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A gigantic polyoxozirconate with visible photoactivity[†]

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We present a gigantic polyoxozirconate nanocluster $(Zr_{18}O_{21}(\mu_2-OH)_2(OOCPh)_{28})$, involving 6, 7 and 8-coordinated Zr atoms. It exhibits visible light driven photocatalytic activity for H₂ evolution. The current results could represent a prelude of polyoxozirconate-based photocatalysis.

Polyoxometalates (POMs) have attracted intensive research attention in both science and industry owing to their rich structures and electronic properties and hence have applications in diverse fields such as catalysis, medicine, and magnetism.¹ A great deal of efforts in POMs have been devoted to d-block elements in high oxidation states, typically for V, Mo, W etc.² Recently, research studies on Ti-based POMs with novel structures and properties have been renewed. Zhang and coworkers have reported fullerene-like polyoxotitanate {Ti₄₂} and {Ti₅₂} clusters which hold the record of the largest titaniumoxo cluster to date.³ Nevertheless, the polyoxozirconates (POZs), being analogous to polyoxotitanate, are less studied and their properties as well as applications are even rarely explored. Low-nuclearity polyoxozirconates containing 2-5 Zr atoms have been prepared as the precursors for ZrO₂ thin film fabrication.⁴ The reported high-nuclearity POZs, including $\{Zr_9\}$, $\{Zr_{10}\}$, and $\{Zr_{12}\}$, can be considered as derivatives from the octahedral Zr_6O_8 parent core (Fig. 1 and Table S1⁺).⁵ Hetero-polyoxozirconates, such as [Co₆Zr₆O₈(pr)₁₂(Hbda)₆] (Hbph)₂·(H₂bph)⁶ and Zr₂₄-cluster substituted poly(polyoxotungstate)⁷ have exhibited distinct properties from pure POZs owing to interactions between Zr and hetero-components. It is noteworthy that the $\{Zr_{24}\}$ core is not isolated from its parent compound. Besides, various Zr-oxo clusters, typically Zr₆ and



Fig. 1 Illustration of the development of polyoxozirconate family. Aqua spheres: Zr; red spheres: O.

Zr₈ have been reported as secondary building units in metalorganic frameworks.⁸

Zirconia has been widely used as an insulating material due to its wide band gap (5 eV). In contrast, titania with a band gap of around 3 eV has been explored as a semiconductor photocatalyst broadly. Zr(w) having d_{10} electron configuration could be explored for photocatalytic applications,^{2c,9} if we are able to narrow the band gap and enable efficient solar spectrum absorption. In this work, we report a gigantic polyoxozirconate of $[Zr_{18}O_{21}(OH)_2(OCCPh)_{28}]$, which, to the best of our knowledge, represents the largest polyoxozirconate so far and exhibits visible light driven photocatalytic activity for H₂ evolution. Another $\{Zr_{18}\}$ cluster coordinating with SO_4^{2-} has been reported without any properties,¹⁰ and the structure is completely different from **POZr₁₈**.

An assembly of ZrCl_4 and benzoic acid with the assistance of thiourea in dried acetonitrile gave rise to pale yellow hexahedra of $[\text{Zr}_{18}\text{O}_{21}(\text{OH})_2(\text{OOCPh})_{28}]$ (Fig. S1,† denoted as **POZr**₁₈), which crystallized in the space group $P2_1/C$ (a = 28.3272(9) Å, b = 20.6226(6) Å, c = 35.7721(11) Å; $\alpha = \gamma = 90^\circ$, $\beta = 95.824^\circ$). As a reference, we failed to obtain **POZr**₁₈ without adding thiourea in the reaction. It is presumed that thiourea functioned as

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alkaline to promote the formation of POZr₁₈. The crystal structure was resolved from single crystal X-ray diffraction data (see details in the ESI[†]). The global structure of POZr₁₈ consists of a $\{Zr_{18}O_{21}(OH)_2\}$ core terminated by twenty-eight bridging carboxylates with a molecular size of $1.9 \times 1.8 \times 1.6 \text{ nm}^3$ (Fig. 2a). Among eighteen Zr atoms, two adopt a six-coordination mode and two are coordinated with eight oxygen atoms as individually marked with yellow and pink polyhedra in Fig. 2b; all other fourteen Zr atoms adopt a seven-coordination mode (green polyhedra). The co-existence of 6, 7 and 8-coordination modes in one single POZ structure has not been found in previous studies yet. Bond valence sum (BVS) calculations revealed that the BVS values of O_{52} and O_{53} (1.18 for O_{52} , 1.14 for O_{53} , respectively) are close to 1, which suggested that O_{52} and O_{53} are the two μ_2 -bridging hydroxyl groups as highlighted with blue spheres in Fig. S2.^{† 11} Here, BVS values were calculated using $s = \exp[(r_0 - r)/B]^{12}$ and the Zr-O distances are listed in Table S3.† Other twenty-one oxygen atoms adopt a μ_3 -bridging mode to connect adjacent Zr atoms.

Benzoate groups can be classified into three types according to their coordination modes: one is mono-dentate (in light blue circle); three individually chelate with a single Zr atom (in orange circles) and twenty-four benzoates bridge two adjacent Zr atoms (in green circle) (Fig. S2[†]). As clearly presented in Fig. 3a, the zirconium atoms in the $\{Zr_{18}O_{21}(OH)_2\}$ core can be described as a C2-symmetrical structure which has a secondary rotation axis through Zr_{10} and Zr_6 (Fig. S3[†]). In addition, the remaining skeleton except Zr10 can formally be divided into two corner-sharing (Zr_6) pentagonal $\{Zr_5Zr(\mu-O)_5\}$ building blocks, and a $\{Zr_3(\mu-O)_5\}$ group is attached side-on to the $\{Zr_5Zr(\mu-O)_5\}$ pentagon (Fig. 3b). Alternatively, the $\{Zr_{18}\}$ skeleton can be disintegrated into four $\{Zr_5(Zr)\}$ pentagons (Fig. 3c-e). Two {Zr₅(Zr)} pentagons share an edge to form $\{Zr_{10}\}\$ units (Fig. 3d) and two $\{Zr_{10}\}\$ units are further connected into $\{Zr_{18}\}$ units via two vertex-sharing edges (Fig. 3e). $\{M_5(M)\}$ units have been found in polyoxomolybdates,13 cerium-oxo nanoclusters¹⁴ and fullerene-like $\{Ti_{42}\}$.^{3a} The $\{Zr_5(Zr)\}$ pentagon identified in POZr₁₈, however, has not been found in the other reported POZ families so far. It could be a new type of building unit to construct large and novel POZ clusters.



b)



Fig. 3 (a) $\{Zr_{18}(OH)_2O_{21}\}$ cores in the POZr₁₈ cluster. (b) Partial zirconium oxide cores ($\{Zr_9O_{10}\}$) in the POZr₁₈ cluster (shadow in (a)), view angle emphasizing the pentagonal $\{Zr_6O_5\}$ substructure. (c–e) The zirconium atom skeleton in POZr₁₈.

The bulk phase purity of POZr18 was examined and confirmed by powder X-ray diffraction (Fig. 4a) and elemental analysis (ESI[†]). The PXRD pattern was identical to the one simulated from the single crystal XRD data. The thermogravimetric analysis revealed that POZr₁₈ is thermally stable up to 200 °C (Fig. S4[†]). The optical absorbance of ZrO₂ and a small POZ cluster mainly originated from ligand (O) and metal (Zr) charge transfer (LMCT). The band gap of ZrO₂ was determined to be in close proximity to 5 eV (Fig. 4b), thereby only exhibiting potential photoactivity in the ultraviolet region. In contrast, the UV-Vis absorption spectrum of POZr18 indicated a strong absorption centered at ca. 300 nm in the UV region and an obvious absorption tail extended into the visible region. The optical band gap of POZr18 was estimated to be 2.75 eV according to the equation $E_g = 1240/\lambda$ ($\lambda = 450$ nm) (Fig. 4b). Obviously, the ligand of benzoates in POZr₁₈ made no contribution to visible absorption. EDS analysis (Fig. S5[†]) indicated that there was no sulfur-related species in the POZr₁₈ cluster, which could cause band-gap narrowing. It has been reported that oxygen vacancies in the crystal have important impact on the electronic properties.¹⁵ The introduction of oxygen vacancies could narrow the band-gap and enhance visible light photocatalytic activity. Electron spin resonance (ESR) was employed to investigate whether there are some oxygen vacancies in the POZr₁₈ cluster. As displayed in Fig. S6,† the line at g = 2.004 was identified as the electrons trapped in



Fig. 4 (a) XRD patterns of POZr₁₈; (b) UV-Vis absorption spectrum of POZr₁₈ cluster (blue) and ZrO₂ (red).

a)

oxygen vacancies.¹⁶ The bulk Zr^{4+} ions adjacent to the bulk oxygen vacancies could capture the electrons resulting in the formation of Zr^{3+} ions. The signal at g = 1.974 can be contributed by the bulk Zr^{3+} ions located at axially symmetric sites.¹⁷ Accordingly, we assumed that the visible absorbance originated from oxygen vacancies in bulk **POZr**₁₈. **POZr**₁₈ represents the largest and the first visible-active polyoxozirconate to date.

The previous studies on polyoxozirconates mainly focused on their structure, characterization and their applications as precursors for ZrO₂ preparation.^{4,5} The photocatalysis application of POZs is restricted by their limited optical absorption. As POZr₁₈ exhibited visible absorption, we are encouraged to investigate its photocatalytic activity for H₂ production using triethylamine (TEA) as the sacrificial agent and Pt nanoparticles as the co-catalyst under visible light irradiation.¹⁸ It should be noted that the photocatalytic H₂ production was performed in a gas-phase photoreactor where TEA and H₂O vapors participated in photocatalytic reaction (see details in the ESI[†]), because the mechanical agitation and the alkaline environment in TEA aqueous solution can destroy the crystal structure, which result in the instability of POZr₁₈ in liquidphase photocatalysis. The evolved hydrogen was monitored by gas chromatography (GC). As displayed in Fig. 5a, the experimental results showed a linear increase in the H₂ amount against irradiation time. Moreover, the cycling experiments revealed that there was no noticeable decrease in photocatalytic activity after three cycles (Fig. 5b), indicating the favorable stability of $POZr_{18}$ under the test conditions. The photogenerated Zr(III) intermediate was believed to be an active center for the photocatalytic activity of Zr-based MOFs including UiO-66-NH2¹⁹ and PCN222.²⁰ Therefore, we speculate that Zr(IV) in POZr₁₈ was reduced to Zr(III) by the photogenerated electron and subsequently, Zr(m) behaved as an active site for H₂ production.

In summary, we successfully synthesized and characterized a polyoxozirconate of $POZr_{18}$, which represented the largest and the first visible-active polyoxozirconate so far. $POZr_{18}$ displayed photocatalytic activity towards H₂ production under visible light irradiation. In spite of the moderate photocatalytic activity, this work may pave the way to explore polyoxozirconates as a new type of visible-active photocatalyst.

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Fig. 5 (a) H_2 production test under visible light illumination (400–780 nm) on the POZr₁₈ cluster. (b) Cyclic performance of H_2 production.

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