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Two Ti_{13}-oxo-clusters showing non-compact structures, film electrode preparation and photocurrent property

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Two benzene dicarboxylate (BDC) and salicylate (SAL) substituted titanium-oxo-clusters, $Ti_{13}O_{10}(o\text{-}BDC)_4(SAL)_4(O^iPr)_{16}$ (**1**) and $Ti_{13}O_{10}(o\text{-}BDC)_4(SAL\text{-}Cl)_4(O^iPr)_{16}$ (**2**), are prepared by one step in a situ solvothermal synthesis. Single crystal analysis shows that the two Ti_{13} clusters take a paddle arrangement with an S_4 symmetry. The non-compact (non-sphere) structure is stabilized by the coordination of BDC and SAL. Film photoelectrodes are prepared by wet coating process using the solution of the clusters and the photocurrent response properties of the electrodes are studied. It is found that the photocurrent density and photoresponsiveness of the electrodes are related with the number of the coating layers and the annealing temperature. Using the ligand coordinated titanium-oxo-clusters as the molecular precursors of TiO_2 anatase films is found to be effective due to the high solubility, appropriate stability in solution and hence the easy controllability.

Introduction

Since the first crystal structure of a titanium-oxo-cluster was determined by X-ray diffraction in 1967,[1] numerous such titanium-oxo-clusters have been structurally characterized with the number of titanium atoms ranging from 3 to 34 and with various multidentate ligands in addition to oxo and alkoxy groups.[2,3] The titanium-oxo-clusters, as the model of the nanoscale titanium oxides, offer the opportunity to understand the information of both bonding structure and stability of the surface modification.[3,4] Consequently, there are considerable interests in designing and synthesizing new titanium-oxo-clusters.[5-7]

In general, [TixOy(OR)z] clusters are synthesized by controlled hydrolysis of titanium alkoxides in the presence of water. As reviewed by Rozes and Sanchez,[2a,b] most of these clusters take compact arrangement to be a sphere-like structures, especially, two large clusters Ti17 and Ti18 join the group of polyoxometalate complexes that display the Keggin structure.[5] The substituted titanium-oxo-clusters constitute an important subclass of titanium-oxo-clusters. Although the smaller clusters exhibit relatively more open structural frameworks (non-compact structures) because of the steric repulsions between the ligand groups, the larger Ti*n* clusters (10< n < 18) still prefer the compact arrangement.[3b,6] Titanium-oxo-clusters with the nuclearity larger than 18 are constructed by fusing two small sphere clusters, such as Ti_{28} and Ti_{34}.[3] It is the self-convergence property of titanium-oxo-clusters. This highly compact arrangement has a great importance in the construction of metal-oxo cores that increases the stability of the clusters in heteropolyanion chemistry.

Most substituted titanium-oxo-clusters are those substituted by carboxylates, acetylacetonate and catecholate derivatives. Salicylic acid (H_2SAL, *o*-hydroxybenzoic acid), including both carboxyl and phenol groups, is a common ligand used in coordination chemistry and is an important component of human medicine (Aspirin). However, the reported number of the titanium-oxo-clusters substituted by this ligand is only single-digit and their nuclearities are less than 10.[8] Using this ligand and phthalic acid (benzene dicarboxylate acid, H_2BDC), we successfully got two new high nuclearity titanium-oxo-clusters, $Ti_{13}O_{10}(o\text{-}BDC)_4(SAL)_4(O^iPr)_{16}$ (**1**) and $Ti_{13}O_{10}(o\text{-}BDC)_4(SAL\text{-}Cl)_4(O^iPr)_{16}$ (**2**), in large single crystals, by one step in situ solvothermal synthesis. Crystal structures of such mixed ligand clusters are obtained by single crystal analysis and the results show that the two clusters are isostructural. Different from the structures of most titanium-oxo-alkoxide clusters with high nuclearities, the two clusters show an unusual non-compact arrangement. The TiO frameworks take a paddle arrangement with an S_4 symmetry. The non central contraction structure is stabilized by the ligands.

On the other hand, a porous nanoscale TiO_2 film (affording a large inherent adsorptive surface area) is very important aspect in the production of highly efficient dye-sensitized solar cells.[9] The development of chemical wet deposition processes for thin films dates to the end of last century and has been experienced a rapid expansion till now.[10] Although sol-gel methods using titanium alkoxides are widely used to manufacture the titanium oxide films, the chemical solution (not sol solution) coating methods still have their advantages

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Electronic Supplementary Information (ESI) available: Crystallographic data CCDC 1417634−1417635 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The XRD, UV, TG and IR spectra can be obtained from DOI: 10.1039/x0xx00000x in solution stability and film processing.[10a,11] Titanium-oxo-clusters have been used as the molecular precursors of TiO$_2$ anatase nanocrystals and the size distribution of these nanocrystals was found to be related to the structures,[12] However, preparation of TiO films using titanium-oxo-clusters is still rarely studied. These surface ligand coordinated clusters are less reactive than those of titanium alkoxides. Therefore, the film preparation using titanium-oxo-clusters can be more easily controlled. In view of the above consideration, films of compounds **1** and **2** are prepared easily using solution coating method and photocurrent responsive properties of these electrodes are investigated. The effects of annealing temperature and coating layers are discussed.

Experimental

General Remarks

All analytically pure reagents are purchased commercially and used without further purification. The IR spectra are recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses of C and H are performed using a VARIDEL III elemental analyzer. Solid-state room-temperature optical diffuse reflectance spectra of the micro crystal samples are obtained with a Shimadzu UV-3150 spectrometer. Room-temperature X-ray diffraction data are collected on a D/MAX-3C diffractometer using a Cu tube source (Cu-Kα, λ = 1.5406 Å). The scanning electron microscope (SEM) measurement was carried out with a JSM-5600LV. Thermoanalytical measurements was performed using a TGA-DCS 6300 microanalyzer and the sample was heated under a nitrogen stream of 100 ml min^{-1} with a heating rate of 10 °C min^{-1}.

Synthesis

Ti$_{13}$O$_{10}$(*o*-BDC)$_4$(SAL)$_4$(O^{i}Pr)$_{16}$ (**1**). Analytically pure Ti(O^{i}Pr)$_4$ (0.1 mL, 0.26 mmol), phthalic acid (0.03 g，0.18 mmol) and salicylic acid (0.015 g，0.10 mmol) are mixed in 0.35 mL mixed solvent of isopropanol-acetone (6:1 in volume). The mixture is placed in a thick Pyrex tube (0.7 cm dia., 18 cm length) and quickly degassed by argon. The sealed tube is heated under autogenous pressure at 120 °C in 5 days to yield greenish-yellow crystals (15 % yield based on Ti(OiPr)$_4$). The crystals are rinsed with ethanol and dried for measurements. The compound is stable under dry environment. Anal. Calcd for C108H144O54Ti13 (MW 2928.54): C, 44.29; H, 4.96. Found: C, 43.86; H, 5.20. Important IR data (KBr, cm^{-1}): 2970(m), 2930(w), 2866(w), 1610(m), 1576(vs), 1476(s), 1426(m), 1393(m), 1257(w), 1125(s), 1014(m), 850(m), 616(w), 546(m).

Ti$_{13}$O$_{10}$(*o*-BDC)$_4$(SAL-Cl)$_4$(O^{i}Pr)$_{16}$ (**2**). Compound **2** was obtained by following a similar procedure to that of **1**, but 2-Cl-salicylic acid (0.014 g，0.08 mmol) was used instead of salicylic acid. Yellow crystals of **2** were obtained in 5 days (10 % yield based on Ti(OiPr)$_4$). The crystals are rinsed with ethanol and dried. The compound is stable and preserved under dry environment. Anal. Calcd for C108H140Cl4O54Ti13 (MW 3066.52): C, 42.30; H, 4.60. Found: C, 41.82; H, 4.76. Important IR data (KBr, cm^{-1}): 2971(m), 2930(w), 2865(w), 1615(m), 1572(vs), 1474(s), 1428(s), 1391(m), 1327(w), 1251(w), 1121(s), 1010(m), 845(s), 735(m), 621(w), 550(m).

X-ray Crystallographic Study

The measurement is carried out on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71075 Å) radiation at 293 K. X-ray crystallographic data for all the compounds are collected and processed using CrystalClear (Rigaku).[13] The structures are solved by direct methods using SHELXS-2014 program and the refinement is performed against F^2 using SHELXL-2014.[14] All the non-hydrogen atoms are refined anisotropically. The hydrogen atoms are positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal data, collection parameters, and refinement results can be found in Table 1.

Table 1 Crystal Data and Structural Refinement Parameters for **1** and **2**

	1	2
formula	$C_{216}H_{288}O_{108}Ti_{26}$	$C_{108}H_{140}Cl_4O_{54}Ti_{13}$
fw	5857.08	3066.69
cryst size (mm^3)	0.30× 0.30 × 0.45	0.30 × 0.35 × 0.40
cryst syst	tetragonal	tetragonal
space group	$I\,4_1/a$	$I\,4_1/a$
a (Å)	25.9224(15)	25.876(3)
b (Å)	25.9224(15)	25.876(3)
c (Å)	41.590(4)	43.429(6)
α (deg)	90.00	90.00
β (deg)	90.00	90.00
γ (deg)	90.00	90.00
V (Å^3)	27947(4)	1790.7(17)
Z	4	8
ρ_{calcd} (g cm^{-3})	1.391	1.401
F(000)	12060	12592
μ (mm^{-1})	0.780	0.825
T (K)	293(2)	293(2)
reflns collected	47613	111842
unique reflns	12061	12264
observed reflns	8389	10316
no. params	810	806
GOF on F^2	1.155	1.218
R_1 [$I>2\sigma(I)$]	0.1167	0.1353
$_wR_2$ [$I>2\sigma(I)$]	0.1693	0.1891

Photocurrent Measurement

The 0.4 mL solution of **1** (8×10^{-3} mmol) in dichloromethane was spin-coated on a cleaned ITO substrate (100 Ω/□) at 1500 rpm/s for 30 s. This procedure yielded uniformly thin layered film electrode of **1** for photocurrent measurements. The electrode of **2** was prepared in the same procedure. The annealing temperatures for the films were 280 and 500 °C treated 10 min in air. A 150 W high-pressure xenon lamp, located 20 cm away from the surface of the ITO electrode, was employed as a full-wavelength light source. The photocurrent experiments were performed on a CHI650E electrochemistry workstation in a three-electrode system, with the sample coated ITO glass as the working electrode mounted on the window with an effective area of 0.385 cm^2 (Φ = 0.7 cm), a Pt plate as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte solution was a 0.1 $mol \cdot L^{-1}$ sodium sulfate aqueous solution. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light.

Results and discussion

Synthesis and characterization

Compounds **1** and **2** are obtained as crystals by a similar in situ solvothermal technique by reacting titanium(IV) isopropoxide, $[Ti(O^iPr)_4]$, with H_2BDC and H_2SAL in a mixed solvent of isopropanol-acetone. The acetone is used as an auxiliary solvent to increase the solubility of H_2BDC. By carefully selecting the mole ratio and the volume of the solvents, bulky crystals of the clusters crystallize directly from the reaction mixtures after a few days. The purity of the samples is confirmed by elemental analysis and by comparing the experimental XRD patterns with the calculated patterns from the crystal data (Fig. S1). To characterize the samples of **1** and **2**, IR, UV-vis and TGA are carried out. For each compound, the FTIR stretches of 1614, 1575 and 1476 cm^{-1} for **1** and 1610, 1568 and 1474 cm^{-1} for **2** indicate the chelating coordination of the carboxyl group of BDC and SAL. Isopropoxy groups are detected by the $\nu_{C–H}$ (between 2970 and 2850 cm^{-1}) and $\nu_{Ti–O–C}$ (about 1110 and 1010 cm^{-1}) vibrations. The bands below about 545 cm^{-1} are attributed to the Ti–O vibrations (Fig. S2, Supporting Information). Optical diffuse-reflection spectra of **1** and **2** were measured and the absorption data are calculated from the reflectance (Fig. S3a). The spectra of **1** and **2** are similar and can be assigned to two main parts. The intense absorption (> 3.5 eV) results from two components, TiO cluster core and organic ligands. The peak at about 3.1 eV is assigned to the charge transfer (CT) band from ligands to TiO cluster. The CT bands extend to the visible range to give the colors, greenish-yellow of **1** and yellow of **2**. Thermal decomposition of **1** and **2** shows two steps in the range of 50 to 800 ˚C (Fig. S3b). In the first step, the mass loss corresponds to the removal of the isopropoxy groups beginning at 260 ˚C and achieving vigorously at 280 ˚C, accompany with the oxo-polymerization. The second step removes the aromatic ligands BDC and SAL molecules at about 400 ˚C and finishes at about 500 ˚C to form TiO_2. The loss weight is by and large in agreement with those of the deduced formula.

Structures of compounds 1 and 2.

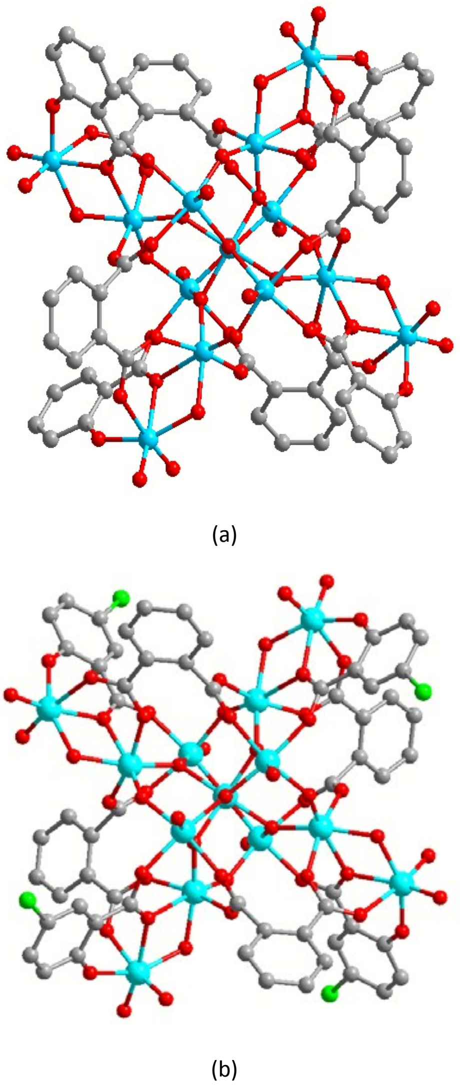
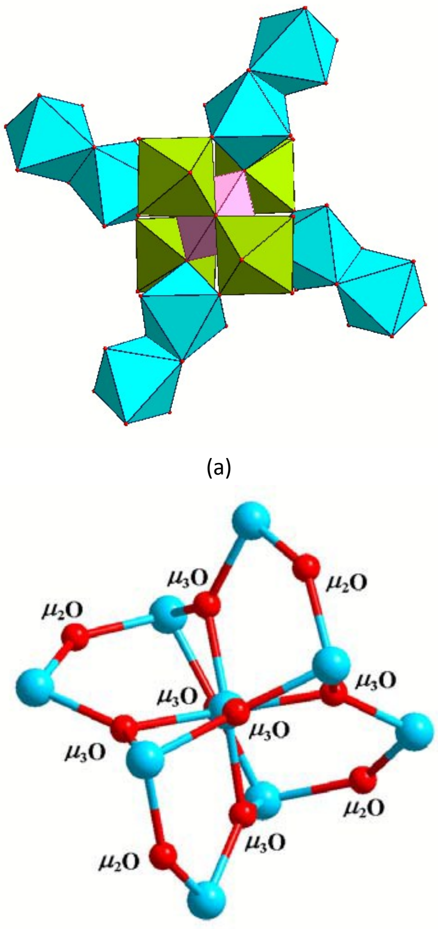


Fig. 1 Structures of compounds **1** (a) and **2** (b), the carbon atoms of isopropane and hydrogens are omitted for clarity.

The ball-stick plots of the structures of **1** and **2** are shown in Fig. 1. The frameworks of the two clusters are isostructral except the chloride atoms of the SAL of **2**. Hence only the structure of **1** is discussed here. Compound **1** is a Ti_{13} oxo cluster with four coordinated BDC and four coordinated SAL ligands. All the Ti(IV) atoms are octahedrally coordinated and assembled through co-sharing edges or corners of the octahedra (Fig. 2a). The central TiO_6 share edges with four neighboring TiO_6 in S_4 symmetry (Ti_5O_{22}) that paves the fundamental character of the structure. Four Ti_2O_{10} (edge-shared two TiO_6) connect with the Ti_5O_{22} core cluster by sharing the corners, forming a paddle-like arrangement. All the oxygen of the central TiO_6 are μ_3-O bridges, which bond to eight titanium atoms and these atoms are bridged by four μ_2-O to form a non-organic cluster core (Fig. 2b). The average distance of central Ti to Oμ_3 is 1.940 Å, while the average distance of Ti–Oμ_2 is 1.828 Å, shorter than the former. The anchoring type of two carboxyl groups of BDC is a μ_2-η^1:η^1 coordination mode and the carboxyl group of the SAL serves as a μ_3-η^2:η^1 coordination mode. The remainder sites of the Ti(IV) atoms are compensated by O^{i}Pr groups. Important Ti-O bond lengths are listed in Table S1 (Supporting Information). The TiO framework is not a compact sphere cluster as the oxo-titanium alkoxides, though the number of titanium is larger than ten. The result indicates that multidentate ligands can stabilize the non sphere structure of the TiO clusters, attributing to the stable chelate coordination and steric effect. To the best of our knowledge, this is a unique example of titanium-oxo-cluster featuring a divergent structure.

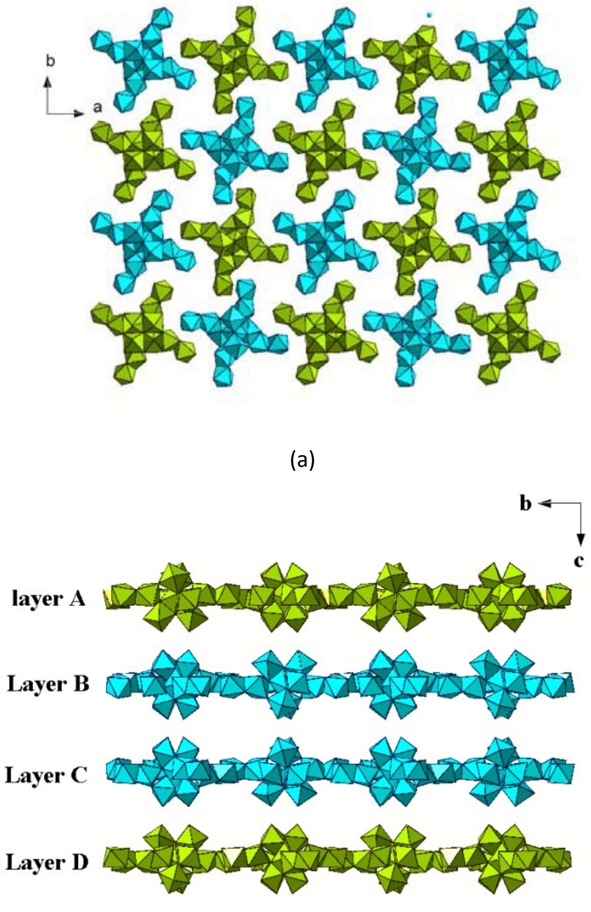


(a)

(b)

Fig. 2 (a) The polyhedron view of the divergent TiO cluster of $Ti_{13}(\mu_3\text{-}O)_8(\mu_2\text{-}O)_4(OR)_{24}$. (b) Ball-stick plots of the cluster core illustrating the μ_3-O and μ_2-O bridges.

Compound **1** crystallizes in the central symmetric space group *I*4$_1$/*a*. The cluster has an S_4 axis with paddles either in a clockwise or a counterclockwise rotation (Fig. 2), and the two rotated clusters are alternately arranged within the layer (the same color clusters in Fig. 3a). Fig. 3b shows the layered arrangement of the clusters viewed along *a* axis. The neighboring layers are cross-packed and face-back arranged in an ABCD manner along the *c* axis.



(a)

(b)

Fig. 3 (a) A two dimensional molecular arrangement of **1** viewed along *c* axis. (b) The ABCD layers packing, viewed along *c* axis.

Studies of the photocurrent response properties

It has been indicated that modification of the structures of titanium alkoxides with coordinated ligands yields oxo-molecular clusters that are substantially different from those of the parent alkoxides.[2] For the advantages in solution stability and film processing mentioned in introduction, photoactive film electrodes were prepared by wet coating process using clusters **1** and **2** as precursors to study the photocurrent response properties of the electrodes. The films were prepared by coating a dichloromethane solution of the compounds on a cleaned ITO substrate (a more detailed description is given in the experimental section). One layer coating and five layers coating films were prepared and they were treated at room temperature, 280 °C and 500 °C annealing temperatures, respectively, to study the film property in different states. The annealing temperatures are chosen according to the results of thermal analysis of crystals **1** and **2** (Fig. S3b). Based on the results of thermal analysis, the three different temperatures correspond to three different states, original cluster, ligand coordinated oxo-polymer (the isopropoxy groups lost) and the titanium oxide state (the organic component decomposed). These electrode films were subjected to scanning electron microscope (SEM) analysis (Fig. 4). The films prepared at room temperature are approximately uniform and become rougher when the layers are increased. Increasing the annealing temperature, the thick film cracked and rough films formed at 500 °C due to the decomposition of the organic components. The IR spectra of the films, prepared at room temperature, after 280 °C annealing and 500 °C annealing, are given in Fig. S4. The IR spectra of the film of **1** prepared at room temperature is similar to that of the crystal, which indicate that the cluster in solution is stable and no chemical change occurs in the process of film preparation (Fig. S4a). The vibrations at about 2970, 1110 and 1014 cm^{-1} disappear after 280 °C annealing that indicates the lost of isopropoxy groups. The stretches of BDC and SAL are still observed and only have some shift and broaden. After annealing at 500 °C, all the organic bands disappear and remain the Ti–O vibrations about 550 cm^{-1}. Similar result for compound **2** is shown in Fig. S4b. The conclusion deduced from the IR spectra of these films is in agreement with the thermal analysis of crystals. The XRD measurement of the 500 ˚C treated samples show that they are nanostructural anatase with weak broadened peaks at 25.5 and 47.8 in agreement with that reported (Fig. S5).[12b,d,15]

To study the photocurrent response of the film electrodes, a three electrodes photoelectrochemical cell consisting of a cluster coated ITO electrode was constructed. Fig. 5 shows the results under different experiment conditions. Fig. 5a shows the photocurrent responses of the solution coated cluster films (not annealing). Under the experiment condition, the photocurrent densities of clusters **1** and **2** are about 0.30 $\mu A \cdot cm^{-2}$ with a sharp response to the irradiation. No obvious difference in intensity for the two compounds, though that of **1** is somewhat larger. Although the response is fast, the shape of the curves is not a strict square wave and exhibits arcs at the top and bottom due to the effect of the non electric active organic components. The films treated with two annealing temperature, 280°C and 500 °C, are used to study the film property in different annealing states. The effect of the number of coating layers on the photocurrent is also studied and the results are displayed in Fig. 5b-5d. (1) The photocurrents are increased along with the increased number of the layers. The current density of a 5 layered film is about 2.5 times of that of the single layered film (Fig. 5c, 5d). (2) The annealing temperature significantly affects the intensity of photocurrent. At room temperature, the current density is about 0.3 $\mu A \cdot cm^{-2}$. After 280°C and 500 °C annealing, the current densities are about 1.0 and 2.2 $\mu A \cdot cm^{-2}$, respectively, for compound **1** (one layer electrodes, Fig. 5a, 5b and 5d). (3) Performance of the electrodes is improved when the annealing temperature is increased. At room temperature, there is delay at top and bottom, while for 280 °C treated electrodes, the delay is reduced. A sharp instant square wave response can be found for curves of 500 °C treated electrodes. The phenomena are also due to the state change mentioned above.

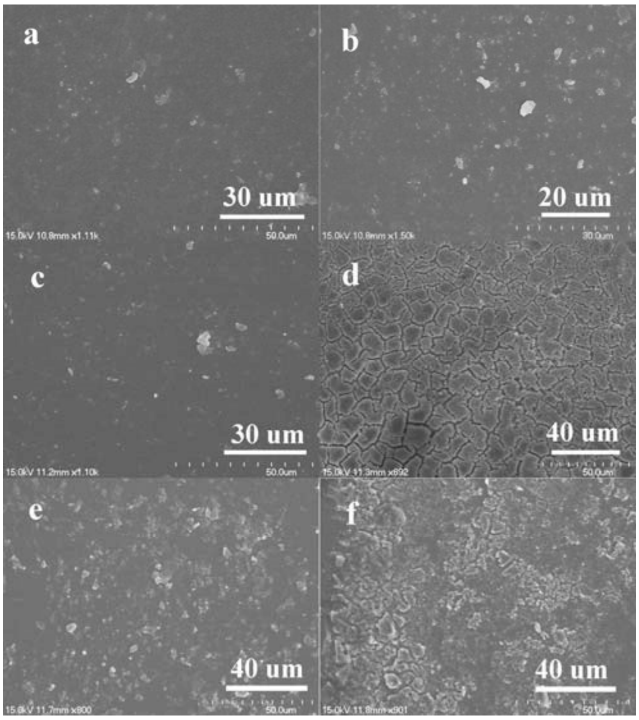
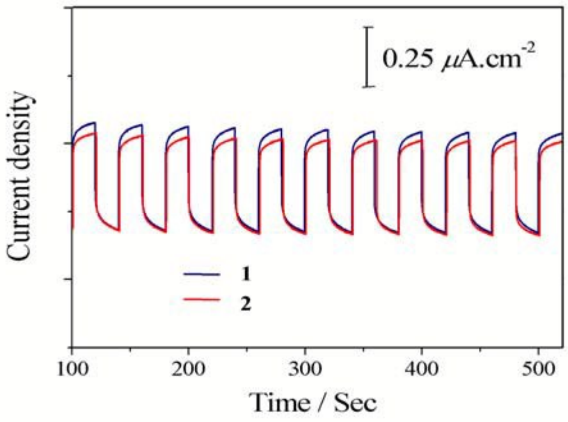
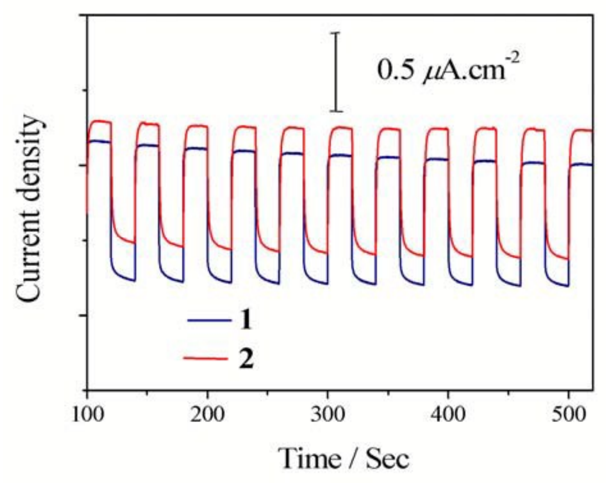


Fig. 4 SEM images of the films of **1** prepared by spin coating method using dichloromethane solutions. (a), (c) and (e) one layer coating; (b), (d) and (f) five layers coating. (a) and (b) room temperature, (c) and (d) after 280 °C annealing, (e) and (f) after 500 °C annealing.



(a)



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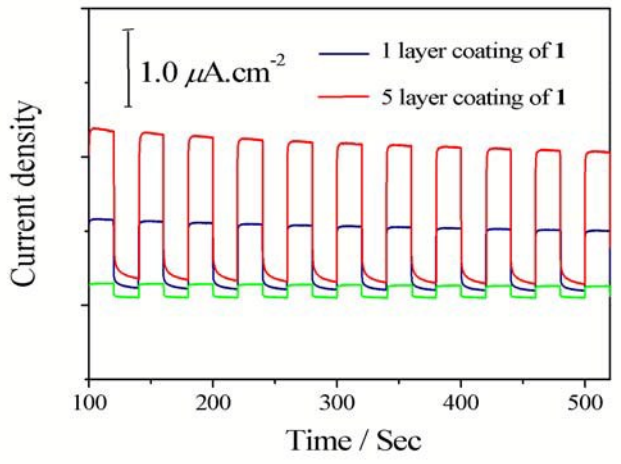
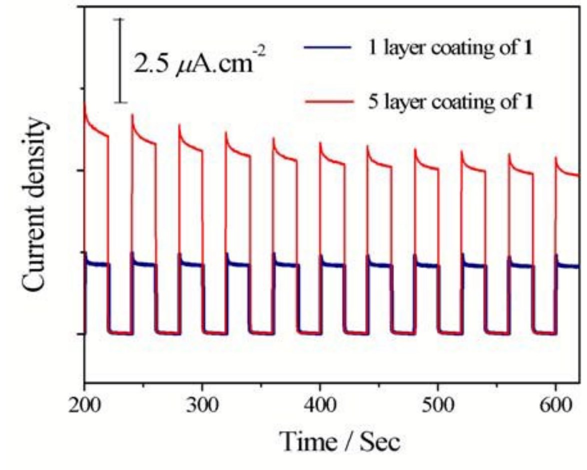


(c)



(d)

Fig. 5 The results of photocurrent densities measured in a three-electrode photoresponsive system (0.10 mol·L^{-1} aqueous solution of Na_2SO_4): (a) using the solution coated cluster **1** and **2** films in one layer); (b) using the 280 °C annealed films of **1** and **2** in one layer; (c) using the 280 °C annealed films **1** in one layer and five layers, along with the blank electrode; (d) using the 500 °C annealed films **1** in one layer and five layers.

Conclusions

In summary, two dicarboxylate and salicylate substituted Ti_{13} titanium-oxo-clusters have been prepared successfully by one step in situ solvothermal synthesis. Single crystal analysis shows that the two Ti_{13} clusters take a paddle-like arrangement with an S_4 symmetry. The non-compact structure is stabilized by the multidentate chelate coordination of BDC and SAL. This is a unique example of titanium-oxo-cluster featuring a divergent structure. Moreover, photoelectrode films were prepared by a simple solution coating process using the clusters as precursors and the photocurrent response properties of the electrodes were studied. The effects of annealing temperature and the number of coating layers on the photocurrent are studied and the results are as follows. (1) The photocurrents are increased along with the number of the increased layers. (2) Raising the annealing temperature significantly increases the intensity of photocurrent. (3) Performance, photoresponsiveness of the electrodes, is also improved when the annealing temperature is increased. Using ligand coordinated titanium oxo-clusters as the molecular precursors of TiO_2 anatase films is found to be effective due to the high solubility, stability in solution and hence easy controllability.

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Two Ti_{13}-oxo-clusters showing non-compact structures, film electrode preparation and photocurrent property

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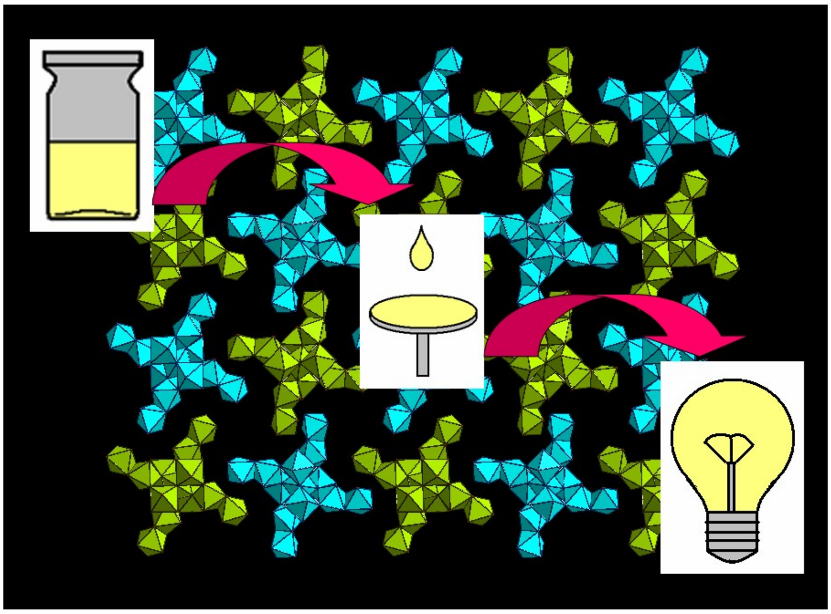
TOC



synopsis

Photoelectrodes are prepared by wet coating process using solutions of two new Ti_{13} clusters that take non-compact structures and the photocurrent response properties of the electrodes are studied.