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Synthesis and Thermal Decomposition of $Zn(tda)H_2O$ [tda = $S(CH_2COO)_2^{2-}$]

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A novel two-dimensional coordination polymer $Zn(tda)H_2O$ [tda = $S(CH_2COO)_2^{2-}$] was synthesized under hydrothermal conditions. The compound crystallized in monoclinic space group $P2_1$ with a = 16.4154(17) Å, b = 5.2133(6) Å, c = 16.4210(17) Å, β = 114.165(2)°, V = 1282.1(2) Å^3, and Z = 8. The structure features two-dimensional, noncentrosymmetric networks with a pseudohexagonal network of Zn^{2+} coordinated by tda and water molecules. $Zn(tda)H_2O$ decomposed at $T > 300$ °C to form a ZnO sponge with a surface area ~ 40 m^2/g, which makes it an attractive precursor for nanoporous ZnO.

With polydentate ligands and transition metals as building units, coordination polymers with desired structural motifs and properties can be synthesized;[1] these can serve as functional materials, such as materials to store hydrogen,[2] catalysts,[3] and nonlinear optical materials.[4] A polycarboxylate compound is one such multidentate ligand used to synthesize coordination polymers. For ligands containing two carboxylate groups, much work has focused on coordination polymers containing iminodiacetate [ida = $HN(CH_2COO)_2^{2-}$] or oxydiacetate [oda = $O(CH_2COO)_2^{2-}$] ions with various metal cations.[5] Coordination polymers containing thiodiacetate ligands [tda = $S(CH_2COO)_2^{2-}$] are rare; only a few metal complexes such as $M(tda)(H_2O)_4$ (M = Ni, Zn)[6] and coordination polymers containing rare-earth cations La^{3+} and Pr^{3+} are reported.[7] We focused on the synthesis of a coordination polymer using tda as a bridging ligand to coordinate with transition metals and found that, under hydrothermal conditions, tda and Zn^{2+} link together to form a new coordination polymer $Zn(tda)H_2O$. The structure comprises Zn^{2+} cations interconnected with pentadentate tda linkers. $Zn(tda)H_2O$ decomposes to form a notable spongelike ZnO for $T > 300$ °C, which makes it an attractive solid precursor for nanoporous ZnO. Although the latter material can be prepared by various methods, such as solution combustion,[8] thermodecomposition,[9] and sol−gel methods,[10] these processes generally need an organometallic precursor[11] or multiple steps to yield this product. The method presented here requires only one solid precursor, and nanoporous ZnO is obtained directly from thermal decomposition. Here we report the detailed synthesis, structural characterization, and thermal decomposition of $Zn(tda)H_2O$.

$Zn(tda)H_2O$ was synthesized hydrothermally from reaction mixtures containing Zn, tda, and H_2O at 180 °C over 2 days. The product exhibits needle-shaped, transparent crystals with a yield near 90% (according to Zn). The compound crystallizes in a new structural type with monoclinic space group $P2_1$ and eight formula units per unit cell. Single-crystal X-ray analysis revealed a novel two-dimensional (2D) network; its three-dimensional (3D) stacking is noncentrosymmetric. The acentric structural feature of $Zn(tda)H_2O$ is confirmed with measurements of second-harmonic generation (SHG). The 3D structure of $Zn(tda)H_2O$ is shown in Figure 1a. There are four independent Zn^{2+} positions in a unit cell; each Zn^{2+} is surrounded with one S and five O atoms in a distorted

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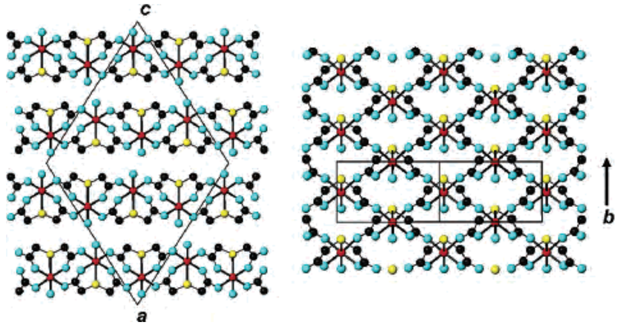

Figure 1. (a) 3D structure of Zn(tda)H_2O projected along [010]. Color code: Zn, red; C, black; O, blue; S, yellow. H atoms are omitted for clarity. (b) 2D structure of Zn(tda)H_2O projected along $[10\bar{1}]$.

octahedral geometry. The S and O atoms at the axial positions are from the tda ligand and H_2O molecule; the other four O atoms at equatorial positions are from three separate tda molecules [$d_{Zn-S} = 2.523(1)$ Å; $d_{Zn-O} = 2.105(4)$ Å]. There are four independent tda molecules in a unit cell; for each tda ligand, the S and O atoms bind to three Zn^{2+} ions; one S and two O atoms at the equatorial position bind to one Zn^{2+} ion, and another two O atoms coordinate to two adjacent Zn^{2+} ions. The binding between Zn^{2+} and tda forms a corrugated 2D network that lies in a plane perpendicular to $[10\bar{1}]$ (Figure 1b). The 2D sheets are stacked together along the $[10\bar{1}]$ direction and are held together by van der Waals interactions. This uncommon structure, containing Zn−S bonds pointing in the opposite direction in adjacent metal centers, is closely related to Cu(oda)$(H_2O)_{0.5}$,[12] but Zn(tda)H_2O forms an undulating pseudohexagonal 2D network instead of a pseudorectangular 2D framework for Cu(oda)$(H_2O)_{0.5}$.

Zn(tda)H_2O is stable in air and water. Thermogravimetric analysis (TGA) shows that Zn(tda)H_2O loses H_2O (12.1% mass loss, expected 12.3%) in the temperature range 250−260 °C to transform to a semitransparent, dehydrated form of Zn(tda). With continued heating, the compound decomposes to form a yellowish foam structure for $T > 300$ °C. The TGA experiment was terminated because of a large expansion of product volume. According to powder X-ray diffraction (XRD) and energy-dispersive spectrometry (EDS) analysis, a solid solution of ZnO/ZnS was observed from a low-temperature product ($T < 500$ °C) because the Zn^{2+} cation in Zn(tda)H_2O is coordinated to both S (×1) and O (×5) atoms. Pure ZnO is prepared upon thermal decomposition of Zn(tda)H_2O at $T > 500$ °C, as confirmed by powder XRD and EDS analysis.

The thermal decomposition of Zn(tda)H_2O was investigated on a powder sample with synchrotron powder XRD for various temperatures in the range of 25−500 °C (NSRRC BL01C2 line, $\lambda = 0.775$ Å); the results appear in Figure 2. Near 25 °C, the powder pattern exhibits complicated features with diffraction signals contributed by water molecules in $[20\bar{2}]$ and $[40\bar{4}]$ diffractions. During dehydration (25 °C < T < 300 °C), the intensities of $[20\bar{2}]$ and $[40\bar{4}]$ decreased gradually from 25 to 300 °C, indicating that H_2O molecules have been released. The powder pattern at $T = 300$ °C has been indexed in a model of monoclinic cell $a = 16.38(2)$ Å, $b = 5.223(4)$ Å, $c = 16.48(2)$ Å, $\beta = 114.0(1)°$, and $V = 1288$ (4) Å^3, similar to the Zn(tda)H_2O pattern except that $[20\bar{2}]$ and $[40\bar{4}]$ reflections are absent. These results indicate that the structure of Zn(tda)H_2O remains intact when all water molecules are removed to form dehydrated Zn(tda). When the dehydrated material was exposed to water, the structure collapsed and converted into a molecular form of Zn(tda)$(H_2O)_4$,[6] indicative of an irreversible process. Zn(tda) began to decompose for $T > 300$ °C. The diffraction pattern for $T = 500$ °C indicated a poorly crystalline nature, with broad reflections corresponding to ZnO. According to the Scherrer equation, the average size of the ZnO particles is ∼10 nm, confirming the presence of a nanocrystalline ZnO phase.

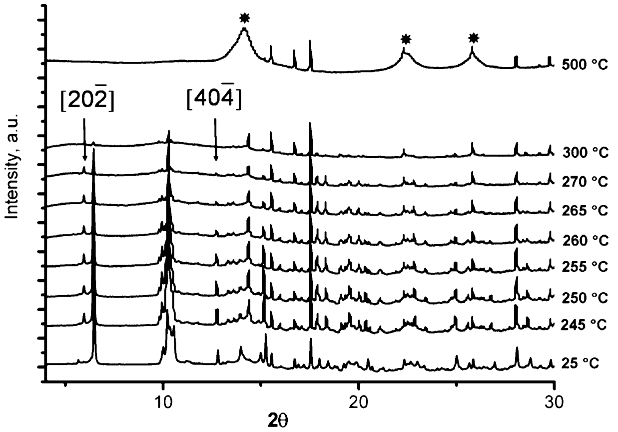

Figure 2. Temperature-dependent synchrotron powder diffraction patterns of Zn(tda)H_2O. Diffraction features marked with asterisks are for ZnO.

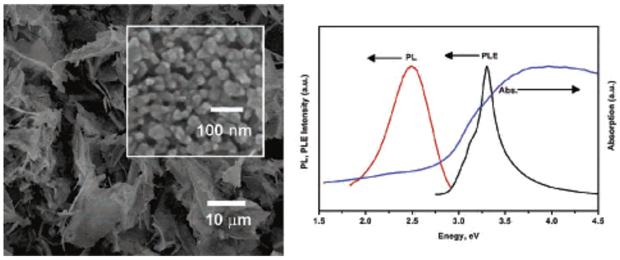

Figure 3. (a) SEM image of ZnO from thermal treatment at $T > 550$ °C. The photograph includes magnified pictures showing the fine structure of ZnO flakes. (b) Excitation, emission, and diffuse-reflectance spectra of porous ZnO at 25 °C.

The resulting material reveals a porous and spongelike structure, which was examined with a scanning electron microscope (SEM). Figure 3a shows porous ZnO with an extensive connection of thick flakes containing large pores of average diameter ∼10 µm. The fine structure of a single flake consists of countless ZnO crystals of average size ∼10 nm, which is consistent with the result from powder diffraction tests (inset of Figure 3a). A reason for the formation of ZnO foam might be the major alteration of coordination modes from an octahedral to a tetrahedral environment for the Zn^{2+} cation. The analogous compound Ni(tda)H_2O was synthesized with the same structure as Zn(tda)H_2O, but thermal decomposition of Ni(tda)H_2O yielded microcrystalline NiS/NiO because coordination of Ni^{2+} in both compounds is the same: six-coordinate.

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Figure 3b shows the photoluminescence (PL) of porous ZnO at 25 °C recorded with an excitation energy of 3.42 eV. A strong UV emission was observed at $E_{\mathrm{MAX}} = 2.49$ eV, which might arise from the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes due to an irregular morphology with crystal defects in these porous materials (Figure 3b).[13] The green light is readily visible with the naked eye when excited with a laboratory UV lamp. For samples collected at varied decomposition temperatures, the intensity of the green emission at $E \sim 2.49$ eV increased significantly as porous ZnO formed (Figure S2 in the Supporting Information), indicative of a large concentration of oxygen vacancies in porous ZnO as synthesized. The UV−visible diffuse-reflectance spectrum shows an onset energy similar to that of the PL excitation spectrum (Figure 3b). The N_2 Brunauer−Emmett−Teller surface area of a porous ZnO sample was 39.8 m^2/g, consistent with the porous structure according to SEM measurements.

In summary, a new coordination polymer, Zn(tda)H_2O, with a novel 2D sheet structure has been synthesized. Zn(tda)H_2O can serve as a single solid precursor for the preparation of nanoporous ZnO. The obtained nanoporous ZnO possesses a large surface area with many pores and walls, beneficial for applications such as a catalyst and a gas sensor. The same idea is applicable to the preparation of new nanoporous materials with a coordination polymer as a precursor. In work in progress, we are employing this precursor to prepare a ZnO thin film for photovoltaic experiments.

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Supporting Information Available: CIF file of Zn(tda)H_2O, UV and PL spectra, a TGA curve, SEM images, and details of experiments. This material is available free of charge via Internet at http://pubs.acs.org.

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