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## Robust Photocatalytic H<sub>2</sub>O<sub>2</sub> Production by Octahedral Cd<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub> Coordination Polymer under Visible Light

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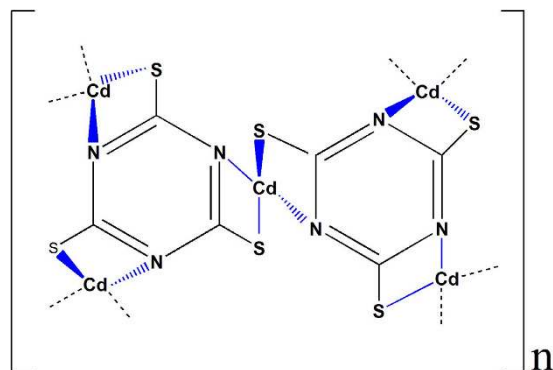
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Herein, we reported a octahedral Cd<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub> coordination polymer as a new noble metal-free photocatalyst for robust photocatalytic H<sub>2</sub>O<sub>2</sub> production from methanol/water solution. The coordination polymer can give an unprecedented H<sub>2</sub>O<sub>2</sub> yield of ca. 110.0 mmol • L<sup>-1</sup> • g<sup>-1</sup> at pH = 2.8 under visible light illumination. The characterization results clearly revealed that the photocatalytic H<sub>2</sub>O<sub>2</sub> production proceeds by a pathway of two-electron reduction of O<sub>2</sub> on the catalyst surface. This work showed the potential perspective of M<sub>x</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>y</sub> (M = transitional metals) coordination polymers as a series of new materials for solar energy storage and conversion.

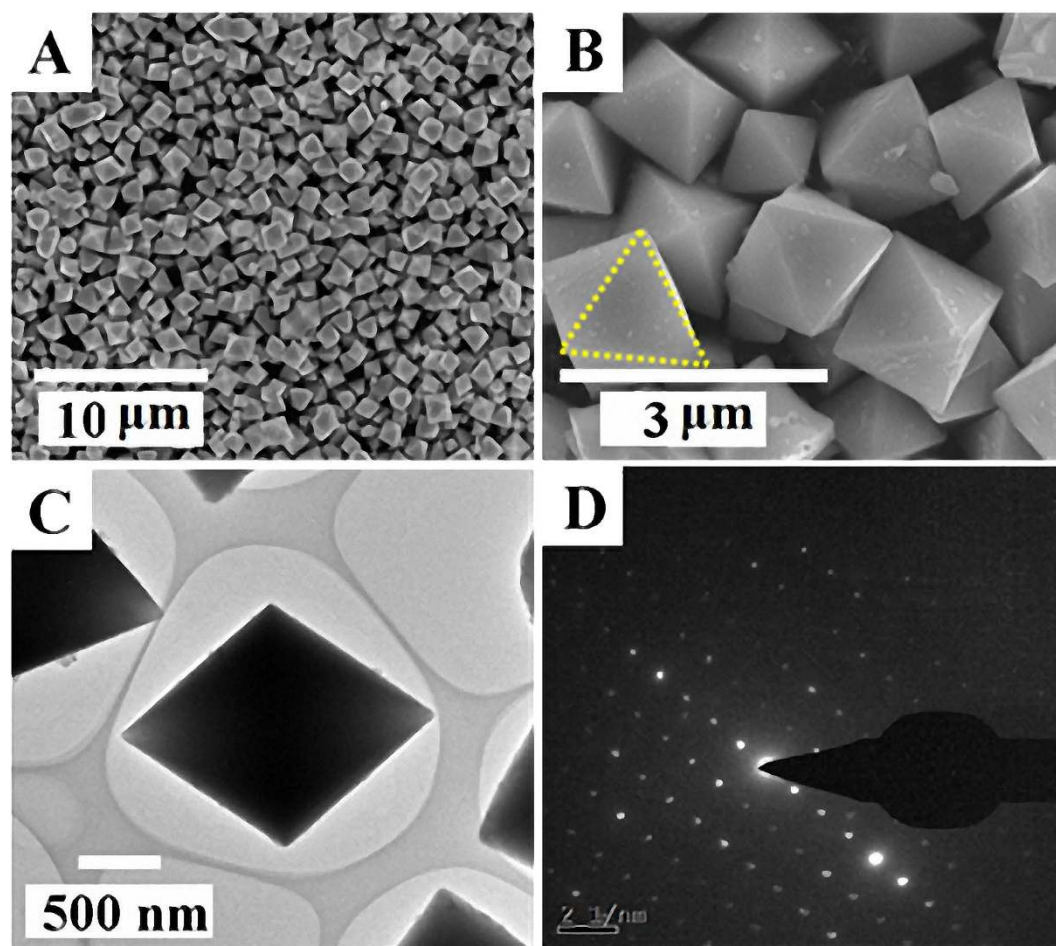
Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an environmentally benign oxidant widely applied in the areas of organic synthesis, the pulp and paper industry, and disinfection<sup>1</sup>. It is also a block building of post-fossil energy framework as a new solar fuel<sup>2-5</sup>. However, the traditional anthraquinone method<sup>6</sup>, also referred as the indirect process, for H<sub>2</sub>O<sub>2</sub> production is contrary to the concept of the modern green chemistry, because it not only involves the multistep reactions of high energy-consuming hydrogenation and oxidation, but also requires large production plants to minimize capital investment and to obtain highly concentrated H<sub>2</sub>O<sub>2</sub> to reduce transportation costs. The direct synthesis of H<sub>2</sub>O<sub>2</sub> by the noble metal-catalyzed reaction of molecular oxygen with hydrogen has proven to be feasible<sup>7-12</sup>, but the high production cost and the unsatisfactory efficiency limited its practical application on-large scale. Moreover, some cares have to be required for safe operation because of the potentially explosive danger of H<sub>2</sub>/O<sub>2</sub> mixture. Recently, the photocatalyzed H<sub>2</sub>O<sub>2</sub> synthesis has attracted more attention as an “ideal green” technique<sup>13-16</sup>. Without the presence of external H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> can be produced on a micromolar order in O<sub>2</sub>-saturated water by ultraviolet irradiation of TiO<sub>2</sub><sup>17</sup>. By suppressing the back reaction, the photocatalytic H<sub>2</sub>O<sub>2</sub> yield can be upgraded to a millimolar level over a surface-fluorinated TiO<sub>2</sub>, but along with a large amount of fluorine contaminant emitted into the aqueous solution<sup>18</sup>. Up to date, much work has devoted to chemically modifying TiO<sub>2</sub> by noble metal loading or nonmetallic doping for H<sub>2</sub>O<sub>2</sub> synthesis<sup>19-21</sup>. Carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and its related composites modified by the electron-deficient aromatic diimide units were recently shown to be also photocatalytically active for H<sub>2</sub>O<sub>2</sub> synthesis under visible light illumination<sup>22-24</sup>, but it yielded H<sub>2</sub>O<sub>2</sub> only on no more than a micromolar level. Thus, the development of visible-light-driven photocatalysts effective for safe H<sub>2</sub>O<sub>2</sub> production on a millimolar and even molar scale remains a formidable challenge.

In natural systems, superoxide dismutases (SODs) are metalloprotein enzymes mildly catalyzed H<sub>2</sub>O<sub>2</sub> production by the dismutation of superoxide into oxygen and hydrogen peroxide<sup>25</sup>. SODs including three major families of CuZn-SOD, Fe/Mn-SOD and Ni-SOD are essentially coordination compounds with late transition metal ions as central atoms and proteins as ligand. Inspired by these macromolecular

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**Figure 1.** Structure of the  $\text{Cd}_3(\text{TMT})_2$  coordination polymer.



**Figure 2.** Typical (A, B) SEM, (C) TEM image and (D) the SAED pattern of the  $\text{Cd}_3(\text{TMT})_2$  coordination polymer.

metalloproteins, we have long looked for metal coordination polymers as robust photocatalysts to mimic the biocatalytic  $\text{H}_2\text{O}_2$  production. Herein, a  $\text{C}_3\text{N}_3\text{S}_3$ -based coordination polymer photocatalyst,  $\text{Cd}_3(\text{C}_3\text{N}_3\text{S}_3)_2$ , was successfully developed to produce  $\text{H}_2\text{O}_2$  on a millimolar level under visible-light irradiation. The yellowish coordination polymer was synthesized by a facile wet-chemical route under the ambient conditions according to the previous work reported by Chudy, J. C. *et al.* who carefully controlled the reaction condition to synthesize the coordination polymer with different stoichiometries<sup>26</sup>. The high stability and low solubility in aqueous solution provided an indicative of the coordination polymer as a catalyst or catalyst support<sup>27</sup>. The elemental analysis of as-synthesized  $\text{Cd}_3(\text{C}_3\text{N}_3\text{S}_3)_2$  was listed

Entry	pH	$h\nu$	Atmosphere	$C(H_2O_2)$ [mmol·L <sup>-1</sup> ]
1 <sup>[a]</sup>	6.7	+	air	negligible
2 <sup>[b]</sup>	6.7	+	air	1.5
3 <sup>[b]</sup>	6.7	–	air	negligible
4 <sup>[b]</sup>	6.7	+	N <sub>2</sub>	negligible
5 <sup>[c]</sup>	5.8	+	air	1.75
6 <sup>[c]</sup>	4.1	+	air	2.0
7 <sup>[c]</sup>	2.8	+	air	8.75
8 <sup>[d]</sup>	6.7	+	air	negligible

**Table 1. Photocatalytic H<sub>2</sub>O<sub>2</sub> evolution over Cd<sub>3</sub>(TMT)<sub>2</sub> under different conditions.** [a] Reaction conditions: 80 mg catalyst dispersed in 20 ml distilled water, visible light ( $\lambda \geq 420$  nm), room temperature, the reaction time is 4 hours; [b] Reaction conditions: 80 mg catalyst dispersed in 19 ml distilled water mixed with 1 ml methanol, other conditions as [a]; [c] pH of the solution was adjusted by *con.* HNO<sub>3</sub>, other conditions as [b]. [d] With the addition of AgNO<sub>3</sub> as electron trapper, other conditions as [b]. The concentration of produced H<sub>2</sub>O<sub>2</sub> was determined by KMnO<sub>4</sub> titration<sup>20</sup>.

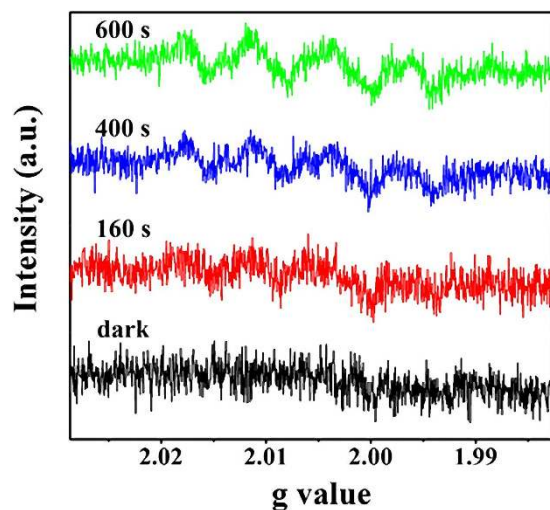
in Table S1, which clearly demonstrates that the molar ratio of C, N, S and Cd elements is 1: 0.98: 0.91: 0.55. The result confirms that the general molecular formula of the resultant product is Cd<sub>3</sub>(C<sub>3</sub>N<sub>3</sub>S<sub>3</sub>)<sub>2</sub>, also denoted as Cd<sub>3</sub>(TMT)<sub>2</sub> where TMT is 2,4,6-trimercaptotriazine anion. The combination of XRD and FTIR characterizations (Fig. S2,S3, Supporting Information) proves the Cd<sup>2+</sup>-bridged structure of the as-synthesized coordination polymer as depicted in Fig. 1<sup>26–28</sup>.

## Results and Discussion

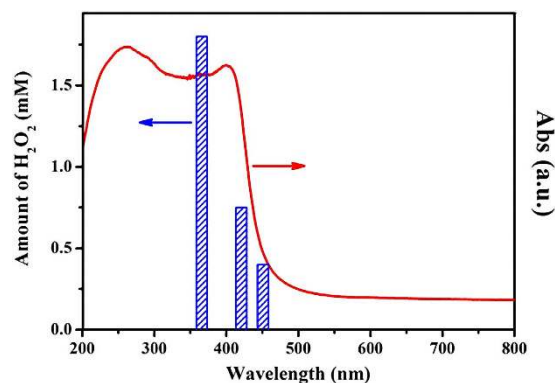
Figure 2 shows the low-magnification scanning electron microscopy (SEM) (Fig. 2A,B) and transmission electron microscopy (TEM) images (Fig. 2C) of the as-synthesized Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer. It well crystallizes as homogeneously dispersed nanocrystals with the perfect octahedron morphology characteristics. Additionally, it appears that the triangular surface of these octahedrons is sporadically covered by some irregular-shaped nanoparticles, which suggests that the formation of the octahedral nanocrystals maybe follow the “Oriented attachment” mechanism, just similar to the case of a previous work by Zeng and coworkers<sup>29</sup>. Namely, owing to the strong coordination capability of TMT with transition metal ions as well as the low  $K_{sp}$  value of Cd<sub>3</sub>(TMT)<sub>2</sub> in water<sup>27</sup>, the addition of TMT ligand into the Cd<sup>2+</sup>aqueous solution leads first to the formation of Cd<sub>3</sub>(TMT)<sub>2</sub> nanoparticulate precipitate, and long reaction time endows the self-aggregation of these nanoparticles to construct the final 3D architectures. This hypothesis is confirmed by the SEM images of products at different reaction time as shown in Fig. S4 (Supporting Information). The TEM image in Fig. 2C further evidences that the product are structurally well-defined octahedrons with solid inner space. The selected area electron diffraction pattern (SAED) shown in Fig. 2D indicates the single crystal feature of the coordination polymer.

The ultraviolet-visible diffuse reflectance spectrum of the Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer (Fig. S5, Supporting Information) displays a typical optical absorption of semiconductor. The corresponding to the optical band-gap energy of *ca.* 2.76 eV. To further investigate the band structure of the Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer, we also carried out electrochemical analysis. The typical Mott-Schottky plot of Cd<sub>3</sub>(TMT)<sub>2</sub> in the dark (Fig. S6, Supporting Information) shows a positive slope of C<sup>-2</sup>-E plot, an indicative of n-type semiconductor<sup>30</sup>. The flat-band potential ( $V_b$ ) of about  $-0.78$  V vs. NHE at pH 7.0 is determined from extrapolation to the X intercept in the Mott-Schottky plot. And by combining with the band-gap energy of *ca.* 2.76 eV estimated from the optical absorption, the valence band position of the Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer is calculated to be 1.98 V vs. NHE at pH 7.0. Thus, it is revealed from the band characteristics as illustrated by the insertion in Fig. S6 that, light-excited electrons in the conduction band of the coordination polymer possess a large thermodynamic driving force to reduce O<sub>2</sub> ( $E^\circ(O_2/\cdot O_2^-) = -0.16$  V), and yet the potential of the photogenerated hole in the valence band is inadequate to oxidize OH<sup>-</sup> to hydroxyl radicals ( $E^\circ(OH^-/\cdot OH) = 2.4$  V). This result clearly indicates that the oxygen reduction reaction over the coordination polymer is feasible.

The activity results of photocatalytic H<sub>2</sub>O<sub>2</sub> production from methanol aqueous solution confirm the conclusion above. As listed in Table 1, in pure water (Entry 1), the Cd<sub>3</sub>(TMT)<sub>2</sub> semiconductor is reluctant to produce H<sub>2</sub>O<sub>2</sub> under the indicated conditions. On the contrary, with the addition of methanol as hole scavenger and proton donor, which is beneficial for the separation of electron-hole pairs, 1.5 mmol·L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> is produced under visible-light irradiation (Entry 2). Notably, this yield is highly comparable to the system using Au-Ag/TiO<sub>2</sub> under ultraviolet light irradiation as previously reported<sup>20</sup>. But in dark (Entry 3), no H<sub>2</sub>O<sub>2</sub> is produced, confirming that the H<sub>2</sub>O<sub>2</sub> production is driven by light absorption. According to the redox potentials of the electron/hole pairs of the coordination polymer, H<sub>2</sub>O<sub>2</sub> can be stoichiometrically formed in an aerated aqueous solution via two different pathways as follows:



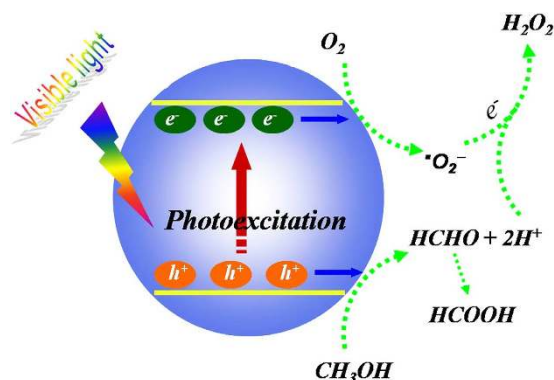
**Figure 3.** ESR spectra of DMPO-•O<sub>2</sub><sup>-</sup>/•OOH adduct in the Cd<sub>3</sub>(TMT)<sub>2</sub>/DMPO system before and after visible light irradiation.



**Figure 4.** Wavelength-dependent hydrogen peroxide evolution by Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer. Reaction conditions: 80 mg catalyst dispersed in 19 ml distilled water mixed with 1 ml methanol, room temperature. The reaction time is 4 hours.



Our control experiments uncover some basic mechanism of the Cd<sub>3</sub>(TMT)<sub>2</sub>-catalyzed H<sub>2</sub>O<sub>2</sub> evolution. When the system is bubbled with N<sub>2</sub> to eliminate O<sub>2</sub>, no H<sub>2</sub>O<sub>2</sub> is detected with KMnO<sub>4</sub> titration method, indicating the participation of O<sub>2</sub> in the photocatalytic H<sub>2</sub>O<sub>2</sub> production. Thus, it can be concluded that the second potential pathway does not contribute to the H<sub>2</sub>O<sub>2</sub> production in our system. This conclusion is also confirmed by our further control experiments (Entries 5–7). If water oxidation, as described by equation (2), is primarily responsible for the photocatalytic H<sub>2</sub>O<sub>2</sub> production, and then increasing the concentration of H<sup>+</sup> will deteriorate the photocatalytic H<sub>2</sub>O<sub>2</sub> production of the Cd<sub>3</sub>(TMT)<sub>2</sub> semiconductor. However, it is shown that, the H<sub>2</sub>O<sub>2</sub> concentration increases with the H<sup>+</sup> concentration in the solution, and the concentration of H<sub>2</sub>O<sub>2</sub> reaches to about 8.75 mmol•L<sup>-1</sup> at pH = 2.8. In addition, when AgNO<sub>3</sub>, which is an often-used electron trapper<sup>31</sup>, was added in the system (Entry 8), no detectable H<sub>2</sub>O<sub>2</sub> is produced in the solution after 4 h of visible-light irradiation. It indicates the pivotal role of photo-electrons for H<sub>2</sub>O<sub>2</sub> generation. Based on the activity results of the control experiments we can confirm that, in the case of Cd<sub>3</sub>(TMT)<sub>2</sub>-photocatalyzed H<sub>2</sub>O<sub>2</sub> production, the overall reaction would be described by the equation (1), which features two-electron reduction of O<sub>2</sub>. It is also noteworthy that, in most cases as previously reported, the produced H<sub>2</sub>O<sub>2</sub>, a more reactive oxidation agent than O<sub>2</sub>, is presumably quick rebound and readily suffers from the reduction reaction by photo-generated electrons



**Figure 5.** Proposed mechanism of the  $\text{H}_2\text{O}_2$  production on the visible-light-activated  $\text{Cd}_3(\text{TMT})_2$  under the ambient condition.

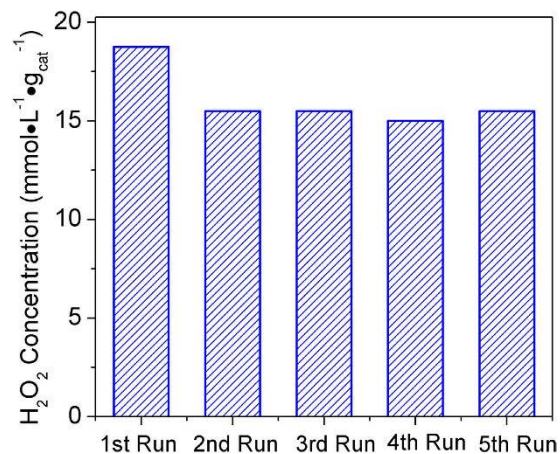
on the catalyst, which results in a very low efficiency of  $\text{H}_2\text{O}_2$  evolution<sup>21</sup>. Interestingly, in the present study, the accumulation of  $\text{H}_2\text{O}_2$  with concentration up to several millimoles per liter is achieved. It should be ascribed to the rapid desorption of  $\text{H}_2\text{O}_2$  from the surface of the  $\text{Cd}_3(\text{TMT})_2$  photocatalyst, which suppresses the photocatalytic  $\text{H}_2\text{O}_2$  decomposition.

5,5-dimethyl-1-pyrroline N-oxide (DMPO) trapping electron paramagnetic resonance (ESR) analysis was used to identify the intermediate oxygen species formed during the  $\text{H}_2\text{O}_2$  evolution, as shown in Fig. 3. No ESR signal can be observed in dark. On the contrary, upon visible light irradiation ( $\lambda \geq 420 \text{ nm}$ ), a set of ESR signals of DMPO- $\bullet\text{O}_2^-/\bullet\text{OOH}$  adduct ( $\bullet\text{O}_2^-$ , a product derived from oxygen reduction reaction:  $\text{O}_2 + e^- = \bullet\text{O}_2^-$ ) is discernable within 160 s, and no ESR signals of DMPO- $\bullet\text{OH}$  adduct occurs (Fig. S7, Supporting Information), indicating the absence of  $\text{H}_2\text{O}_2$  decomposition induced by reduction reaction with electrons (e.g.  $\text{H}_2\text{O}_2 + e^- = \text{OH}^- + \bullet\text{OH}$ )<sup>32</sup>. Furthermore, the intensity of the DMPO- $\bullet\text{O}_2^-/\bullet\text{OOH}$  adduct signals increase gradually with irradiation time. All these facts are in good agreement with the activity results, indicating that the  $\text{H}_2\text{O}_2$  evolution over the  $\text{Cd}_3(\text{TMT})_2$  coordination polymer proceeds via the  $\text{O}_2$  reduction process, as illustrated by equation (1).

The spectrum action of  $\text{H}_2\text{O}_2$  production as shown in Fig. 4 further validates that the photoreaction proceeds through light-excitation of the coordination polymer. It appears that the  $\text{H}_2\text{O}_2$  amount produced in the system decreases with increasing the incident light wavelength, matching well with the optical spectrum. This result clearly indicates that the  $\text{H}_2\text{O}_2$  production is intrinsically a photocatalytic process driven by photoexcitation of the coordination polymer semiconductor. Therefore, we can propose a reasonable mechanism of  $\text{Cd}_3(\text{TMT})_2$ -photocatalyzed oxygen activation for  $\text{H}_2\text{O}_2$  production, as illustrated in Fig. 5. Under visible light irradiation, the electron-hole pairs are produced, and then methanol is oxidized by holes into formaldehyde and proton (eq. 3), which contributes to the separation of charge carriers and  $\text{H}^+$ <sup>33–35</sup>. The adsorbed oxygen molecules are spontaneously reduced by electrons to form superoxide radicals (eq. 4), which further react with protons to produce  $\bullet\text{OH}_2$  radicals (eq. 5). The  $\bullet\text{OH}_2$  radicals can readily undergo further reduction with  $e^-$  (eq. 6), producing  $\text{HO}_2^-$  anions. Finally, just as demonstrated by equation (7), the negatively-charged  $\text{HO}_2^-$  reacts with  $\text{H}^+$ , leading to the evolution of the final  $\text{H}_2\text{O}_2$  product<sup>36</sup>.



In order to clearly verify the photocatalytic reaction mechanism, the concentration of formic acid and formaldehyde has been further measured by the ion chromatography and acetylacetone spectrophotometry, as shown in Fig. S8. The concentration of HCHO and HCOOH gradually increases with the enhancement of reaction time under 24 h of visible-light irradiation, which is good consistent with the above reaction mechanism. Although the accumulated  $\text{H}_2\text{O}_2$  can further oxidize HCHO into HCOOH, which will lead to some  $\text{H}_2\text{O}_2$  loss, a stable  $\text{H}_2\text{O}_2$  concentration in the aqueous solution can be achieved once



**Figure 6.** Stability testing of photocatalytic activity of the Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer.

a production-decomposition balance of H<sub>2</sub>O<sub>2</sub> is reached, just as demonstrated by Fig. S9 (Supporting Information) representing a time curve of enzyme-biocatalyzed H<sub>2</sub>O<sub>2</sub> evolution, over the coordination polymer from methanol aqueous solution. As we all known, the formation and decomposition of H<sub>2</sub>O<sub>2</sub> follow zero- and first-kinetics toward H<sub>2</sub>O<sub>2</sub> concentration, respectively<sup>14,20</sup>. Therefore, the kinetic data can be modeled and explained by the equation:  $[H_2O_2] = (k_f/k_d)\{1 - \exp(-k_d t)\}$ , where  $t$  is time,  $k_f$  (mM h<sup>-1</sup>) and  $k_d$  (h<sup>-1</sup>) are the formation and decomposition rate constants for H<sub>2</sub>O<sub>2</sub>, respectively. The  $k_f$  and  $k_d$  values of Cd<sub>3</sub>(TMT)<sub>2</sub> polymer are 0.39 mM h<sup>-1</sup> and 0.04 h<sup>-1</sup>, respectively, indicating that the Cd<sub>3</sub>(TMT)<sub>2</sub> polymer is a robust photocatalyst for H<sub>2</sub>O<sub>2</sub> production. To check the photo-stability of the as-prepared photocatalyst, the photocatalytic evolution of H<sub>2</sub>O<sub>2</sub> was repeated up to five cycles under the same conditions (Fig. 6). It can be clearly seen that after five successive operations, the coordination polymer still maintains the high photocatalytic activity for H<sub>2</sub>O<sub>2</sub> production. In addition, its crystal structure does not change after photocatalytic reaction, as shown in Fig. S10 (Supporting Information). Those results indicate that the Cd<sub>3</sub>(TMT)<sub>2</sub> polymer is able to serve as a stable, reusable photocatalyst for H<sub>2</sub>O<sub>2</sub> generation from methanol/water solution.

According to the characterization results above, we believe that the Cd<sub>3</sub>(TMT)<sub>2</sub> coordination polymer can fulfill as a versatile visible-light photocatalyst. The activity results of photocatalytic degradation of Rhodamine B over Cd<sub>3</sub>(TMT)<sub>2</sub> shown in Fig. S11 (Supporting Information) also confirms that it indeed enables the destruction of organic pollutants due to the  $\cdot O_2^-$  generation. Importantly, a considerable amount of H<sub>2</sub>O<sub>2</sub> is simultaneously produced along with the Rhodamine B photodegradation in the solution<sup>37</sup> (Fig. S12, Supporting Information). This result suggests that the sacrificial agent, methanol, will be hopefully replaced by waste organic dyes for H<sub>2</sub>O<sub>2</sub> production in the future, synchronously achievement of environmental remediation.

In summary, a bioinspired metal coordination polymer with a general molecular formula of Cd<sub>3</sub>(TMT)<sub>2</sub> was reported for the first time to fulfill as a visible light photocatalyst effective for H<sub>2</sub>O<sub>2</sub> evolution with the aid of methanol. The coordination polymer features a well-defined octahedral morphology and high crystallinity and shows robust photocatalytic H<sub>2</sub>O<sub>2</sub> production on a millimolar level. The electrochemical analysis and ESR characterizations clearly reveal that the photocatalytic H<sub>2</sub>O<sub>2</sub> evolution over the coordination polymer follows a mechanism of two-electron reduction of O<sub>2</sub>. This work shows the potential promising of the transitional metal coordination polymers in solar energy storage and conversion, especially organic photosynthesis.

## Methods

**Materials.** Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and sodium hydroxide (NaOH) were supplied by Sinopharm chemical reagent Co., Ltd (Shanghai, China), trithiocyanuric acid (H<sub>3</sub>TMT) was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). All materials are analytical grade purity without further purification prior to use. Deionized (DI) water used in the synthesis was obtained from local sources.

**Catalyst Preparation.** The monodisperse Cd<sub>3</sub>(TMT)<sub>2</sub> octahedrons are prepared by a facile template-free wet-chemical synthesis at room temperature. Typically, 0.015 mol cadmium nitrate, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, was dissolved in 200 mL DI water under mechanically stirring to form a transparent solution (denoted as solution A). Trithiocyanuric acid (0.01 mol) was dissolved in 200 mL 0.15 mol·L<sup>-1</sup> NaOH aqueous solution to form yellowish homogenous solution, which is denoted as solution B. In order to avoid the formation of cadmium hydroxide precipitation, solution B was slowly added into solution A drop-by-drop under vigorously stirring. Afterwards, the system was aged for 24 h with mildly stirring. The products were then separated by filtration, washed by DI water, and fully dried at 333 K in oven to get the final resultants, namely Cd<sub>3</sub>(TMT)<sub>2</sub> octahedrons.

**Characterizations.** The phase composition of the as-prepared samples was determined on a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu K $\alpha$  radiation at 40 kV and 40 mA in the  $2\theta$  ranging from 20° to 80° with a scan rate of 0.02° per second. Field-emission scanning electron microscopy (FE-SEM) was used to characterize the morphology and elemental distribution of the as-prepared samples on a FEI Nova NANOSEM 230 spectrophotometer. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) were obtained using a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The optical properties of the as-prepared samples were analyzed by UV-vis diffuse reflectance spectroscopy (DRS) using a UV-vis spectrophotometer (Cary 500, Varian Co.), in which BaSO<sub>4</sub> was employed as the internal reflectance standard. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a Thermo Scientific ESCA Lab 250 spectrometer which consists of a monochromatic Al K $\alpha$  as the X-ray source, a hemispherical analyzer and sample stage with multi-axial adjustability to obtain the surface composition of the sample. All of the binding energies were calibrated by the C 1s peak at 284.6 eV. The concentration of formic acid was measured by the ion chromatography (Dionex, ICS-1100). Electron spin resonance (ESR) signal of the radicals spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was recorded on a Bruker EPR A300 spectrometer. The irradiation source ( $\lambda \geq 420$  nm) was a 300 W Xe arc lamp system and the whole ESR experiment was measured under room temperature. The settings for the ESR spectrometer were as follows: center field = 3507 G, microwave frequency = 9.84 GHz and power = 6.36 mW. The Mott-Schottky experiments were obtained on a Precision PARC workstation. The electrochemical analysis was carried out in a conventional three-electrode cell using a Pt plate and an Ag/AgCl electrode as the counter electrode and reference electrode, respectively. For electrode preparation, indium-tin oxide (ITO) glass was firstly cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using scotch tape. 5 mg of sample was dispersed in 0.5 mL ethanol by sonication to get a slurry. The slurry was spread onto the pretreated ITO glass. After air drying, the working electrode was further dried at 393 K for 2 h to improve adhesion. Then the scotch tape was unstuck and the uncoated part of the electrode was isolated with epoxy resin. The exposed area of the working electrode was 0.25 cm<sup>2</sup>. Mott-Schottky experiments were measured in a sodium sulfate electrolyte solution (0.2 M) (pH = 6.8), the potential ranged from -0.2 V to 0.8 V, and the perturbation signal were 10 mV with the frequency at 1 K Hz.

**Photocatalytic activity test.** In a typical photocatalytic reaction, a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co., Ltd.) with a UV-CUT filter to cut off light of wavelength <420 nm was used as the irradiation source. 80 mg of photocatalyst was added into 20 mL of the methanol aqueous solution (19 mL H<sub>2</sub>O with 1 mL methanol). Before visible light illumination, the above suspension was stirred in the dark for 1 h to ensure the establishment of adsorption-desorption equilibrium between the sample and reactant. During the process of the reaction, 5 mL of sample solution was collected after 4 hours of visible light irradiation and centrifuged to remove the catalyst completely at 12000 rpm. Afterward, the concentration of H<sub>2</sub>O<sub>2</sub> was determined by KMnO<sub>4</sub> titration ( $c_{\text{KMnO}_4} = 1 \text{ mmol} \cdot \text{L}^{-1}$ ) with the addition of 5 mL 1 M H<sub>2</sub>SO<sub>4</sub> solution. When the solution becomes the pink after the addition of KMnO<sub>4</sub> solution and keeps the color of solution for 30 s, the concentration of KMnO<sub>4</sub> solution is equivalent to the concentration of H<sub>2</sub>O<sub>2</sub>. All of the experimental processes were conducted under ambient temperature.

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## Author Contributions

H.Q.Z and J.L.L. wrote the manuscript and carried out the most of experiments. L.F.Y., J.X., F.Y.L., Z.Z.Z. and H.X.L. did the ESR and SEM measurements, and obtained the data and figures. J.L.L. and X.X.W. analyzed the data and revised the manuscript. All authors reviewed the manuscript.

## Additional Information

**Supplementary information** accompanies this paper at <http://www.nature.com/srep>

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