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Communication

A hydrated amorphous iron oxide nanoparticle as active water oxidation catalyst

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ABSTRACT

Developing efficient water oxidation catalysts (WOCs) with earth-abundant elements still remains a challenging task for artificial photosynthesis. Iron-based WOC is a promising candidate because it is economically cheap, little toxic and environmentally friendly. In this study, we found that the catalytic water oxidation activity on amorphous iron-based oxide/hydroxide (FeO_x) can be decreased by an order of magnitude after the dehydration process at room temperature. Thermogravimetric analysis, XRD and Raman results indicated that the dehydration process of FeO_x at room temperature causes the almost completely loss of water molecule with no bulk structural changes. Based on this finding, we prepared hydrated ultrasmall (ca. 2.2 nm) FeO_x nanoparticles of amorphous feature, which turns out to be extremely active as WOC with turnover frequency (TOF) up to 9.3 s^{-1} in the photocatalytic $\text{Ru}(\text{bpy})_3^{2+}\text{-Na}_2\text{S}_2\text{O}_8$ system. Our findings suggest that future design of active iron-based oxides as WOCs requires the consideration of their hydration status.

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Artificial photosynthesis that converts solar energy into storable chemical fuels including H_2 is one of the most promising ways to meet the energy demands of future generations [1,2]. In this process, water oxidation reaction involving four electron transfer process and various high-energy intermediates is quite challenging from both thermodynamic and kinetics point of view [3,4]. To achieve efficient water oxidation, many water oxidation catalysts (WOCs) consisting of earth-abundant transition metal elements have been investigated [5–8]. Iron is the second most abundant metal element in the earth's crust, which has redox properties. Many iron-based compounds such as iron enzymes or complexes have been reported to exhibit biological or biomimetic activities for oxygen activation [9]. Therefore, it is desirable to develop active and robust

iron-based WOCs for solar energy conversion to chemical fuels.

A number of iron-based oxides have been reported as WOCs [10–13]. In order to fast screening iron-based oxides for water oxidation, much research has been devoted to correlating the catalytic activity with a specific descriptor or feature of the catalyst. For example, Parmon et al. [14] suggested that the surface hydroxyls with stronger acidities on iron-based WOCs could lead to higher water oxidation activity. Berlinguette et al. [15] found that amorphous Fe_2O_3 showed improved electrochemical water oxidation activity over crystalline Fe_2O_3 . However, the influence of hydration state on the catalytic water oxidation activity of iron-based oxides has been neglected. Lyons et al. [16] proposed that the electrochemical water oxidation reaction at hydrated iron oxide surface involves the active

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participation of octahedrally coordinated anionic iron oxyhydroxide surface complexes to form the porous hydrated layer. This result suggested that the hydration state may affect the catalytic water oxidation activity of iron-based oxides.

In this study, we found that the turnover frequency (TOF) for water oxidation on hydrated amorphous iron oxide (FeO_x -hydrated) with a broad size distribution ranging from 3 to 100 nm is an order of magnitude higher than that of dehydrated one (FeO_x -dehydrated). Based on this finding, we further prepared a hydrated amorphous iron oxide nanoparticles with small size (ca. 2.2 nm) that is extremely active towards water oxidation, with TOF value up to 9.3 s^{-1} in the photocatalytic $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ system.

FeO_x -hydrated sample was prepared following the literature [17]. The dehydration of FeO_x -hydrated was carried out at room temperature in vacuum and this process could be confirmed by its weight loss from thermogravimetry (TG) curve in Fig. 1(a). A significant amount of water was removed at room temperature for FeO_x -hydrated while only a minor amount of water lost for FeO_x -dehydrated powder which was likely caused by adsorbed moisture. Fig. 1(b) shows the Raman spectra of FeO_x -hydrated and FeO_x -dehydrated samples. A Raman peak around 3400 cm^{-1} assigned to the water stretching mode can be clearly observed for the FeO_x -hydrated sample. This peak disappears for the FeO_x -dehydrated, confirming the loss of

water after drying at room temperature. This indicates that the adsorbed water molecule is weakly bonded with the surface of amorphous FeO_x -hydrated [18]. In short, both the TG and Raman results confirm the dehydration process occurs at room temperature for FeO_x -hydrated sample.

Water oxidation activities of FeO_x -hydrated and FeO_x -dehydrated were investigated in photocatalytic $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ system (Fig. S1, ESI†) [19]. No obvious oxygen evolution was detected when $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Na}_2\text{S}_2\text{O}_8$ were used under irradiation in the absence of catalyst, suggesting that the catalyst is essential for the water oxidation reaction (Fig. S2, ESI†). Interestingly, after the dehydration process, TOF value of water oxidation on FeO_x -dehydrated decreased by an order of magnitude (Fig. 1(c) and Fig. S3, ESI†). We noted that after dehydration process, TOF value of amorphous FeO_x -dehydrated is still several times higher than those of typical crystalline Fe-based oxides (Table S1, ESI†) [15].

XRD patterns in Fig. 1(d) show no distinct changes between FeO_x -hydrated and FeO_x -dehydrated samples. In addition, a Raman peak around 690 cm^{-1} and the corresponding overtone peak around 1378 cm^{-1} assigning to Fe-O vibration are observed for FeO_x -hydrated and FeO_x -dehydrated samples with almost the same peak position and intensity (Fig. 1(b)) [20]. Both XRD and Raman results confirm no bulk structural changes of iron oxide after the dehydration process. This is

Fig. 1. (a) TG curves of FeO_x -hydrated and FeO_x -dehydrated. (b) Raman spectra of FeO_x -hydrated and FeO_x -dehydrated. (c) Comparing water oxidation activities between FeO_x -hydrated and FeO_x -dehydrated. The activity tests are carried out in 50 mmol/L pH 8 borate buffer containing 1 mmol/L $\text{Ru}(\text{bpy})_3^{2+}$ and 10 mmol/L $\text{Na}_2\text{S}_2\text{O}_8$ under the photoirradiation. (d) XRD patterns of FeO_x -hydrated and FeO_x -dehydrated.

reasonable since the dehydration process is carried out at room temperature. To exclude the possibility that different sizes between FeO_x -hydrated and FeO_x -dehydrated nanoparticles contribute to their different water oxidation activities, dynamic light scattering (DLS) was carried out which shows they have almost the same size distribution (Fig. S4). The catalysts recycled after water oxidation were analyzed using Raman to check for structural changes (Fig. S5). Comparison of Raman spectra of recycled FeO_x -hydrated and FeO_x -dehydrated revealed that both of them did not undergo any observable change after reaction. This indicates that they are true WOCs instead of acting as precursors and they are relatively stable in water oxidation conditions.

Dehydration at room temperature would result in the loss of free water and surface weakly bounded water molecules. Water oxidation is a multiple electron-transfer process which involves the coordination of the substrate H_2O molecule to the surface active sites, namely the surface bounded H_2O participating in forming O–O bond [21]. FeO_x -hydrated surface can be considered as compounds with great affinity to the H_2O molecule [14]. We guess that during the dehydration process, the FeO_x -hydrated sample undergoes surface reconstructing and the obtained FeO_x -dehydrated shows much lower affinity to the substrate H_2O molecule, thus becoming unfavorable for catalytic water oxidation. Further investigations are needed to examine the surface structural changes of FeO_x -hydrated during the dehydration process as well as its interaction with the substrate H_2O molecule.

Inspired by the above results that FeO_x -hydrated exhibited much higher catalytic water oxidation activity than FeO_x -dehydrated, we tried to prepare hydrated amorphous FeO_x nanoparticles with small sizes possessing more active sites to achieve even higher water oxidation activity. The synthetic route involves using tris(hydroxymethyl)aminomethane (Tris) to inhibit the growth of FeO_x nanoparticles. Tris molecule is reported as good capping agent to prepare metal oxide nanoparticles with small sizes [22]. Hereafter, the as-prepared iron-based nanoparticles is denoted as FeO_x -Tris for simplicity.

Fig. 2(a) and (b) gives the representative TEM image and histogram of size distribution of FeO_x -Tris nanoparticles which shows they are well-dispersed with an average size of about 2.2

nm according to random statistics of 100 nanoparticles. The existence of large FeO_x -Tris nanoparticles can be excluded from the dynamic light scattering measurements (Fig. S6, ESI†). As a comparison, the size of FeO_x -hydrated sample prepared without using Tris as capping agent is much bigger and more broadly distributed, ranging from 3 to 100 nm (Fig. S7, ESI†). These results indicate that the Tris molecule plays a crucial role in limiting the growth of FeO_x -Tris. The selected area electron diffraction (SAED) pattern of FeO_x -Tris in the inserted Fig. 2(a) shows no diffraction spots or rings for FeO_x -Tris, indicating its amorphous feature.

Fig. 3(a) presents the oxygen evolution rates catalyzed by different concentrations of FeO_x -Tris catalysts. TOF value was calculated assuming that every iron atom is involved in catalytic water oxidation. An average TOF value up to 9.3 s^{-1} towards water oxidation can be obtained using FeO_x -Tris as WOC according to five times' parallel test results (Fig. S8, ESI†) in the photocatalytic $\text{Ru}(\text{bpy})_3^{3+}$ - $\text{Na}_2\text{S}_2\text{O}_8$ system. This value is much higher than those of reported iron-based oxides WOCs as well as typical iron oxides such as $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-FeOOH}$ prepared according to reported methods [23] (Fig. S9, ESI†), as listed in Table S1. The TOF value of FeO_x -Tris is even comparable to that of the very active Fe-based polyoxometalate WOC [24].

The initial quantum efficiency of oxygen evolution on FeO_x -Tris nanoparticles is calculated to be 67% based on the number of evolved O_2 molecules and the irradiation spectrum of the halogen lamp (Fig. S10, ESI†). This further indicated the outstanding activity of hydrated FeO_x -Tris nanoparticles for water oxidation.

A general advantage of heterogeneous WOCs is their robustness compared with homogeneous WOCs. We immobilized the FeO_x -Tris nanoparticle on SiO_2 surface (denoted as " $\text{FeO}_x/\text{SiO}_2$ ") to investigate its stability, since the small FeO_x -Tris nanoparticles of only 2.2 nm is difficult to isolate from the post-solution after water oxidation test. SiO_2 is oxidation-stable as well as hydrolysis-stable which is suitable to act as support for FeO_x -Tris nanoparticle. FeO_x -Tris nanoparticles can be effectively mobilized on the surface of SiO_2 from the color changes of SiO_2 (Fig. S11, ESI†). About 98% of FeO_x -Tris nanoparticles are adsorbed on the SiO_2 surface as determined from the UV-vis spectra (Fig. S12, ESI†).

Fig. 2. (a) HRTEM image FeO_x -Tris nanoparticles. The insert shows selected electron diffraction pattern. (b) Size distribution histogram of FeO_x -Tris nanoparticles.

Fig. 3. (a) O₂ evolution rates with different concentrations of FeO_x-Tris. The activity tests are carried out in 50 mmol/L pH 8 borate buffer containing 1 mmol/L Ru(bpy)₃²⁺ and 10 mmol/L Na₂S₂O₈ under the photoirradiation. (b) Stability test of FeO_x/SiO₂ catalyst in water oxidation. After each run of water oxidation test, the FeO_x/SiO₂ catalyst is recycled from the post solution, and a new batch of Ru(bpy)₃²⁺, Na₂S₂O₈ as well as borate buffer is added to the reaction solution.

After each run of photocatalytic test, a new batch of Ru(bpy)₃²⁺, Na₂S₂O₈ and borate buffer in the same concentration as the original one were added to the recycled FeO_x catalyst to examine its stability. Fig. 3(b) shows the time course of oxygen evolution with FeO_x/SiO₂ catalyst for repetitive use. The oxygen evolution rates of FeO_x/SiO₂ catalyst decreased slightly after 2 cycles of water oxidation tests, which may be ascribed to the loss of FeO_x/SiO₂ during the recycling process. This result indicates that FeO_x-Tris is stable during water oxidation process as WOC. The high catalytic activity of FeO_x-Tris WOC combining with its robustness suggests its potential application in artificial photosynthesis devices.

In summary, dehydration process would greatly reduce the catalytic water oxidation activity of amorphous iron-based oxide. Based on this result, we prepared hydrated amorphous FeO_x nanoparticles with an average size down to 2.2 nm, which shows extremely high activity as WOC with a TOF value up to

9.3 s⁻¹ in the photocatalytic Ru(bpy)₃²⁺-Na₂S₂O₈ system.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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A hydrated amorphous iron oxide nanoparticle exhibits high water oxidation activity with TOF of 9.3 s⁻¹ in the photocatalytic Ru(bpy)₃²⁺-Na₂S₂O₈ system.

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水合状态的无定形氧化铁用作高效水氧化催化剂

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摘要: 由于传统化石燃料的不可再生性和使用过程中对环境的污染, 近年通过太阳光驱动催化水分解制备氢气或CO₂还原制备甲醇等高能化学燃料是人工光合作用制备太阳能燃料领域的研究重点. 水的氧化反应是制备太阳能燃料的重要半反应, 为质子或CO₂的还原提供必需的质子和电子, 开发基于非贵金属氧化物的高效水氧化催化剂是人工光合作用制备太阳能燃料的重要挑战之一. 最近我们课题组的研究发现, 无定形氧化钴作为水氧化催化剂时, 其本征活性比结晶态的高出一个数量级. 与氧化钴催化剂相比, 铁基氧化物作为水氧化催化剂具有许多优点, 比如成本低、环境友好、对动植物不产生生理毒性. 基于此, 本文探索了开发制备具有高催化活性的铁基氧化物作为水氧化催化剂.

结果发现, 氧化铁水氧化催化剂活性不但受其结晶度影响, 还与其水合状态密切相关. 水合氧化铁在进行室温真空干燥脱水处理后, 在Ru(bpy)₃²⁺-Na₂S₂O₈光催化水氧化体系中, 其催化水氧化活性降低了一个数量级. 热重分析、XRD和拉曼测试等结果表明, 室温下进行脱水处理后, 氧化铁基本不含有水分子的信号, 其体相结构没有发生显著的变化. XRD和拉曼结果表明, 催化水氧化测试后回收的氧化铁催化剂结构没有发生改变, 表明该水合状态的氧化铁是水氧化过程中真实的催化剂成分, 并不是充当前驱体的角色.

基于此, 我们进一步制备了尺寸较小且为水合状态的无定形氧化铁纳米粒子, 后者在Ru(bpy)₃²⁺-Na₂S₂O₈光催化水氧化体系中显示出极高的催化活性, TOF值高达9.3 s⁻¹, 基于产生的氧气分子计算的光催化量子效率达到67%. 该尺寸较小的水合状态氧化铁纳米粒子还可以有效地负载在SiO₂表面进行催化水氧化反应, 循环测试结果表明, 负载的水合状态氧化铁纳米粒子连续进行三个催化水氧化循环测试, 其活性未明显衰减, 显示了较高的稳定性. 该结果表明, 未来设计铁基氧化物作为高活性的水氧化催化剂时, 需要特别考虑其水合状态.

关键词: 人工光合作用; 水氧化; 氧化铁; 水合状态; 无定形

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