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Oxidative Degradation of Chitosan to the Low Molecular Water-Soluble Chitosan over Peroxotungstate as Chemical Scissors

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Abstract

Low molecular water-soluble chitosan was prepared by the depolymerization of chitosan in the presence of a series of catalysts with active $W(O_2)$ sites. Both the peroxo species $[W_2O_3(O_2)_4]^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}^{3-}$ showed high efficiency in the degradation of chitosan, indicating that the degradation mechanism did not follow the radical mechanism. That means •OH is not the active species, which has been proven by the fluorescence spectra. H_2O_2 acted as an oxidant to regenerate the active $W(O_2)$ sites in the depolymerization of chitosan. The developed catalyst $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ is recoverable.

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Introduction

Chitosan is a biopolymer obtained by partial deacetylation of chitin, which is the second most abundant polysaccharide in nature after cellulose[1,2]. However, chitosan has a high molecular weight and low solubility in most solvents, which limits its applications in agriculture[3,4], food and beverages[5], waste water treatment[6-8], pharmaceuticals[9,10] and biomaterials[11]. By the degradation process chitosan can be converted into the low-molecular-weight chitosan which exhibits good water solubility. To date, acid hydrolysis, basic hydrolysis and oxidation-based methods are commonly used for the preparation of the low-molecular water-soluble chitosan (LMWSC). Catalytic oxidation with hydrogen peroxide is particularly attractive from the economical and environmental benefits. However, oxidative degradation of chitosan using H_2O_2 without additives is inefficient. Thus, the combined methods for degradation of chitosan by using H_2O_2 and chemical or physical techniques, such as the catalysis of Fe^{2+}, Cu^{2+}, heterpoly compounds, ultraviolet, microwave irradiation and gamma radiation, have been studied[12–15]. Recently, Huang et al. reported that a Keggin heterpoly acid, $H_3PW_{12}O_{40}$, can efficiently catalyze oxidative degradation of chitosan with H_2O_2 to the LMWSC[16–18]. The authors presumed that 1) the peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ formed by phosphotungstic acid in the presence of H_2O_2 is the real catalyst. 2) the peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ accelerates the formation of free radicals by the disassociation of hydrogen peroxide. 3) the free radicals can attack the β-(1–4) glucosidic bond of chitosan to obtain the LMWSC. To the best of our knowledge, however, little experimental data is available to support this conjecture. Besides, some researchers[19,20] have reported that heteropolyacids with the Keggin structure ($H_3PW_{12}O_{40}$) are degraded in the presence of H_2O_2 to form two peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4]^{2-}$ (**Figure 1**). These results motivated us to reconsider why the real catalyst is not $[W_2O_3(O_2)_4]^{2-}$ but the peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$, also it is not clear why the peroxo species $[W_2O_3(O_2)_4]^{2-}$ formed from $H_3PW_{12}O_{40}$ showed no catalytic activity.

In this report, the isolated peroxo species $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ and $K_2[W_2O_3(O_2)_4]$ were directly employed as the catalyst to degrade chitosan. We demonstrated that not only the peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$, but also $[W_2O_3(O_2)_4]^{2-}$ are highly efficient catalysts. The peroxo species itself can efficiently degrade chitosan without hydrogen peroxide. Moreover, the $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ catalyst can be recycled.

Experiment Section

Materials

$H_3PW_{12}O_{40}$, $Na_3PW_{12}O_{40}$, K_2WO_4, $(NH_4)_2WO_4$, Na_2WO_4, EDTA, KSCN, $SnCl_2$ and $TiCl_3$ (AR) were purchased from Aladdin Industrial Corporation. H_2O_2 (Hydrogen peroxide, 30%) and Chitosan (DD≥90%) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used was distilled.

Synthesis of $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$

The $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ was prepared according to the literature[19,21]. Hydrogen peroxide (30%) (10 mL, 100 mmol) was added to a solution of $H_3PW_{12}O_4$ (1.65 g in 1 mL water). After 30 min, an aqueous solution of tetrabutylammonium chloride (1.6 mmol in 3 mL) was slowly added. The resulting white precipitate was filtered out, washed several times with water, and then air dried. IR(KBr): $\nu(PO_4)$:1084, 1053 cm^{-1}, $\nu(W=O)$: 964 cm^{-1}, $\nu(O–O)$: 845 cm^{-1}, $\nu_{asym}[W(O)_2]$: 593 cm^{-1}, ν_{sym}

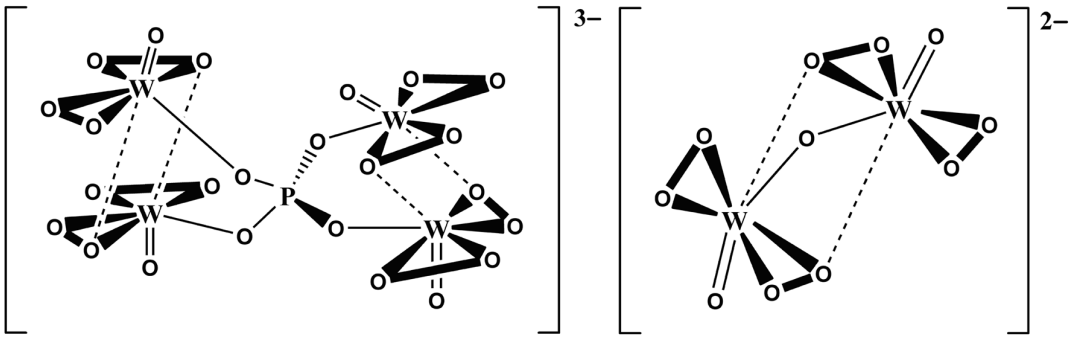

Figure 1. The chemical structure of peroxo species.
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[$W(O)_2$]: 523 cm^{-1}. Raman (in CH_3CN): $v(PO_4)$:1050, 1024 cm^{-1}, $v(W=O)$: 957 cm^{-1}, $v(O–O)$: 848 cm^{-1}, $v_{asym}[W(O)_2]$: 591 cm^{-1}, v_{sym} [$W(O)_2$]: 520 cm^{-1}.

Synthesis of $K_2[W_2O_3(O_2)_4]$

$K_2[W_2O_3(O_2)_4]$ was prepared according to the literature[19–21]. A solution of K_2WO_4 (5.0 g in 10 mL water) was placed in an ice-water bath. 30% H_2O_2 (10 mL) was slowly added, and the solution turned light yellow. Dilute hydrochloric acid was added into the solution until the color just disappeared at pH = 2~3. Then the ethanol was added. The resulting white precipitate was filtered out, washed several times with ethanol and dried in air. IR (KBr): $v(W=O)$: 966 cm^{-1}, $v(O–O)$: 854 cm^{-1}, $v_{asym}[W(O)_2]$: 550 cm^{-1}, v_{sym} [$W(O)_2$]: 615 cm^{-1}, $v_{asym}[W_2O]$: 764 cm^{-1}. Raman (solid): $v(W=O)$: 958 cm^{-1}, $v(O–O)$: 861 cm^{-1}, $v_{asym}[W(O)_2]$: 553 cm^{-1}, v_{sym} [$W(O)_2$]: 537 cm^{-1}, $v_{asym}[W_2O]$: 763 cm^{-1}, $v_{sym}[W_2O]$: 450 cm^{-1}.

The typical procedure of the degradation of chitosan

In a typical reaction, a mixture of 0.200 g of chitosan, 4.2 μmol tungsten (W) in the catalyst, 5 mL of the distilled water, 1 mL of 30% H_2O_2, were stirred in the 50 mL round-bottomed flask for 20 min at different temperature. After the reaction, NaOH was added to the filtrate until pH = 7. The products were extracted with ethanol. The obtained white precipitate was filtered out, dried in vacuum and then analyzed.

Determination of tungsten

The filtrate was evaporated and calcinated at 400°C. Then the samples were digested by microwave with the digestion solvent of 40 mL NaOH solution (0.025 g/mL). After being digested for 30 min by medium-high level microwaves, the sample was cooled to room temperature, and 1 g EDTA and 30 mL deionized water were added into the beaker. Then the solution was transferred into 100 mL volumetric flask (**1**).

2 mL KSCN (0.5 g/mL), 4.5 mL $SnCl_2$ (0.008 g/L) and 1.5 mL $TiCl_3$ (0.15 g/mL) were added into 10 mL (**1**) solution, transferred 25 mL volumetric flask. Then the solution was measured on the Spectrophotometer 721 at λ = 406 nm.

Analytical method

The degradation ratio of chitosan was defined as follows:

$$R\% = \frac{M_0 + M_{cat} - M_x}{M_0} \times 100$$
$$R\% = \frac{M_0 - M_x}{M_0} \times 100 \quad (1)$$

where R refers to the degradation ratio of chitosan, M_0 refers to the quantity of the original chitosan, M_{cat} refers to the quantity of the catalyst, M_x refers to the quantity of the collected solid after degradation under different conditions.

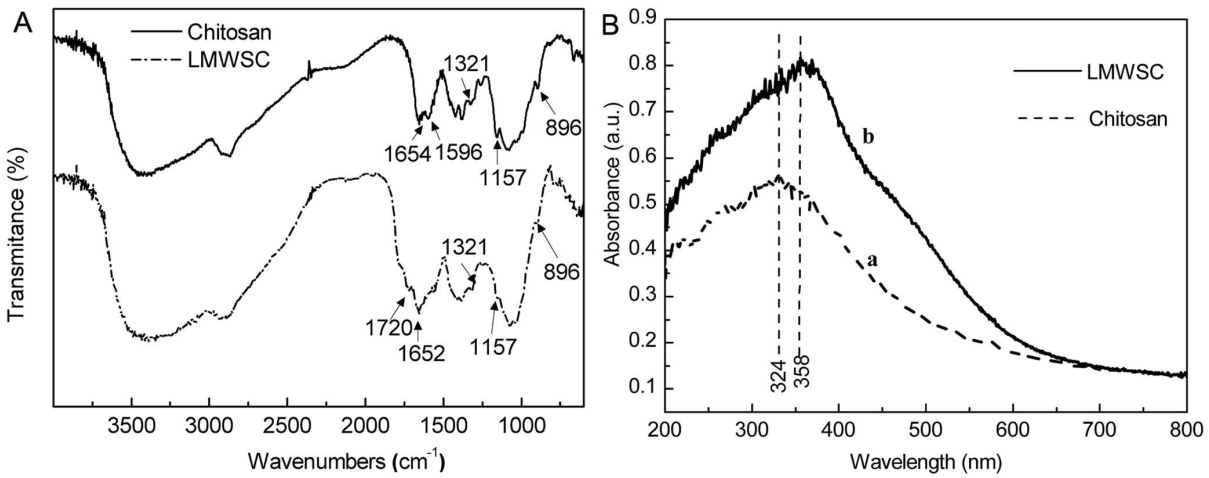

Figure 2. The characterization of chitosan and the LMWSC, FTIR spectra (A) and DRS patterns (B).
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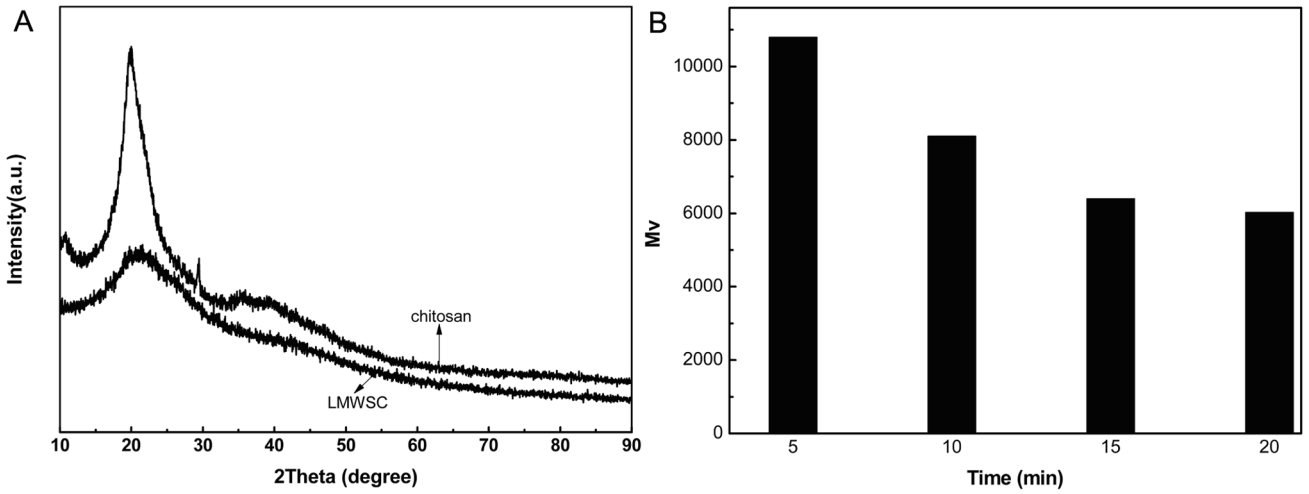

Figure 3. The characters of chitosan and the LMWSC, XRD patterns (A), and the effect of the reaction time on the Mv of LMWSC (B).
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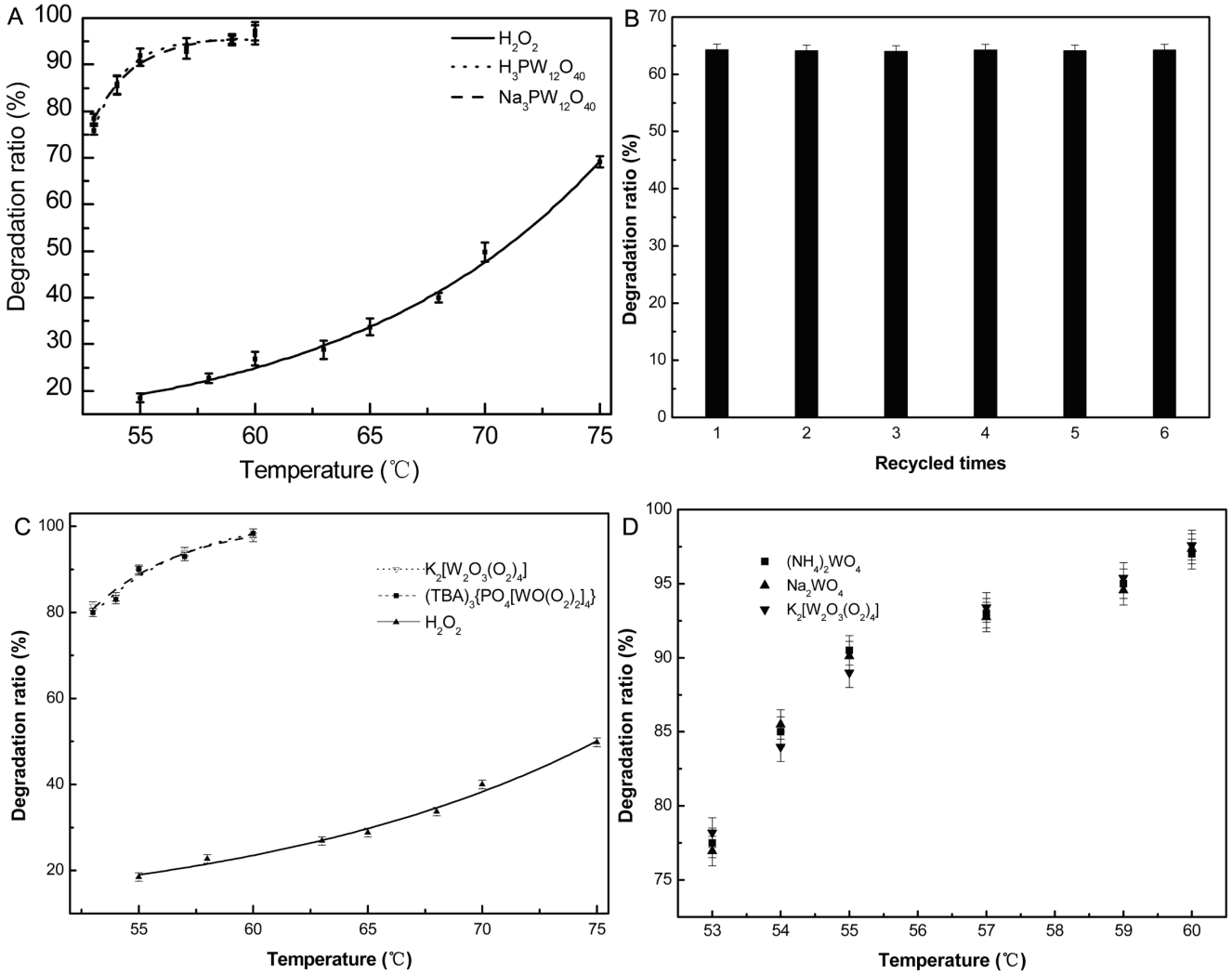

Figure 4. The oxidative degradation of chitosan, (A) $H_3PW_{12}O_{40}$ (0.35 μmol), $Na_3PW_{12}O_{40}$ (0.35 μmol) and H_2O_2 without any additives. (C) $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ (1.05 μmol), $K_2[W_2O_3(O_2)_4]$ (2.1 μmol) and H_2O_2 without any additives. (D) Na_2WO_4 (4.2 μmol), $(NH_4)_2WO_4$ (4.2 μmol) and $K_2[W_2O_3(O_2)_4]$ (2.1 μmol). Under the same reaction conditions: H_2O_2 (1 mL), H_2O(5 mL), 20 min. (B) Recycling of the filtrate at 65°C, 1 mL H_2O_2.
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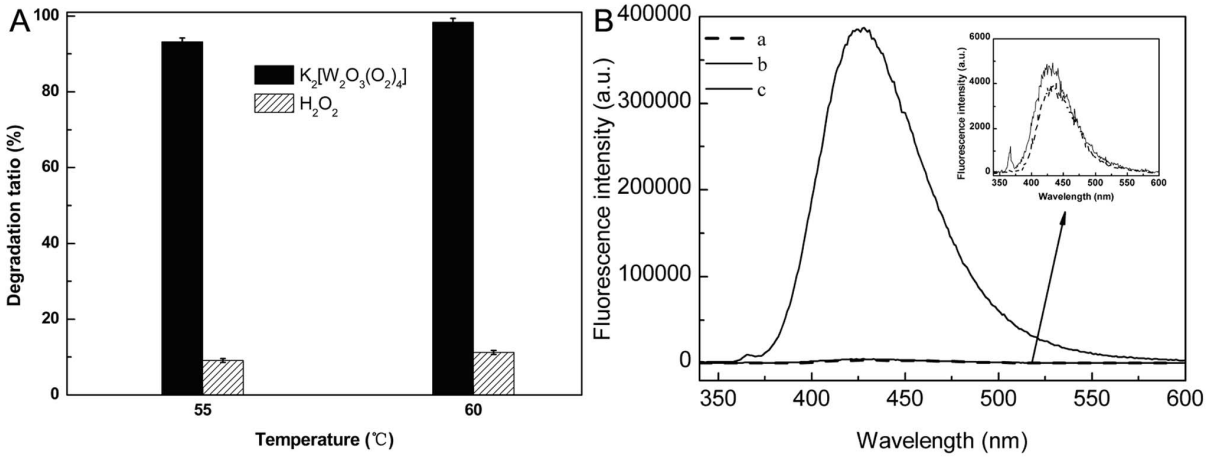

Figure 5. The comparison of different peroxo species, the peroxo species K_2 $[W_2O_3(O_2)_4]$ (2.5 mmol) and H_2O_2 (10 mmol), respectively, under the same reaction conditions: 5 mL H_2O, 20 min (A), and the Fluorescence spectra changes (excitation at 315nm) with different addtives (B), a. terephthalic acid (5 $\times10^{-5}$ M), Na_2WO_4 (4.2 μmol), H_2O_2 solution (100 μL) b. terephthalic acid (5 $\times10^{-5}$ M) and H_2O_2 solution (100 μL). c. terephthalic acid (5 $\times10^{-5}$ M), $K_2[W_2O_3(O_2)_4]$ (2.1 μmol), H_2O_2 solution (100 μL), under the same reaction conditions: 55°C, 2 min.
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The Ubbe-lodhe viscosimeter was used to determine the intrinsic viscosities at 303 K. Chitosan was dissolved in 0.1mol/L CH_3COONa–0.2 mol/L CH_3COOH solution. The viscosity average molecular weight (M_v) was calculated according to the following equation[16–18].

$$[\eta]=\frac{\eta_{sp}+3In\eta_r}{4C} \quad (2)$$

$$[\eta]=1.81\times10^{-3}M_v^{0.93} \quad (3)$$

Here,η_{sp},η_r refer to the incremental viscosity and the relative viscosity respectively, C is the concentration of the LMWSC (g/mL). M_v is the viscosity average molecular weight.

The FT-IR spectra of samples were recorded on a NEXUS 670 FT-IR spectrometer with KBr pellets prepared by manual grinding. Raman spectra of samples were recorded on Renishaw RM1000 ($\lambda = 514.5$ nm). Fluorescence spectra were acquired with an FLSP920 spectrofluorometer (Edinburgh Instruments Ltd, UK) at 20±1°C, equipped with a temperature-controlled circulator (Julabo, Germany). X-ray diffraction (XRD) patterns of samples were carried out on a PW 3040/60 X-ray diffractometer (Philips, Netherlands) with Cu Kα target at 40 kV and 40 mA. The samples were scanned from 5°to 70°of 2θ. The UV-vis absorption spectra of the samples were measured in the range of 100–800 nm on a UV-vis spectrometer (Nilcolet Evolution 500, Thermo). The metal content of the product solution was measured on the Spectrophotometer 721 (Shanghai Analysis Instrument Company).

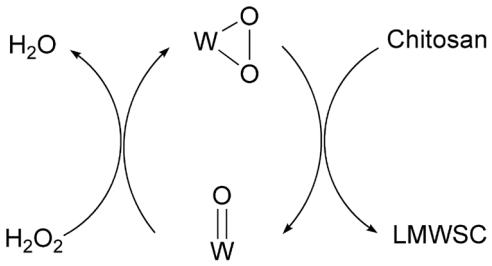

Figure 6. The mechanism of degradation of chitosan.
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Results and Discussion

The characterization of chitosan

The chitosan and the LMWSC were characterized by FTIR in **Figure 2A**. The main bands of chitosan were as follows. The band at around 3422 cm^{-1} could be ascribed to the stretching vibration of O-H and N-H. The absorption peak at 1599 cm^{-1} corresponds to the binding vibration of the amido groups. An apparent carboxyl (-C = O) band at 1654 cm^{-1} is attributed to the residual acetyl. The band in the range 1157 cm^{-1} to 896 cm^{-1} belongs to the special absorb peaks of β-1,4 glycoside bond in chitosan[22]. The similar characteristics in the FTIR spectrum of the LMWSC can also be observed. Besides, a new absorption peak at 1720 cm^{-1} is observed in the spectrum of the LMWSC, which is assigned to the absorption of the carboxylic group (–COOH). It indicates the existence of the carboxylic group in the LMWSC.

To further identify the carboxylic group of the LMWSC, DRS analysis are given in **Figure 2B**. There is an absorption band at 324 nm in the original chitosan, which is caused by the n→π* transition of residual acetyl (DD>90%). Compared with that of chitosan, the DRS spectrum of the LMWSC has a new absorption band at 357 nm caused by the n→π* transition of a carboxylic group in the LMWSC. Consequently, the DRS patterns reflected that the carboxylic group was formed, which coincided with the analysis of the FTIR spectra.

The X-ray powder patterns of chitosan and the LMWSC are shown in **Figure 3A**. The pattern of chitosan shows two characteristic peaks at 2θ = 10.4° and 20.0° which correspond to (1 0 0) and (0 2 0) reflections of the L-2 polymorph of chitosan[23]. For the LMWSC, the peak at 2θ = 10.4° disappeared, and the strength of the peak at 2θ = 20.0° decreased. It indicated the crystalline structure of the LMWSC was destroyed and the crystallinity decreased. LMWSC became more amorphous than chitosan[24]. It manifests that the

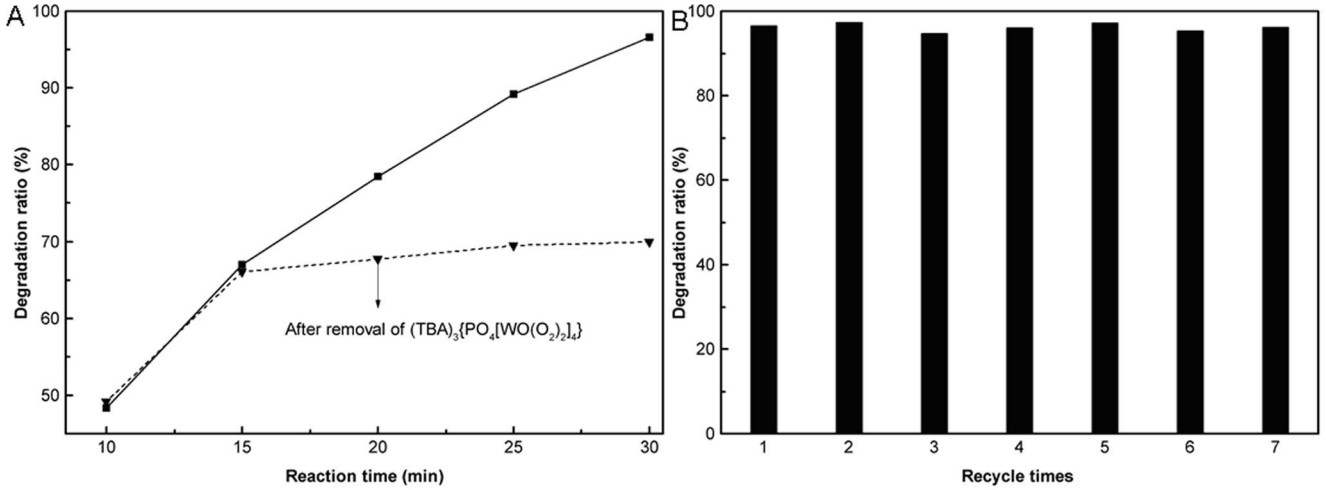

Figure 7. The catalytic activity of the filtrate and the catalyst. The filtrate (A) and the catalyst (B), 0.0125 mmol $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$, 1 mL H_2O_2, 65°C.
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degradation of chitosan occurred preferentially from the amorphous region to the water-soluble molecular, which dissolved in the water. With the further degradation, the crystalline structure was destroyed thoroughly. **Figure 3B** shows the viscocity average molecular weight (Mv) of the LMWSC versus time on the $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ catalyst. After 20min the Mv of theLMWSC can reach 5892.

The catalytic activities of the catalysts

We first reinvestigated the oxidative degradation of chitosan with $H_3PW_{12}O_{40}$ and H_2O_2. Compared with H_2O_2, the degradation efficiency increased significantly (**Figure 4A**). This could be expected considering that both the acid hydrolysis of chitosan and the oxidative dagredation of chitosan might occur in the presence of $H_3PW_{12}O_{40}$. Thus, we switched to the salt $Na_3PW_{12}O_{40}$. Interestingly, the degradation ratio of chitosan is not significantly changed when three Na^+ substituted the position of protons in $H_3PW_{12}O_{40}$, which allowed us to exclude the contribution of Brønsted acid catalysis for the reaction. In an attempt to interpret the results, we added an aqueous solution of tetrabutylammonium chloride to the solution of $H_3PW_{12}O_{40}$ and 30% H_2O_2. The obtained white precipitate $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ was filtered out. It is worthwhile to note that the filtrate is still active for the degradation of chitosan although the catalytic activity is low. And most interestingly, the filtrate can be reused six times without loss of reactivity (**Figure 4B**). The results can be explained if $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ is not completely filtered out or the peroxo species $[W_2O_3(O_2)_4]^{2-}$ dissolved in the filtrate is also an active species. Therefore, we turned our attention to the two peroxo species $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and $[W_2O_3(O_2)_4]^{2-}$, which are always formed in the presence of H_2O_2.

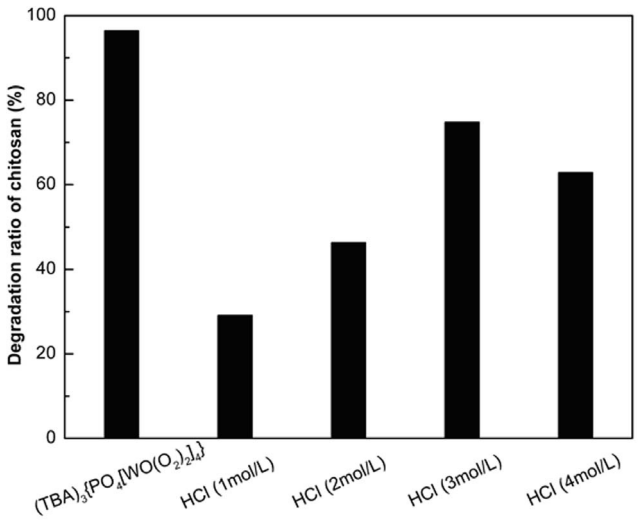

Figure 8. Degradation ratio of chitosan by different methods.
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The catalytic activity of the peroxo species

Next, we examined the oxidative degradation of chitosan by $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ and $K_2[W_2O_3(O_2)_4]$ with H_2O_2, seperately. The results are shown in **Figure 4C**. We can see that the degradation ratio of chitosan is still high for the peroxo species, while only a very small amount of chitosan is degraded in the absence of peroxo species. Most interestingly, no significant change in the degradation ratio of chitosan was observed when $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ (the content of W atom: 4.2 μmol) and $K_2[W_2O_3(O_2)_4]$ (the content of W atom: 4.2 μmol) were used. The catalyst $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ is almost insoluble and $K_2[W_2O_3(O_2)_4]$ is highly soluble in water. By further investigation we found 1.05 μmol $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ was not soluble in 5 mL water at room temperature. However, when heated to 50°C, the catalyst $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ was soluble in water. When cooled to room temperature, it precipitated as a solid. Increasing the amount of the catalyst (10 μmol) in 5 mL water, part of the catalyst was still not soluble when heated at 50°C. Thus, we can conclude that the catalyst ascribed to the ionic compound has a certain solubility in the water when the water was heated, so that $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ and $K_2[W_2O_3(O_2)_4]$ with the same W content gaved almost the same activities under the present reaction condition. The results also motivated us to revisit the structure of the two peroxo species (**Figure 1**). Both of the peroxo species possess the same unit of $W(O_2)$. It indicates that the unit of $W(O_2)$ might be the active sites for oxidative degradation of

chitosan. In order to prove the above suggestion, Na_2WO_4 or $(NH_4)_2WO_4$ with H_2O_2 which could also form the active $W(O_2)$ sites[21,25] were used as the catalysts to degrade chitosan. As shown in **Figure 4D**, the two samples exhibit the degradation ratio of chitosan as high as that of $K_2[W_2O_3(O_2)_4]$, which is consistent with our suggestion of the $W(O_2)$ active sites.

Except where noted, we are interested to know whether the $K_2[W_2O_3(O_2)_4]$ containing the active $W(O_2)$ sites can behaved as the efficient oxidant without H_2O_2 in the preparation of LMWSC. Therefore, some comparative experiments were carried out and the results are summarized in **Figure 5A**. It is clear that the degradation ratio of chitosan was high with $K_2[W_2O_3(O_2)_4]$ in the absence of H_2O_2, while that was low with only H_2O_2. Moreover, the results further supported the hypothesis that the structure of $W(O_2)$ is the real active site in the degradation of chitosan because both of them contain an equal quantity of the peroxo group(10 - mmol). To the best of our knowledge, this is the first example of highly efficient utilization of the peroxo group to obtain the LMWSC. The peroxo species $K_2[W_2O_3(O_2)_4]$ itself was more efficient for the degradation of chitosan than hydrogen peroxide. This intriguing finding shows that we need to know more about the oxidative degradation of chitosan by $K_2[W_2O_3(O_2)_4]$ with H_2O_2.

The mechanism of the degradation of chitoan

It has been well documented in previous work that the unit of $W(O_2)$ is the active sites for oxidative different substrate such as epoxidation of olefins[26,27], desulfurization of fuels[28], and oxidation of alcohols[29]. Our work also lead to the conclusion that $W(O_2)$ structures are the active sites. There are efficient for the degradation of chitosan, even in the absence of H_2O_2. However, in the previous work,[13,15] decomposition of H_2O_2 to free radicals is considered as a key factor in the degradation of chitosan. To further investigate the role of H_2O_2 in the oxidative degradation of chitosan by $K_2[W_2O_3(O_2)_4]$ with H_2O_2, the decomposition of H_2O_2 was detected according to the literature[30,31]. The results were summarized in **Figure 5B**. The fluorescence signal at 426 nm can be assigned to 2-hydroxyterephthalic acid, which results from the capture of ·OH by terephthalic acid. Compared with the fluorescence of the system with only H_2O_2, that of the system with an extra Na_2WO_4 or $K_2[W_2O_3(O_2)_4]$ was much weaker under the same conditions(**Figure 5B a,c**), which indicated a low content of ·OH was in the system and the peroxo species exhibited its inherent poor activity for the decomposition of hydrogen peroxide[32–35]. Combining the above facts, H_2O_2 was suggested to act as an oxidant to re-form the structure of $W(O_2)$, on which chitosan was degraded. Hence, a plausible reaction mechanism might contain the active $W(O_2)$ sites cutting the β-1,4 glycoside bond in chitosan to obtain the LMWSC and the regeneration of the active sites (**Figure 6**).

Recycling of the catalyst $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$

The catalyst $K_2[W_2O_3(O_2)_4]$ can be dissolved in water, which is not beneficial for the recycle of the catalyst. Hence, we turned our attention to the water insoluble catalyst $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$. When the reaction had proceeded for 15 min, the vessel was cooled to room temperature. Then the catalyst was filtered and the filtrate was used for the next run. The results were shown in **Figure 7A.** After removal of the catalyst, the degradation ratio of chitosan was obviously decreased, and only 0.6 μg/mL W was determined in the product solution. The degradation ratio of chitosan was slightly increased after 15 min probably due to the minute amount of W remained in the filtrate. Then, the recycling experiment of the catalyst was investigated. The results in **Figure 7B** show that the degradation ratio could still reach a high level of 96.2% after recycling 7 times. For comparison, the acid hydrolysis method was also used in the degradation of chitosan and hydrochloric acid of different concentration acid was employed (**Figure 8**). With the increase in the concentration of HCl, the degradation ratio of chitosan increased. Although the degradation ratio could reach 74.8% in 3mol/L HCl, the degradation ratio decreased to 62.9% in 4mol/L HCl. It could be ascribed that the low concentration of hydrochloric acid favors the chitosan dissolving in solution, while high concentration of hydrochloric acid restrains the chitosan dissolution[36]. What's more, large amounts of inorganic acid are not friendly for the environment. It's clear that the novel catalyst developed herein is promising for application in preparation of LMWSC.

Conclusions

In conclusion, this study showed that the peroxo species $K_2[W_2O_3(O_2)_4]$ itself was more efficient for the degradation of chitosan than hydrogen peroxide. Both the peroxo species $[W_2O_3(O_2)_4]^{2-}$ and $\{PO_4[WO(O_2)_2]_4\}$ are effective catalysts for the oxidative degradation of chitosan to obtain LMWSC in water with high efficiency of hydrogen peroxide utilization. The structure of $W(O_2)$ was considered to be the active site. In addition, the new catalyst $(TBA)_3\{PO_4[WO(O_2)_2]_4\}$ was efficient for the degradatiion of chitosan, and the recovered catalyst could achieve a high degradation ratio of 96.2% after 7 times.

Author Contributions

Conceived and designed the experiments: ZM YW YH WW. Performed the experiments: ZM WW. Analyzed the data: ZM YW YH WW. Contributed reagents/materials/analysis tools: YW TW. Wrote the paper: ZM YW WW.

References

1. Gallezot P (2012) Conversion of biomass to selected chemical products. Chem. Soc. Rev41: 1538–1558.
2. Schnepp Z (2013) Biopolymers as a flexible resource for nanochemistry. Angew.Chem. Int Ed. 52: 1096–1108.
3. Pospieszny H, Chirkov S, Atabekov J (1991) Induction of antiviral resistance in plants by chitosan. Plant Sci79: 63–68.
4. Nge KL, Nwe N, Chandrkrachang S, Stevens WF (2006) Chitosan as a growth stimulator in orchid tissue culture. Plant Sci170: 1185–1190.
5. No HK, Meyers SP, Prinyawiwatkul W, Xu Z (2007) Applications of chitosan for improvement of quality and shelf life of foods: a review. J. Food Sci72: R87–100.
6. Swayampakula K, Boddu VM, Nadavala SK, Abburi K (2009) Competitive adsorption of Cu (II), Co (II) and Ni (II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent. J. Hazard. Mater170: 680-689.
7. Ngah WSW, Kamari A, Fatinathan S, Ng PW (2006) Adsorption of chromium from aqueous solution using chitosan beads. Adsorption 12: 249–257.
8. Boddu VM, Abburi K, Randolph AJ, Smith ED (2008) Removal of Copper (II) and Nickel (II) Ions from Aqueous Solutions by a Composite Chitosan Biosorbent. Separ. Sci. Technol43: 1365–1381.
9. Ueno H, Yamada H, Tanaka I, Kaba N, Matsuura M, et al. (1999) Accelerating effects of chitosan for healing at early phase of experimental open wound in dogs. Biomaterials 20: 1407–1414.
10. Dai T, Tanaka M, Huang YY, Hamblin MR (2011) Chitosan preparations for wounds and burns: antimicrobial and wound-healing effects. Expert Rev Anti-infe9: 857–879.
11. Kumar MNVR, Muzzarelli RAA, Muzzarelli C, Sashiwa H, Domb AJ (2004) Chitosan Chemistry and Pharmaceutical Perspectives. Chem. Rev104: 6017–6084.
12. Hien NQ, Phu DV, Duy NN, Lan NTK (2012) Degradation of chitosan in solution by gamma irradiation in the presence of hydrogen peroxide. Carbohydr. Polym87: 935–938.

13. Makuuchi K (2010) Critical review of radiation processing of hydrogel and polysaccharide. Radiat. Phys. Chem79: 267–271.
14. Wang S-M, Huang Q-Z, Wang Q-S (2005) Study on the synergetic degradation of chitosan with ultraviolet light and hydrogen peroxide. Carbohydr. Res340: 1143–1147.
15. Yin H, Du Y, Zhang J (2009) Low Molecular Weight and Oligomeric Chitosans and Their Bioactivities. Curr. Top. in Med. Chem9: 1546–1559.
16. Huang QZ, Zhuo LH, Guo YC (2008) Heterogeneous degradation of chitosan with H2O2 catalysed by phosphotungstate. Carbohydr. Polym72: 500–505.
17. Huang QZ, Wang SM, Huang JF, Zhuo LH, Guo YC (2007) Study on the heterogeneous degradation of chitosan with hydrogen peroxide under the catalysis of phosphotungstic acid. Carbohydr. Polym68: 761–765.
18. Huang QZ, Meng ZH, Feng YQ, Shi HZ (2010) Study on the heterogeneous degradation of chitosan with H_2O_2 catalyzed by a new supermolecular assembly crystal: $[C_6H_8N_2]_6H_3[PW_{12}O_{40}]\cdot 2H_2O$. Carbohydr. Res345: 115–119.
19. Aubry C, Chottard G, Platzer N, Bregeault JM, Thouvenot R, et al. (1991) Reinvestigation of epoxidation using tungsten-based precursors and hydrogen peroxide in a biphase medium. Inorg. Chem30: 4409–4415.
20. Campbell NJ, Dengel AC, Edwards CJ, Griffith WP (1989) Studies on transition metal peroxo complexes. Part 8. The nature of peroxomolybdates and peroxotungstates in aqueous solution. J. Chem. Soc., Dalton Trans. 1203–1208.
21. Duncan DC, Chambers RC, Hecht E, Hill CL (1995) Mechanism and Dynamics in the $H_3[PW_{12}O_{40}]$-Catalyzed Selective Epoxidation of Terminal Olefins by H_2O_2. Formation, Reactivity, and Stability of $\{PO_4[WO(O_2)_2]_4\}^{3-}$. J. Am. Chem. Soc117: 681–691.
22. Peniche C, Argüelles-Monal W, Davidenko N, Sastre R, Gallardo A, et al. (1999) Self-curing membranes of chitosan/PAA IPNs obtained by radical polymerization: preparation, characterization and interpolymer complexation. Biomaterials 20: 1869–1878.
23. Saito H, Tabeta R, Ogawa K (1987) High-resolution solid-state carbon-13 NMR study of chitosan and its salts with acids: conformational characterization of polymorphs and helical structures as viewed from the conformation-dependent carbon-13 chemical shifts. Macromolecules 20: 2424–2430.
24. Kurita K, Sannan T, Iwakura Y (1977) Studies on chitin, 4. Evidence for formation of block and random copolymers of N-acetyl-D-glucosamine and D-glucosamine by hetero- and homogeneous hydrolyses. Die Makromolekulare Chemie 178: 3197–3202.
25. Hou S-Y, Zhou Z-H, Lin T-R, Wan H-L (2006) Peroxotungstates and Their Citrate and Tartrate Derivatives. Eur. J. Inorg. Chem2006: 1670–1677.
26. Ishii Y, Yamawaki K, Ura T, Yamada H, Yoshida T, et al. (1988) Hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridinium chloride. Epoxidation of olefins and allylic alcohols, ketonization of alcohols and diols, and oxidative cleavage of 1,2-diols and olefins. J. Org. Chem53: 3587–3593.
27. Kamata K, Yamaguchi K, Mizuno N (2004) Highly Selective, Recyclable Epoxidation of Allylic Alcohols with Hydrogen Peroxide in Water Catalyzed by Dinuclear Peroxotungstate. Chem. – .Eur. J.10: 4728–4734.
28. Zhang B, Jiang Z, Li J, Zhang Y, Lin F, et al. (2012) Catalytic oxidation of thiophene and its derivatives via dual activation for ultra-deep desulfurization of fuels. J. Catal287: 5–12.
29. Buonomenna MG, Drioli E (2008) Solvent free selective oxidation of benzyl alcohol to benzaldehyde using a membrane contactor unit. Appl. Catal., B: Environ79: 35–42.
30. Fang X, Mark G, von Sonntag C (1996) OH radical formation by ultrasound in aqueous solutions Part I: the chemistry underlying the terephthalate dosimeter. Ultrason. Sonochem3: 57–63.
31. Ishibashi K-i, Fujishima A, Watanabe T, Hashimoto K (2000) Quantum yields of active oxidative species formed on TiO_2 photocatalyst. J. Photochem. Photobiol, A134: 139–142.
32. Bregeault J-M (2003) Transition-metal complexes for liquid-phase catalytic oxidation: some aspects of industrial reactions and of emerging technologies. Dalton Trans: 3289–3302.
33. Kamata K, Hirano T, Kuzuya S, Mizuno N (2009) Hydrogen-Bond-Assisted Epoxidation of Homoallylic and Allylic Alcohols with Hydrogen Peroxide Catalyzed by Selenium-Containing Dinuclear Peroxotungstate. J. Am. Chem. Soc131: 6997–7004.
34. Lane BS, Burgess K (2003) Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. Chem. Rev103: 2457–2474.
35. Mizuno N, Yamaguchi K, Kamata K (2005) Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates. Coord. Chem. Rev249: 1944–1956.
36. Horowitz ST, Roseman S, Blumenthal HJ (1957) The Preparation of Glucosamine Oligosaccharides. I. Separation1,2. J. Am. Chem. Soc79: 5046-5049.