match that of the (044) crystallographic planes of α-Mn_2O_3. These crystallographic planes have been clearly identified in the figures.

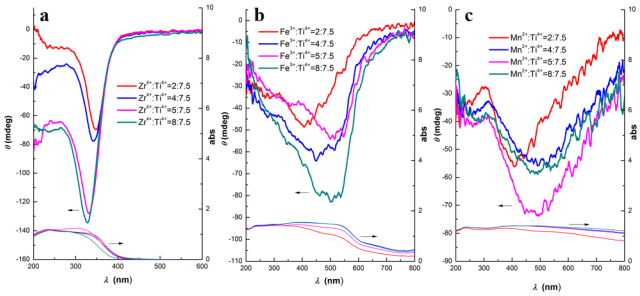

Figure S4. DRUV-Vis and DRCD spectra of calcined chiral metal oxides complexes synthesized with different ratio of metal ion to Ti^{4+} .

In Fig. S4a, with increasing molar ratio of Zr^{4+}/Ti^{4+}, the DRCD spectra of the metal oxides complex were gradually blue-shifted due to the ZrO_2 with absorption band in the range of 200-260 nm shorter than TiO_2. In Fig. S4b and Fig. S4b, with increasing of molar ratio of Fe^{3+}/Ti^{4+} and Mn^{2+}/Ti^{4+}, the DRCD spectra of the metal oxides complex were gradually red-shifted because of Fe_2O_3 and Mn_2O_3 with absorption band in the range of 400-600 nm longer than TiO_2.