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Communication

Odd-membered cyclic hetero-polyoxotitanate nanoclusters with high stability and photocatalytic H₂ evolution activity

Ya-Jie Liu^{a,b}, Lin Geng^{a,c}, Yao Kang^a, Wei-Hui Fang^{a,*}, Jian Zhang^{a,#}^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, Fujian, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, Fujian, China

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ABSTRACT

We investigated the hydrolysis of Ti^{IV} along with naturally abundant Al^{III} ions and reported the formation of a stable and semiconducting nanocluster. Interestingly, this compound exhibits an unusual odd-membered ring structure and also represents the largest Al-containing polyoxotitanium cluster (PTC) observed thus far. The presence of a shell of organic ligands as well as the incorporation of hetero-Al^{III} ions endowed the nanocluster with high air, thermal, and pH stabilities. The present compound exhibited a record photocatalytic hydrogen evolution of 402.88 μmol g⁻¹ h⁻¹ among PTC materials. This work not only paves the way towards stable PTC materials but also provides new insights into the design of novel photocatalysts.

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The use of solar energy is a promising approach to address the current energy crisis and environmental issues [1,2]. As one of the most promising photocatalysts, titania is a highly stable and environmentally benign material [3,4]. However, assumptions and theoretical optimizations are required to understand the mechanism of the photocatalysis process. To avoid extensive theoretical and experimental studies, crystalline polyoxotitanium clusters (PTCs) with precise structural information, which can be considered as structural models of titania, have attracted considerable attention in recent years [5–7]. Wright et al. [8,9] illustrated the applications of functional ligand-modified and metal ion-doped PTCs. A majority of the PTCs containing terminal alkoxy groups investigated thus far are readily hydrolyzed by the moisture in the air. As a result, investigations of their photocatalytic performance are largely limited

by their poor stability, and only a few cases have been demonstrated for photocatalysis [10,11].

To improve the stability of PTCs, modifying the inorganic titanium-oxo core with a π -conjugated organic shell has proved to be an effective approach, such as in the case of carboxylate- and phenol-coordinating PTCs [12,13]. In addition, metal dopants provide an opportunity to modify the microscopic electronic structure and affect macroscopic photocatalytic performances [8,14–17]. As the most abundant metal in the biosphere, aluminum is of major environmental importance [18,19]. A broad range of hydrolysis compounds of aluminum are present on the earth's surface. Hence, it would be significantly interesting to study the hydrolysis and photocatalysis chemistry of titanium with naturally abundant aluminum ions. However, only a few structurally characterized Al-containing

* Corresponding author. E-mail: fwh@fjirsm.ac.cn

Corresponding author. Tel/Fax: +86-591-63179450; E-mail: zhj@fjirsm.ac.cn

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PTCs have been reported to date, including tetrametallic Ti_3Al [20], pentametallic Ti_3Al_2 [21], hexametallic Ti_3Al_3 [22], heptametallic Ti_6Al , as well as octametallic Ti_7Al clusters (Fig. 1a) [23]. All these compounds were obtained through a stepwise approach. Therefore, the preparation and exploration of the properties of high-nuclearity Al-containing PTCs is a highly challenging but interesting task.

Herein, we successfully improved the stability of PTCs through a combination of carboxylate shell protection and hetero-metal doping. The hydrolysis of titanium and aluminum ions resulted in the isolation of a fascinating core-shell wheel nanocluster (up to 2.5 nm), $[\text{Al}_7\text{Ti}_{14}(\mu_2\text{-O})_7(\mu_3\text{-O})_{14}(\text{L})_{35}]\cdot 2\text{CH}_3\text{CN}$ (**1**; L = benzoic acid) (Fig. 1b). The binding modes of the carboxylate to the semiconductor surfaces were determined unambiguously via single-crystal X-ray diffraction (XRD) methods. Notably, the semiconducting core-shell cluster was highly stable in both acidic and basic aqueous solutions. The crystalline material was able to generate large photocurrents and exhibited good photochromic and photocatalytic properties.

Colorless single crystals of complex **1** were obtained through straightforward hydrolysis of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Al}(\text{O}^i\text{Pr})_3$ in the presence of benzoate. The phase purity of the experimental sample was identified using powder XRD (PXRD) analysis (Fig. S1). To further characterize the bulk sample of compound **1**, we performed infrared (IR), thermogravimetric analysis (TGA), optical diffuse-reflection spectroscopy, and energy-dispersive X-ray spectroscopy (EDX) measurements (Figs. S2–S5). The oxidation states of metal ions and oxo bridges were established by a combination of charge balance considerations and bond valence sum (BVS) calculations (Table S2) [24].

The prominent feature of **1** is the presence of an uncommon

Fig. 1. (a) Summary of reported Al-containing PTCs: inorganic cores of Ti_3Al , Ti_3Al_2 , Ti_3Al_3 , Ti_6Al , and Ti_7Al clusters; (b) core-shell wheel nanocluster of compound **1**. Hydrogen atoms and guest acetonitrile molecules are omitted for clarity.

odd-membered cyclic cluster. According to the literature, cyclic compounds are generally high-symmetry, even-membered systems such as the giant Mn_{84} single-molecule magnets and the well-known protein-sized Mo_{368} cluster [25–29]. Similarly, most cyclic clusters previously reported in the PTC area are even-membered, such as Ti_8 [30–32], Ti_{10} [33], $\text{Ti}_{12}\text{In}_6$ [12], $\text{Ti}_{12}\text{Cr}_6$ [34], Ti_{20} [35], and Ti_{32} [36]. Odd-membered cyclic clusters are uncommon [37]. Herein, we synthesized a 21-membered inorganic core fully surrounded by organic ligands. The most notable structural feature of the inorganic core was the presence of a typical $[\text{Ti}_{14}\text{O}_{21}]^{14+}$ ring built from seven trigonal $[\text{Ti}_3\text{O}_3]^{6+}$ segments sharing their inner Ti atoms (Fig. 2a). To our knowledge, no such $[\text{Ti}_{14}\text{O}_{21}]^{14+}$ ring with a seven-vertex star configuration has been reported to date. Subsequently, the seven Al atoms acted as bridges and effectively linked the neighboring $[\text{Ti}_3\text{O}_3]^{6+}$ segments into a wheel-shaped assembly, yielding a $[\text{Ti}_{14}\text{Al}_7(\mu_3\text{-O})_{21}]^{35+}$ heterometallic cluster (Fig. 2b). Owing to its high electropositivity, the corrugated wheel was further surrounded and charge-compensated by 35 ligands, exclusively in a bridging bidentate mode (Fig. 2c, 2d). Unlike single-stranded wheels [30–32,38,39], $\{\text{Ti}_{14}\text{Al}_7\}$ exhibited a donut-like ring structure with an inner diameter of approximately 0.8 nm and an outer diameter of 1.35 nm. All metal

Fig. 2. (a) Ball-and-stick representation of the $[\text{Ti}_{14}\text{O}_{21}]^{14+}$ ring. (b) Ball-and-stick representation of the $\{\text{Ti}_{14}\text{Al}_7\}$ heterometallic ring. (c,d) Top/side views of ball-and-stick representations of **1**. (e) 3-D supramolecular packing of **1** viewed along the b axis. (f) Simplified 3-D supramolecular packing of **1**. Hydrogen atoms and guest acetonitrile molecules are omitted for clarity.

ions possessed an octahedral coordination geometry. Each Al^{3+} ion resided in an octahedral environment with four carboxylate oxygen atoms (O_{COO}) from four organic ligands and two $\mu_3\text{-O}$ atoms (Fig. S6a, S6b). Every external Ti^{4+} ion had similar coordination environment to Al^{3+} (Fig. S6c, S6d), and each internal Ti^{4+} ion was coordinated by two O_{COO} from two organic ligands, two $\mu_3\text{-O}$, and two $\mu_2\text{-O}$ bridges (Fig. S6e, S6f). The lengths of the Ti–O and Al–O bonds ranged from 1.722 to 2.279 Å and 1.861 to 1.925 Å, respectively (Table S2), which were comparable to those of related complexes [40–42]. Noticeably, two acetonitrile guest molecules were trapped in each molecular unit and could be crystallographically identified (Fig. S7). The $\{\text{Ti}_{14}\text{Al}_7\}$ wheels in compound **1** were further packed together through weak supramolecular interactions (hydrogen bonding and van der Waals forces) (Figs. 2e and S8). In the *ac* plane, each $\text{Al}_7\text{Ti}_{14}$ wheel was surrounded by six crystallographically equivalent units, forming a hexagonal array (Fig. 2e). Moreover, when viewed along the *b* axis, the wheels exhibited two types of spatial orientations staggered in an $\cdots\text{ABAB}\cdots$ motif (Fig. 2f). According to the Cambridge Crystallographic Data Centre (CCDC) database, this heterometallic nanocluster not only represents a rare example of an odd-membered cyclic compound but also an unusual case of high nuclearity in Ti/Al-related crystalline materials.

Before exploring the photophysical properties of the present compounds, we investigated their stability. The crystals of **1** could survive longer than 6 months in the air, as monitored

and confirmed using PXRD. In addition, **1** exhibited remarkable thermal stability in air and water below 100 °C for 24 h (Fig. S9). Furthermore, we checked the stability of **1** in aqueous solutions with pH ranging from 1 to 12 for a period of 12 h. No evident crystallinity loss could be detected *via* PXRD (Fig. 3a), which highlights the potential of the present system for heterogeneous catalysis in aqueous media. Such high stability can be ascribed to the significantly stronger coordination bonds between the organic carboxylate shell and the inorganic Ti/Al core.

At present, studies of the photocatalytic applications of PTCs are rare, although TiO_2 nanomaterials exhibit distinct photo-physical properties [43–48], which may be due to the low stability of PTCs in aqueous solution. Based on the excellent stability of **1**, we carried out water-splitting H_2 production tests under UV-vis light irradiation, in which **1** was used as photocatalyst and lactic acid served as a sacrificial reducing agent. As shown in Fig. 3b, the H_2 generation from **1** exhibited a linear increase during the entire testing period. The H_2 production rate of **1** reached about $402.88 \mu\text{mol g}^{-1} \text{h}^{-1}$. Although this value was not higher than that of titanium oxide, it was comparable to the rates of most PTCs and of some other materials (e.g., covalent- or metal-organic frameworks as well as perovskite oxides) reported in the literature, as summarized in Tables S3 and S4 [49]. After removing **1** from the reaction system, the H_2 production rate was only $14.46 \mu\text{mol g}^{-1} \text{h}^{-1}$. The cycling tests and unchanged PXRD patterns confirmed the stability of **1**

Fig. 3. (a) PXRD patterns of **1** (simulated or immersed in aqueous solution at pH = 1, 3, 5, 7, 9, and 12 (adjusted with H_2SO_4 or NaOH) for 12 h). (b) Comparison of H_2 evolution profiles under UV-visible (UV-vis) light, obtained with or without **1**. (c) Cycling tests of H_2 evolution from **1** under UV-vis light irradiation. (d) Transient photocurrent responses of **1** under +0.2 V bias potential and UV-vis light irradiation with and without lactic acid.

during the photocatalytic experiments (Figs. 3c, S10, and S11).

To explore the possible mechanism, we first measured the electron paramagnetic resonance (EPR) spectra of compound **1**. After 20 min of light irradiation, the colorless compound **1** immersed in a mixture solution of H₂O and lactic acid changed to black. The EPR spectrum of this black sample showed an obvious signal at $g = 1.950$, corresponding to the paramagnetic Ti³⁺ ions (Fig. S12) [50,51]. However, no EPR resonance was observed in the dark. In the absence of the sacrificial agent, another obvious photochromic feature was observed in the air: instead of turning dark, the color of compound **1** only changed to yellow upon UV irradiation, even after exposure for several hours (Figs. S13 and S14). Then, the emission intensity of complex **1** was reduced, and the peak position exhibited a redshift of 90 nm compared with that of benzoate, indicating a ligand-to-metal charge transfer (LMCT) process (Fig. S15) [52–54]. Moreover, in order to understand the charge separation mechanism, we measured the photoluminescence decay spectrum of compound **1**, which presented an average lifetime of 4.12 ns (Fig. S16). This value is larger than that of pristine TiO₂ (2–4 ns) [55,56], suggesting that the Al dopant and the protection of the organic shell effectively promoted charge separation [57–59]. Furthermore, the transient photocurrent responses of **1** were measured to study the charge separation efficiency. A weak photocurrent response was detected when the experiment was carried out in a 0.2 mol/L Na₂SO₄ electrolyte solution without any sacrificial agent (Fig. 3d). However, the current densities exhibited a dramatic improvement (with the density value increasing up to 1.5 $\mu\text{A}/\text{cm}^2$) when lactic acid was added to the electrolyte solution. This result could be attributed to the rapid transfer of photogenerated holes in **1** to lactic acid and is fully consistent with the H₂ evolution results discussed above.

On the basis of the above experimental results, we propose the photocatalytic mechanism shown in Fig. S17. Upon irradiation with a xenon lamp, a photogenerated excited electron is transferred from the benzoate ligands to the {Ti₁₄Al₇} cluster, forming the Ti³⁺ species. Then, H⁺ ions accept the electron from Ti³⁺ to produce H₂ and Ti⁴⁺. Lactic acid, serving as sacrificial agent, fills the holes in the benzoate ligands restoring their ground state, thus completing the photocatalytic cycle [60–64].

In summary, we have successfully prepared and characterized the first examples of odd-membered core-shell wheel nanoclusters through a one-step synthesis. Upon carboxylate shell protection and hetero-metal incorporation, the nanoclusters showed high air, thermal, and pH stability, as well as obvious photochromic properties. Moreover, they exhibited excellent photocatalytic H₂ evolution capabilities compared to other PTCs. The materials investigated in this work not only expand the very small family of Al-containing PTC compounds but also exhibit promising potential in applications based on photochemical and photocatalytic reactions.

Electronic supporting information

Supporting information associated with this article contains chemical and physical measurements and detailed synthesis is

available in the online version of this article. CCDC 1985014 contains the supplementary crystallographic data for compound **1**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] W. Zhang, W. Lai, R. Cao, *Chem. Rev.*, **2017**, 117, 3717–3797.
- [2] J. Qi, W. Zhang, R. Cao, *Adv. Energy Mater.*, **2018**, 8, 1701620.
- [3] S. Horikoshi, N. Serpone, *Catal. Today*, **2020**, 340, 334–346.
- [4] C. H. A. Tsang, K. Li, Y. Zeng, W. Zhao, T. Zhang, Y. Zhan, R. Xie, D. Y. C. Leung, H. Huang, *Environ. Int.*, **2019**, 125, 200–228.
- [5] W. H. Fang, L. Zhang, J. Zhang, *Chem. Soc. Rev.*, **2018**, 47, 404–421.
- [6] P. Coppens, Y. Chen, E. Trzop, *Chem. Rev.*, **2014**, 114, 9645–9661.
- [7] L. Rozes, C. Sanchez, *Chem. Soc. Rev.*, **2011**, 40, 1006–1030.
- [8] P. D. Matthews, T. C. King, D. S. Wright, *Chem. Commun.*, **2014**, 50, 12815–12823.
- [9] N. Li, P. D. Matthews, H. K. Luo, D. S. Wright, *Chem. Commun.*, **2016**, 52, 11180–11190.
- [10] J. X. Liu, M. Y. Gao, W. H. Fang, L. Zhang, J. Zhang, *Angew. Chem. Int. Ed.*, **2016**, 55, 5160–5165.
- [11] Y. Y. Wu, X. W. Lu, M. Qi, H. C. Su, X. W. Zhao, Q. Y. Zhu, J. Dai, *Inorg. Chem.*, **2014**, 53, 7233–7240.
- [12] S. Liu, W. Hu, J. K. Nath, J. Tong, X. Hou, W. Liu, J. Yang, B. Liu, *Dalton Trans.*, **2017**, 46, 678–684.
- [13] X. Fan, H. Fu, M. Y. Gao, L. Zhang, J. Zhang, *Inorg. Chem.*, **2019**, 58, 13353–13359.
- [14] Y.-J. Liu, W.-H. Fang, L. Zhang, J. Zhang, *Coord. Chem. Rev.*, **2020**, 404, 213099.
- [15] J. D. Xiao, L. Han, J. Luo, S. H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.*, **2018**, 57, 1103–1107.
- [16] Q. Yang, Q. Xu, S.-H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.*, **2016**, 55, 3685–3689.
- [17] K. Sun, J. Shen, Q. Liu, H. Tang, M. Zhang, S. Zulfiqar, C. Lei, *Chin. J. Catal.*, **2020**, 41, 72–81.
- [18] W. H. Casey, *Chem. Rev.*, **2006**, 106, 1–16.
- [19] Z. L. Mensinger, W. Wang, D. A. Keszler, D. W. Johnson, *Chem. Soc. Rev.*, **2012**, 41, 1019–1030.
- [20] S. Aguado-Ullate, J. J. Carbó, O. González-del Moral, M. Gómez-Pantoja, A. Hernán-Gómez, A. Martín, M. Mena, J. M. Poblet, C. Santamaría, *J. Organomet. Chem.*, **2011**, 696, 4011–4017.
- [21] A. Hernan-Gomez, A. Martin, M. Mena, C. Santamaria, *Inorg. Chem.*, **2010**, 49, 8401–8410.
- [22] O. Gonzalez-del Moral, A. Hernan-Gomez, A. Martin, M. Mena, C. Santamaria, *Dalton Trans.*, **2008**, 44–46.
- [23] G. A. Timco, A. Fernandez, A. K. Kostopoulos, C. A. Muryn, R. G. Pritchard, I. Strashnov, I. J. Vitorica-Yrezabal, G. F. S. Whitehead, R. E. P. Winpenny, *Angew. Chem. Int. Ed.*, **2017**, 56, 13629–13632.
- [24] G. P. Shields, P. R. Raithby, F. H. Allen, W. D. S. Motherwell, *Acta Crystallogr.*, **1999**, B56, 455–465.
- [25] A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.*, **2004**, 43, 2117–2121.
- [26] A. Müller, B. Botar, S. K. Das, H. Bögge, M. Schmidtman, A. Merca, *Polyhedron*, **2004**, 23, 2381–2385.
- [27] M. Affronte, S. Carretta, G. A. Timco, R. E. P. Winpenny, *Chem. Commun.*, **2007**, 1789–1797.
- [28] E. Garlatti, M. A. Albring, M. L. Baker, R. J. Docherty, H. Mutka, T. Guidi, V. Garcia Sakai, G. F. S. Whitehead, R. G. Pritchard, G. A. Timco, F. Tuna, G. Amoretti, S. Carretta, P. Santini, G. Lorusso, M. Affronte, E. J. L. McInnes, D. Collison, R. E. P. Winpenny, *J. Am.*

- Chem. Soc.*, **2014**, 136, 9763–9772.
- [29] T. Kajiwara, H. Wu, T. Ito, N. Iki, S. Miyano, *Angew. Chem. Int. Ed.*, **2004**, 43, 1832–1835.
- [30] C. Artner, M. Czakler, U. Schubert, *Chem. Eur. J.*, **2014**, 20, 493–498.
- [31] T. Frot, S. Cochet, G. Laurent, C. Sassoie, M. Popall, C. Sanchez, L. Rozes, *Eur. J. Inorg. Chem.*, **2010**, 2010, 5650–5659.
- [32] H. Barrow, D. A. Brown, N. W. Alcock, H. J. Clase, M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, **1995**, 1231–1232.
- [33] H. Assi, G. Mouchaham, N. Steunou, T. Devic, C. Serre, *Chem. Soc. Rev.*, **2017**, 46, 3431–3452.
- [34] J. Zhang, W. Hu, J. Zhang, S. Liu, J. Tong, X. Hou, W. Liu, J. Yang, B. Liu, *J. Phys. Chem. C*, **2017**, 121, 18326–18332.
- [35] W. T. Jin, F. Yang, L. Deng, M. L. Chen, J. F. Chen, H. B. Chen, Z. H. Zhou, *Inorg. Chem.*, **2018**, 57, 14116–14122.
- [36] C. Zhao, Y. Z. Han, S. Dai, X. Chen, J. Yan, W. Zhang, H. Su, S. Lin, Z. Tang, B. K. Teo, N. Zheng, *Angew. Chem. Int. Ed.*, **2017**, 56, 16252–16256.
- [37] G. Kickelbick, U. Schubert, *Eur. J. Inorg. Chem.*, **1998**, 159–161.
- [38] P. King, T. C. Stamatatos, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.*, **2006**, 45, 7379–7383.
- [39] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.*, **1994**, 116, 823–832.
- [40] Z. Janas, L. B. Jerzykiewicz, P. Sobota, K. Szczegot, D. Wiczeniewska, *Organometallics*, **2005**, 24, 3987–3994.
- [41] S. K. Mandal, P. M. Gurubasavaraj, H. W. Roesky, R. B. Oswald, J. Magull, A. Ringe, *Inorg. Chem.*, **2007**, 46, 7594–7600.
- [42] C. Krüger, R. Mynott, C. Siedenbiedel, L. Stehling, G. Wilke, *Angew. Chem. Int. Ed. Engl.*, **1991**, 30, 1668–1670.
- [43] P. Wang, S. Xu, F. Chen, H. Yu, *Chin. J. Catal.*, **2019**, 40, 343–351.
- [44] Z.-W. Zhang, Q.-H. Li, X.-Q. Qiao, D. Hou, D.-S. Li, *Chin. J. Catal.*, **2019**, 40, 371–379.
- [45] Y. Zhu, Z. Zhang, N. Lu, R. Hua, B. Dong, *Chin. J. Catal.*, **2019**, 40, 413–423.
- [46] D. Ren, Z. Liang, Y. H. Ng, P. Zhang, Q. Xiang, X. Li, *Chem. Eng. J.*, **2020**, 390, 124496.
- [47] D. Ren, R. Shen, Z. Jiang, X. Lu, X. Li, *Chin. J. Catal.*, **2020**, 41, 31–40.
- [48] R. Shen, L. Zhang, X. Chen, M. Jaroniec, N. Li, X. Li, *Appl. Catal. B-Environ.*, **2020**, 266, 118619.
- [49] F.-M. Zhang, J.-L. Sheng, Z.-D. Yang, X.-J. Sun, H.-L. Tang, M. Lu, H. Dong, F.-C. Shen, J. Liu, Y.-Q. Lan, *Angew. Chem. Int. Ed.*, **2018**, 57, 12106–12110.
- [50] M. Y. Gao, L. Zhang, J. Zhang, *Chem. Eur. J.*, **2019**, 25, 10450–10455.
- [51] Y. Y. Wu, W. Luo, Y. H. Wang, Y. Y. Pu, X. Zhang, L. S. You, Q. Y. Zhu, J. Dai, *Inorg. Chem.*, **2012**, 51, 8982–8988.
- [52] H. Wu, B. Yan, R. Liang, V. Singh, P. Ma, J. Wang, J. Niu, *Dalton. Trans.*, **2020**, 49, 388–394.
- [53] L. Xue, C. Liu, H. Jiang, *Chem. Commun.*, **2009**, 1061–1063.
- [54] P. Ashokkumar, V. T. Ramakrishnan, P. Ramamurthy, *J. Phys. Chem. A*, **2011**, 115, 14292–14299.
- [55] H. N. Ghosh, S. Adhikari, *Langmuir*, **2001**, 17, 4129–4130.
- [56] J. Zhou, Y. Zhang, X. S. Zhao, A. K. Ray, *Ind. Eng. Chem. Res.*, **2006**, 45, 3503–3511.
- [57] J. Hu, L. Zhan, G. Zhang, Q. Zhang, L. Du, C.-H. Tung, Y. Wang, *Inorg. Chem.*, **2016**, 55, 8493–8501.

Graphical Abstract

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Odd-membered cyclic hetero-polyoxotitanate nanoclusters with high stability and photocatalytic H₂ evolution activity

Ya-jie Liu, Lin Geng, Yao Kang, Wei-Hui Fang*, Jian Zhang*

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences;

University of Chinese Academy of Sciences;

Fujian Normal University

Crystalline polyoxotitanates continue to be of great interest for their potential application in photocatalysis. Apart from high stability, the core-shell Ti₁₄Al₇ nanocluster presented a record photocatalytic H₂ evolution among other compounds in this area.

- [58] N. Xiao, S. Li, S. Liu, B. Xu, Y. Li, Y. Gao, L. Ge, G. Lu, *Chin. J. Catal.*, **2019**, 40, 352–361.
- [59] R. Shen, J. Xie, Q. Xiang, X. Chen, J. Jiang, X. Li, *Chin. J. Catal.*, **2019**, 40, 240–288.
- [60] Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, *Angew. Chem. Int. Ed.*, **2012**, 51, 3364–3367.
- [61] Y. Horiuchi, T. Toyao, M. Saito, K. Mochizuki, M. Iwata, H. Higashimura, M. Anpo, M. Matsuoka, *J. Phys. Chem. C*, **2012**, 116, 20848–20853.
- [62] D. Sun, Y. Fu, W. Liu, L. Ye, D. Wang, L. Yang, X. Fu, Z. Li, *Chem. Eur. J.*, **2013**, 19, 14279–14285.
- [63] G. Zhang, G. Kim, W. Choi, *Energy Environ. Sci.*, **2014**, 7, 954–966.
- [64] Z.-F. Hong, S.-H. Xu, Z.-H. Yan, D.-F. Lu, X.-J. Kong, L.-S. Long, L.-S. Zheng, *Cryst. Growth Des.*, **2018**, 18, 4864–4868.

具有高稳定性以及光催化产氢活性的奇数环状异金属钛氧纳米团簇

刘雅洁^{a,b}, 耿琳^{a,c}, 康遥^a, 方伟慧^{a,*}, 张健^{a,#}

^a中国科学院福建物质结构研究所结构化学国家重点实验室, 福建福州350002

^b中国科学院大学, 北京100049

^c福建师范大学 化学与材料学院 福建福州350007

摘要: 利用太阳能是解决当前能源危机和环境问题的有效途径. 二氧化钛是一种稳定性高、环境友好的新型光催化剂. 近年来, 具有精确结构信息的晶态钛氧团簇(PTCs)作为TiO₂的分子结构模型受到广泛关注. 目前大多数PTCs含有烷氧基, 在空气中易发生水解. 这在很大程度上限制了对其光催化性能的研究.

在无机钛氧簇的外围修饰大量的共轭有机配体是一种有效提升PTCs稳定性的方法. 此外, 异金属的嵌入有助于修饰微观电子结构, 从而也将影响光催化性能. 铝是地球上最丰富的金属元素, 其水解产物也大量存在于地壳表面. 因此, Ti和Al的水解和光催化研究引起了我们的兴趣. 目前, 只有少数几例低核的Al掺杂PTCs晶态材料被报道, 且其制备过程都需要多步反应. 因此, 合成高核的包含Al的PTCs材料是一项有趣且充满挑战的工作.

本文利用有机配体的保护和异金属离子的掺杂成功地提高了PTCs晶体材料的稳定性. 通过研究Ti和Al离子的水解, 制备了一例核-壳型的纳米轮簇[Al₇Ti₁₄(μ₂-O)₇(μ₃-O)₁₄(L)₃₅]·2CH₃CN (**1**; L = 苯甲酸). 该轮簇中包含罕见的奇数环状结构, 是目前核数最高的包含Al的PTC. 借助单晶X射线衍射可以清晰观察到无机{Al₇Ti₁₄}核与有机保护配体之间的配位模式. 此外, 利用红外光谱、热重和漫反射光谱对该化合物进行了进一步表征. 有机配体层和Al³⁺占据了Ti⁴⁺周围的烷氧基位点, 使得该化合物呈现较高的空气、热以及酸碱稳定性. 在已报道的PTCs晶态材料中, 该化合物也展现出较高的光催化产氢速率(402.88 μmol g⁻¹ h⁻¹). 借助催化过程中的光致变色现象、电子顺磁共振谱、荧光光谱以及光电流响应, 我们推测了该化合物催化水分解产氢机理. 该项工作不仅为制备稳定的PTCs材料提供了基础, 也为新型光催化剂的设计提供了新的思路.

关键词: 钛氧簇; 异金属簇; 纳米簇; 水分解产氢

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*通讯联系人. 电子信箱: fwh@fjirsm.ac.cn

#通讯联系人. 电话/传真: (0591)63179450; 电子信箱: zhj@fjirsm.ac.cn

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