



Synthesis, structure, and photocatalytic hydrogen of three environmentally friendly titanium oxo-clusters



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ABSTRACT

In this paper, three environmentally friendly titanium oxo-clusters, $\text{Ti}_6\text{O}_4(\text{OEt})_4(\text{OPr}^i)_4(\text{OOC}_6\text{H}_5)_8$ (**1**), $\text{Ti}_6\text{O}_4(\text{OEt})_8[\text{OOC}(\text{CH}_3)_3]_8$ (**2**) and $\text{Ti}_6\text{O}_4(\text{OCH}_3)_8[\text{OOC}(\text{CH}_3)_3]_8$ (**3**), were obtained under three similar solvent-thermal reactions of titanium(IV) isopropoxide, alcohols and carboxylic acids, and structurally characterized by single-crystal X-ray diffraction, TGA and IR analysis. All the compounds were crystallized in the space group $P2_1/c$ and the arrangements of the titanium atoms are similar. In addition, the UV-light photocatalytic hydrogen evolution activities have been observed for them, which showed good photocatalytic activity for hydrogen production from water.

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Metal oxo-clusters are widely studied by material chemists because of their potential applications in catalysis, electric conductivity, magnetism, nonlinear optics and medicine [1] as well as their intriguing variety of architectures and topologies. Titanium and titanium oxide show almost the highest activity for water splitting, which are considered to be one of the most promising environment-friendly materials, because of its highly active, low toxicity, stable chemical properties, abundance and low cost advantage [2]. Early in 1977, Schrauzer reported the first example where TiO_2 was used as photocatalyst for water splitting under UV irradiation [3]. Thereafter, some metal-substituted titanium complexes [4] and Ti-MOF (metal-organic framework) complexes, such as $\text{La}_4\text{Ti}_3\text{O}_7$ [5], BaTi_4O_9 [6], $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [7], and MIL-125(Ti) [8] have also been studied for catalytic hydrogen production under UV light, and Ti-MOF-NH₂ and Pt/Ti-MOF-NH₂ [9] under visible-light. However, they are complicated as catalysts in photocatalytic reactions, and photocatalytic hydrogen production of pure titanium oxo-clusters without any cocatalyst has rarely been reported to date.

Until now, a number of titanium oxo-clusters have been reported, with metal nuclearity ranging from 2 to 34. The largest titanium oxo-clusters $[\text{Ti}_{34}\text{O}_{50}(\text{OPr}^i)_{30}\text{DMABA}_6]$ has been reported by Sokolow in 2012 [10]. Titanium oxo-clusters contain three types: Titanium polyoxoalkoxy structures $[\text{Ti}_n\text{O}_m(\text{OR})_{4n-2m}]$, oxo and alkoxy groups $[\text{Ti}_n\text{O}_{2n-x/2-y/2}(\text{OR})_x(\text{L})_y]$, and purely carboxo-clusters $[\text{Ti}_n\text{O}_m(\text{OOCR})_y]$ [11], whereas the second type is more stable than the others [12]. Generally, the titanium oxo-clusters are obtained under solvent-thermal conditions, in which toxic solvents such as toluene [13] and acetonitrile [8,13(a)] were used. Here in our work, environmentally friendly alcohols were used instead. Three titanium oxo-clusters,

$\text{Ti}_6\text{O}_4(\text{OEt})_4(\text{OPr}^i)_4(\text{OOC}_6\text{H}_5)_8$ (**1**), $\text{Ti}_6\text{O}_4(\text{OEt})_8[\text{OOC}(\text{CH}_3)_3]_8$ (**2**) and $\text{Ti}_6\text{O}_4(\text{OCH}_3)_8[\text{OOC}(\text{CH}_3)_3]_8$ (**3**), were prepared by the combination of titanium isopropoxide, different carboxylic acid heated at 100 °C for 6 h in a sealed 12 mL Teflon-lined stainless steel vessel under autogeneous pressure [14]. Our reaction schemes are comparatively different from that of Moraru [15] and Kickelbick [16], who had reported the compounds with the similar Ti_6O_4 structural core as described in this work. But in those cases, Ti_6O_4 clusters were obtained under the conditions of 4 °C for 3 weeks.

The Ti_6O_4 structural core belongs to the second class of titanium oxo-clusters mentioned above. Single-crystal X-ray diffraction analysis reveals that all the compounds are crystallized in the same space group $P2_1/c$, but the organic ligands of them are different. Crystal data and structure refinement for compounds **1**, **2**, and **3** [17] are shown in Table S1. Due to the fact that the structures of **1–3** are similar (Fig. 1), the structure of **1** will be described in detail as a representative. As shown in Fig. 1d, the six Ti atoms of **1** form a circular arrangement in which all of them are six coordinated with oxygen atoms ($\mu_2\text{-O}$ and $\mu_3\text{-O}$), exhibiting distorted octahedral geometries. The Ti_6O_4 core of molecule $[\text{Ti}_6\text{O}_4(\text{OR})_8(\text{OOCR})_8]$ is built of two asymmetric units linked by a center of symmetry as shown in Fig. 2. The bridging of Ti(1), Ti(2) and Ti(3) is asymmetrical; one carboxylate bridge ($\mu_2\text{-O}$) and one alkoxy ($\mu_3\text{-O}$) bridge between Ti(1) and Ti(2), one carboxylate ($\mu_2\text{-O}$) bridge between Ti(2) and Ti(3) and no bridge between Ti(1) and Ti(3). The distances of Ti and $\mu_2\text{-O}$ [1.741(3) Å – 2.071(3) Å] and Ti and $\mu_3\text{-O}$ [1.953(3) Å – 2.074(3) Å] are similar to other titanium oxo-clusters [18]. There exists a 3D supramolecular structure via $\pi\text{-}\pi$ stacking interactions (face-to-face: 3.56 Å, centroid-to-centroid: 3.88 Å), which could be responsible for the cohesion and stability of the structure. Apart from these, no other classic hydrogen bonds or weak interactions are found (Fig. 3).

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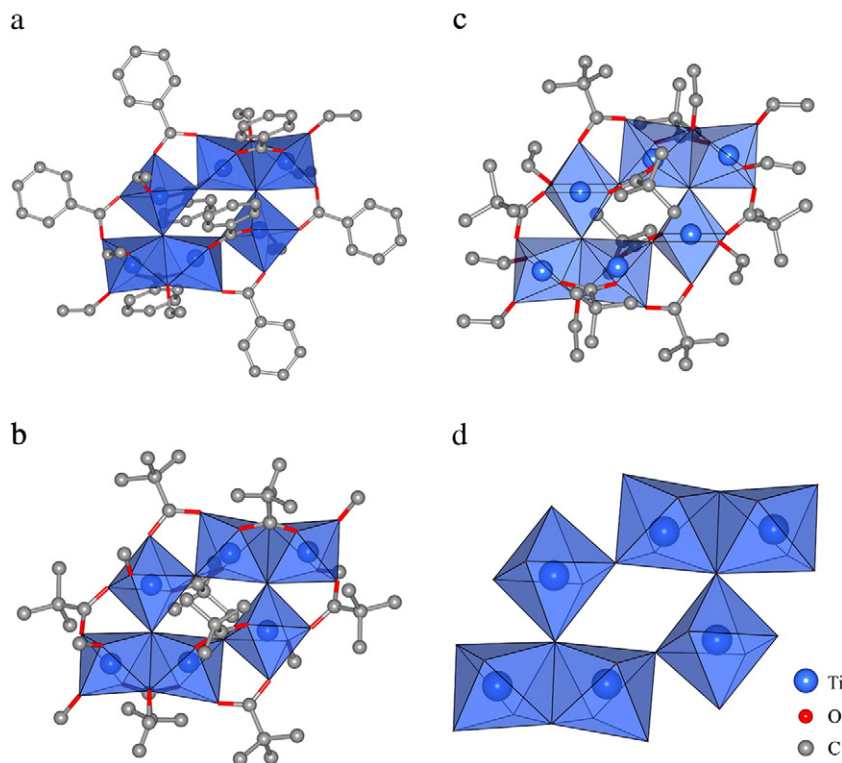


Fig. 1. a), b) and c) Polyhedral/ball-and-stick representation of compounds **1**, **2** and **3** respectively, d) linking of the coordination polyhedra of Ti_6O_4 structure core in the three similar structure. All hydrogen atoms are omitted for clarity.

To study the thermal stability of the complexes, thermogravimetric analyses (TGA) were performed on crystalline samples under nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The thermal behaviors of compounds **1–3** are similar and the TG diagrams display continuous weight losses between 165 to $530\text{ }^\circ\text{C}$. The remaining weight may correspond to the final products of TiO_2 (**1**: obs 27.7%, calc 27.2%; **2**: obs 33.1%, calc 33.7%; **3**: obs 35.7%, calc 36.6%).

Photocatalytic reactions were carried out in a closed gas circulation system by using a 500 W mercury lamp for UV irradiation. Fig. 4 shows the yields and rate of H_2 evolution in the presence of 10% methanol as a sacrificial electron donor with compounds **1–3** (0.1 g respectively) as the UV light photosensitizer and catalyst as time goes by. The details are shown in Table 1. Efficiently H_2 evolved even without co-catalysts such as Pt from water. Highest rates of compounds **1–3** are $326\text{ }\mu\text{mol/h/g}$, $210\text{ }\mu\text{mol/h/g}$ and $236\text{ }\mu\text{mol/h/g}$ respectively, while it was reported that rates of pure TiO_2 nanowires (1 g), nanotubes (1 g) and nanosheets (1 g) without co-catalysts were $54\text{ }\mu\text{mol/h/g}$ [19], $285\text{ }\mu\text{mol/h/g}$ [20] and $117.6\text{ }\mu\text{mol/h/g}$ [21] respectively under the same condition. As shown in Fig. 4(a) and (b), both the trends of yields and rates change analogously for compounds **1–3**, mainly

due to their titanium clusters' similar arrangements, even though the ligands are different. In additions, the good agreement between the XRD patterns before and after photocatalytic reaction reveals the stability and prospects of compound **1** in photocatalysis (Fig. S1).

In summary, we have successfully synthesized and structurally characterized three hexanuclear titanium oxo-clusters, $\text{Ti}_6\text{O}_4(\text{OEt})_4(\text{OPr}^i)_4(\text{OOC}_6\text{H}_5)_8$, $\text{Ti}_6\text{O}_4(\text{OEt})_8[\text{OOC}(\text{CH}_3)_3]_8$ and $\text{Ti}_6\text{O}_4(\text{OCH}_3)_8[\text{OOC}(\text{CH}_3)_3]_8$, under three similar solvent-thermal reactions with environmentally friendly alcohols. Their similar structures and high activity in photocatalytic hydrogen from water under UV light have been investigated in detail. The discovery of these new titanium oxo-clusters affords new opportunities for developing metal oxo-clusters chemistry and exploring highly efficient photocatalysts.

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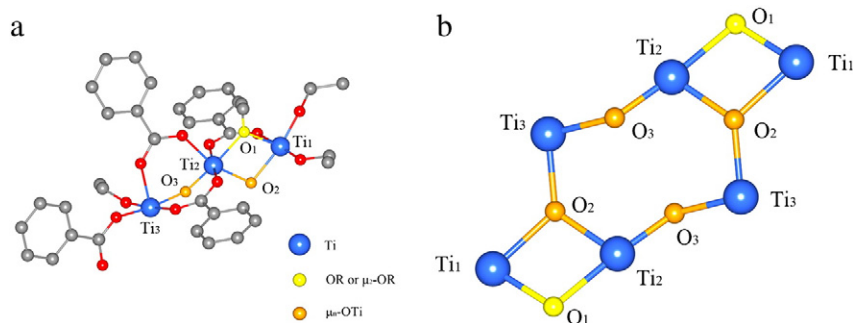


Fig. 2. a) View of the asymmetric unit of compound **1** shows the connectivity. b) Schematic representation of the polyhedral arrangement of $\text{Ti}_6\text{O}_4(\text{OR})_8(\text{OOCR})_8$.

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