Synthesis and Thermodecomposition Study of $Zn(tda)H_2O$

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Using polydentate ligands and transition metals as building units, coordination polymers with varies connections from one- to three-dimensional (3D) networks can be synthesized. Polycarboxylate ligand is one of such multidentate ligands that have been used to synthesize coordination polymers. Our recent study has focused on the synthesis of coordination polymer using thiodiacetate ligands (tda = $S(CH_2COO)_2^{2-}$) as the bridge ligand. We found that under hydrothermal condition, the Zn^{2+} ions coordinate to tda and H_2O molecules to form a new coordination polymer $Zn(tda)H_2O$. Herein, we report the detail synthesis, structure characterization and thermodecomposition behaviors of $Zn(tda)H_2O$.

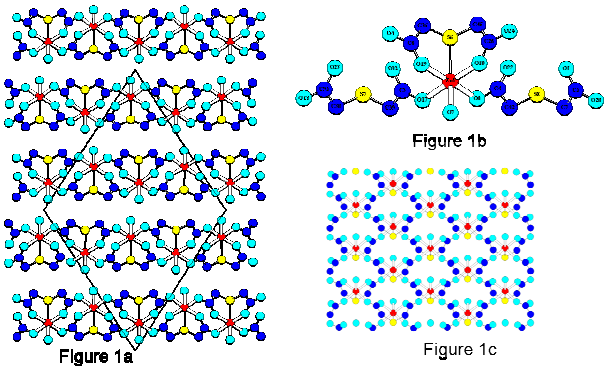

Figure 1. a) The three dimensional structure $Zn(tda)H_2O$ projected along [010]. Red, light blue, dark blue and yellow circles are Zn, O, C, and S atoms, respectively. Hydrogrn atoms are omitted for clearity. b) Coordination environment of Zn. c) 2D structure. $Zn(tda)H_2O$ Crystal data: 0.2×0.1×0.5 mm^3, monoclinic, $P2_1$ (Z = 4), a = 15.56 Å, b = 5.187 Å, c = 17.391 Å, β =114.571°, V = 1276.6 $Å^3$.

The product exhibits colorless crystal with the yield close to 90 % (according Zn). Single crystal X-ray studies revealed a novel two dimensional network and its three dimensional stacking is noncentrosymmetric. The structure of $Zn(tda)H_2O$ is shown in Fugure 1. There are four independent Zn^{2+} positions in a unit cell. Each Zn^{2+} is surrounded by one sulfur and five oxygen atoms in a distorted octahedral geometry (Figure 1b). The S and O atoms on the axial positions are from tda ligand and H_2O molecule, the other four O atoms in the equatorial positions are from three different tga molecules (d_{Zn-S} = 2.50 A, d_{Zn-O} = 2.10). There are four independent tda molecules in a unit cell. Both the sulfur and oxygen atoms in a tda ligand are binding to three different Zn^{2+} ions, one S and two O atoms on the equatorial position bond to one and other two O atoms coordinate to two adjacent Zn^{2+} ions. The binding between the Zn^{2+} and tda constructs the corrugated 2-D network that lies in the plane perpendicular to [10-1] (Figure 1c). The 2D sheets are stacked together alone [10-1] direction that are held together by van der Wall interactions. This unusual structure, containing Zn-S bonding pointed in opposite direction in adjacent metal center, is closely related to $Cu(oda)H_2O$ (oda = $O(CH_2COO)_2^{2-}$). However, the Zn^{2+} atoms form an undulate hexagonal network instead of a rectangle structure for Cu^{2+} atoms in $Cu(oda)H_2O$.

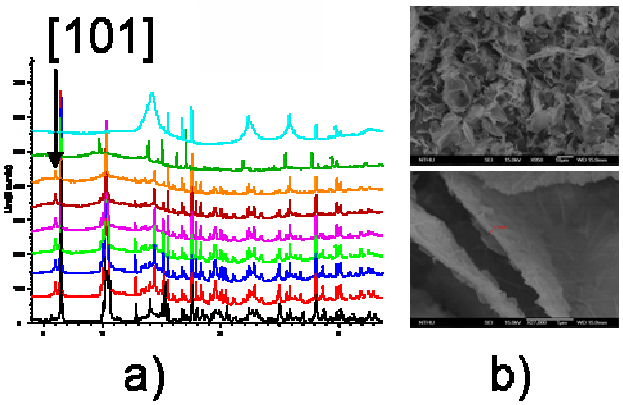

Figure 2. a)Temperature-resolved powder pattern recorded at 25, 245, 250, 255, 260, 265, 270, 300, 500 °C (from left to right), and complete dehydrate reaction occurs to ZnO by the heating stage 500°C. The [101] peak from $Zn(tda)H_2O$ and diffractions from ZnO are labeled. b) SEM images of porous ZnO.

The temperature dependent Powder X-ray diffraction data were collected using synchrotron radiations at NSRRC BL01C2 beam line. The results indicate that the structure of $Zn(tda)H_2O$ was maintained during the dehydration process (Figure 2a). The intensity of diffraction peak [101] decreases as the temperature increases, which is corresponding to the H_2O releasing. The last powder pattern shows that the as-synthesized $Zn(tda)H_2O$ decomposed completely at the final heating stage (T > 500°C) to form porous ZnO; PXRD pattern indicates broadening of diffraction peak with estimated ZnO particle size ~ 10-20 nm using the Scherer equation, which is in consistent with the particle size of ZnO from SEM images (Figure 2b).

In summary, a new coordination polymer, $Zn(tda)H_2O$, with a novel two-dimensional sheet structure has been synthesized. $Zn(tda)H_2O$ can be used as a single precursor to prepare nanoporous ZnO. The obtained nanoporous ZnO contains high surface area with large number of pores and walls, which can be of benefit for studies or applications such as catalyst or gas sensor.