

## Porous MnO<sub>2</sub>/CNT catalysts with a large specific surface area for the decomposition of hydrogen peroxide

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**Abstract**—H<sub>2</sub>O<sub>2</sub> vapor sterilization is an effective and safe method for removing various pathogens. To improve the efficiency of this technique, the time required for sterilization must be shortened. The aeration time constitutes a large portion of the total sterilization time; therefore, the development of a catalyst for H<sub>2</sub>O<sub>2</sub> decomposition is necessary. Bulk MnO<sub>2</sub> is typically used in H<sub>2</sub>O<sub>2</sub> decomposition, but it has a low specific surface area. To increase H<sub>2</sub>O<sub>2</sub> decomposition activity, specific surface area and electron transfer ability of catalyst need improvement. In this study, MnO<sub>2</sub>/CNT(x), where x denotes the weight ratio of CTAB to H<sub>2</sub>O in the catalyst preparation, was synthesized using a soft template method with varying amounts of the template. Overall, the catalyst specific surface area remarkably increased to 190–200 m<sup>2</sup>/g from 0.043 m<sup>2</sup>/g for bulk MnO<sub>2</sub>, and these increased surface areas resulted in superior H<sub>2</sub>O<sub>2</sub> decomposition activity. Among the CNT-supported catalysts tested, MnO<sub>2</sub>/CNT (1.0) exhibited the highest activity, which was 570 times that of bulk MnO<sub>2</sub>. Aeration times were also calculated with some assumptions and the aeration can be finished within 1 hr (bulk MnO<sub>2</sub> needs about 25 hr).

Keywords: Manganese Oxide Catalyst, Soft Template Method, Large Surface Area, Hydrogen Peroxide Decomposition, Aeration

### INTRODUCTION

Development of effective sterilization techniques has recently attracted attention due to the outbreak of devastating infectious diseases and development of biochemical weapons, such as anthrax bacillus. For example, the recent Middle East respiratory syndrome (MERS) outbreak in 2012 brought 1,728 infections and 624 deaths by 2016 [1]. Although many types of pathogens can be transmitted between people through a variety of pathways, many of the infected and deceased were infected after admission to a hospital in which other patients diagnosed with MERS were being treated. Therefore, sterilization of hospital beds, equipment, tools, rooms and other spaces is crucial to prevent nosocomial transmission. Depending on the applications, sterilization methods involve the use of heat [2], chemicals [3], irradiation [4], or high pressure [5] to remove these viruses and bacteria. In particular, chemical sterilization is appropriate for application to larger spaces, such as hospital rooms. Ethylene oxide (EO) is a representative sterilant that is used for chemical sterilization. EO sterilization has a mild operating temperature that ranges from 49 °C to 63 °C [6], and therefore, this approach is primarily used when the materials that need to be sterilized cannot withstand heat. However, time weighted average

(TWA), which is a measure of the permissible exposure limit, of ethylene oxide is 0.1 ppm. This legal limit was set because a longer exposure to a higher amount may induce cancer or genetic damage [7]. The use of hydrogen peroxide as a sterilant offers advantages related safety compared to ethylene oxide because its TWA is 1 ppm. Hydrogen peroxide sterilization has been used as an effective method, and Bioquell is a representative company that provides hydrogen peroxide vapor sterilization equipment.

The hydrogen peroxide sterilization cycle consists of evaporation, dwell and aeration steps. Vaporized hydrogen peroxide can remove pathogens over a large space within a short time. During aeration, the hydrogen peroxide concentration is reduced below its toxic threshold. To improve the operational efficiency of the hydrogen peroxide vapor sterilization equipment, the run time of the equipment must be reduced, especially that of the aeration step because it accounts for more than 50% of the total time [8]. To reduce the aeration time, the development of an active catalyst for hydrogen peroxide decomposition is necessary because adjusting only the air condition is restrictive due to the safe hydrogen peroxide concentration level being 1 ppm [9], which is very low. In addition, the catalyst must exhibit excellent decomposition activity because the amount of catalyst that is used is limited in the sterilization machine.

Hydrogen peroxide can be decomposed by various precious metals (e.g., Pd and Pt [10–14]) or transition metal oxides (e.g., MnO<sub>2</sub> [15], Fe<sub>2</sub>O<sub>3</sub> [16] and Al-La-Mn oxide [17]) and perovskite [18]. Recently, metal-Schiff base complexes (e.g., Mn<sub>2</sub>A, A=3,5-bis[(2-hydroxy-40-sodiumsulphatoethyl sulphonyl)azobenzene-methyl-

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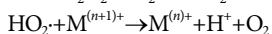
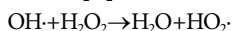
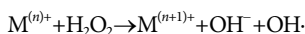
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<sup>\*</sup>This article is dedicated to Prof. Ki-Pung Yoo on the occasion of his retirement from Sogang University.

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neimino]-benzoic acid) have been reported as the catalysts with a high  $\text{H}_2\text{O}_2$  decomposition activity [19,20]. However, precious metals are expensive, and metal-Schiff base catalyst synthesis has several drawbacks, including a long synthesis time and the use of a hazardous organic solvent. Therefore, transition metal oxides as heterogeneous catalysts for hydrogen peroxide decomposition are attractive materials.

Hydrogen peroxide decomposition via transition metal oxides is based on redox catalysis, and the corresponding reaction mechanism is as follows [21]:



(M: transition metal,  $\cdot$ : radical)

$\text{H}_2\text{O}_2$  exchanges an electron with  $\text{M}^{(n)+}$  and decomposes into  $\text{OH}^-$  and  $\text{OH}\cdot$ , and finally into  $\text{H}_2\text{O}$  and  $\text{O}_2$ . According to this mechanism, the electron transfer ability of catalyst is expected as a factor of  $\text{H}_2\text{O}_2$  decomposition.

Nonprecious metal catalysts have been used in various catalytic reactions due to being inexpensive [22-24]. Manganese oxide is also used as a catalyst for various reactions [25-29] and exhibits a high  $\text{H}_2\text{O}_2$  decomposition activity, resulting from facile reversible changes in its oxidation state. However, the commercially available  $\text{MnO}_2$  catalyst has a low specific surface area that is less than  $10 \text{ m}^2/\text{g}$  [30], and many studies have focused on increasing the surface area of catalysts. A porous catalyst structure is commonly studied, and a porous transition metal oxide may also be possible. Many of the porous  $\text{MnO}_2$  structures exhibited improvements over the bulk  $\text{MnO}_2$  regarding the catalytic reactions such as the HCHO decomposition [31], the  $\text{H}_2\text{O}_2$  decomposition [32], and the reaction in the electrical capacitor [33,34].

In this study, we synthesized porous  $\text{MnO}_2$ /carbon nanotube (CNT), using a soft template method, that has a large specific surface area of  $\text{MnO}_2$ , which was related to the porous structure and thin layer of  $\text{MnO}_2$  on the CNT. In addition, the conductive car-

bon materials (e.g., CNT and graphene) enhance the electron transferability of catalyst [35]. The porous oxide on CNT can be achieved using the soft template method with appropriate organic surfactants [35-37]. The soft template method provides a facile synthesis method for porous materials due to its mild conditions in the absence of a hydrothermal treatment and calcination. To determine the effect of the template amount on the catalytic properties, the CTAB amount was varied during the catalyst synthesis.

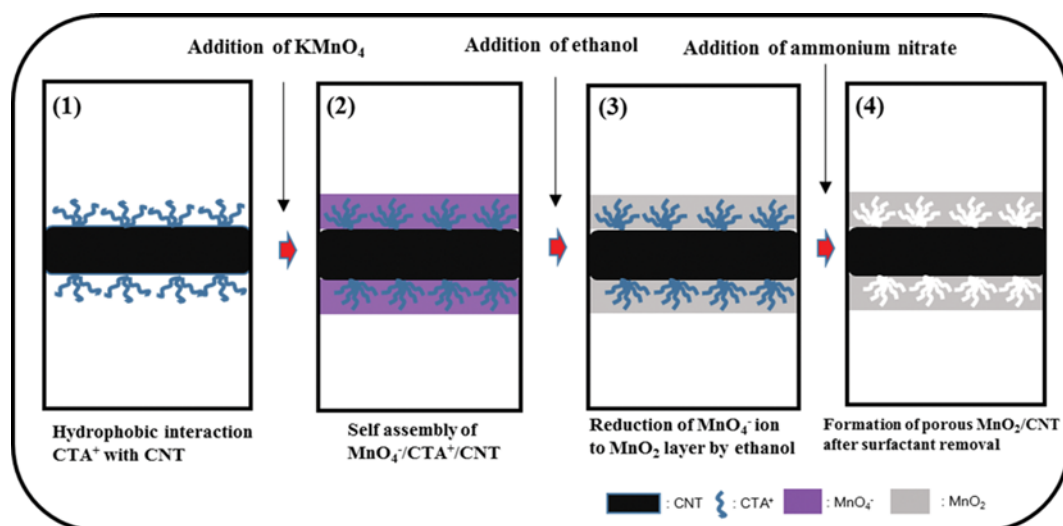
## EXPERIMENTAL

### 1. Materials

Absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.5%, Sigma-Aldrich), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , 98%, Sigma-Aldrich), multi-wall carbon nanotube (CNT, 98%, Sigma-Aldrich), cetyltrimethyl ammonium bromide (CTAB, 98%, Sigma-Aldrich), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 35 wt% in  $\text{H}_2\text{O}$ , Sigma-Aldrich), sulfuric acid solution ( $\text{H}_2\text{SO}_4$ , 0.1 N, Fluka), manganese dioxide ( $\text{MnO}_2$ , 99%, Sigma-Aldrich), potassium permanganate ( $\text{KMnO}_4$ , 99%, Sigma-Aldrich), potassium iodide solution (KI, 0.1 N, Samchun), and sodium thiosulfate solution ( $\text{Na}_2\text{S}_2\text{O}_3$ , 0.1 N, Fluka) were used without further purification.

### 2. Catalyst Preparation

Porous  $\text{MnO}_2$ /CNT was synthesized using a soft template method based on a previously reported [35]. Scheme 1 shows the catalyst preparation process, which is composed of the following steps: (1) hydrophobic interaction of  $\text{CTA}^+$  with CNT, (2) electrostatic interaction of  $\text{MnO}_4^-$  with  $\text{CTA}^+$  and self-assembly of  $\text{MnO}_4^-/\text{CTA}^+/\text{CNT}$ , (3)  $\text{MnO}_4^-$  reduction to  $\text{MnO}_2$  via ethanol addition, and (4) template removal using ion exchange. Details of the procedure are provided below. First, CTAB (0.6 g, 0.8 g, 1 g, 1.2 g) was dissolved in 90 mL of DI water, and 70 mg of CNT was added to the solution. The mixture was sonicated for 4 h, and then 10 mL of a  $\text{KMnO}_4$  solution (0.1 M) was added before stirring for 1 h. In this step,  $\text{MnO}_4^-$  ions were attached to  $\text{CTA}^+$  which had formed layer on CNT via electrostatic interactions. Finally, 40 mL of absolute ethanol was added to reduce permanganate to manganese oxide, and the



Scheme 1.  $\text{MnO}_2$ /CNT preparation process.

mixture was stirred for 12 h. The catalysts were filtered and washed with ethanol. The recovered products were dried overnight at 80 °C. To achieve a porous structure, CTAB was removed via ion exchange with ammonium nitrate. The catalyst was dispersed in an ethanol solution for which the ammonium nitrate was dissolved, followed by stirring for 30 min at 60 °C. Similar to previous recovery processes, the catalysts were filtered and washed. The CTAB/water solvent weight ratios are denoted as *x* in MnO<sub>2</sub>/CNT (*x*) (*x*=0.6, 0.8, 1.0, 1.2).

### 3. Characterization

Using a BELSORP-max (BEL Japan Inc. Osaka, Japan), nitrogen adsorption-desorption isotherms of MnO<sub>2</sub>/CNT were measured. The specific surface areas of the catalysts were calculated using the Brunauer-Emmett-Teller (BET) equation. The degassing conditions were 100 °C and 6 hr under reduced pressure.

To measure the mass fraction of MnO<sub>2</sub> in the catalysts, inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using a JY Ultima2C (Jobin Yvon, France) dual ICP-OES spectrometer. The samples were pretreated by dissolution in a mixture consisting of aqua regia and hydrofluoric acid. The analysis was carried out at 200 °C under reduced pressure, provided by the Korean Basic Science Institute (KBSI).

X-ray diffraction (XRD) was performed to investigate the structure of MnO<sub>2</sub>/CNT using a D8 Advanced LynxEye (Bruker). The scanning speed was 2°/min, and the scanning range was 10° to 90°. The beam source was Cu-K $\alpha$  irradiation ( $\alpha=1.5406$  Å).

Scanning transmission electron microscopy (STEM) images of MnO<sub>2</sub>/CNT were obtained to identify the structure of the composite using a Tecnai G<sup>2</sup> 11 F30 instrument (FEI Company, OR, USA). The catalysts were dispersed in ethanol and sampled on a Cu grid. To identify the Mn element in the catalyst structure, energy-dispersive X-ray (EDX) spectroscopy was also performed.

To measure the Mn electronic state, X-ray photoelectron spectroscopy (XPS) was performed on an ESCA2000 (VG microtech: U.K.). The operating conditions were 10<sup>-10</sup> Torr with an AlK $\alpha$  X-ray anode source.

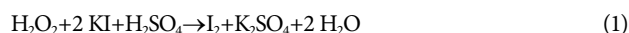
### 4. Hydrogen Peroxide Decomposition

The decomposition of hydrogen peroxide was in a 200 mL double jacket glass reactor. The initial concentration of H<sub>2</sub>O<sub>2</sub> was set to 1,000 ppm by diluting 35 wt% H<sub>2</sub>O<sub>2</sub> in 100 mL of DI water. 10 mg of each catalyst was added to the reaction solvent and stirred with a magnetic stirrer (1,200 rpm). The reaction temperature was maintained at 25 °C using a circulator. To examine the time progression of the change in the H<sub>2</sub>O<sub>2</sub> concentration, we sampled the solution three times at an interval of 10 min. The concentration was measured via iodide titration. To compare the H<sub>2</sub>O<sub>2</sub> decomposition activity, the hydrogen peroxide decomposition was also performed using bulk MnO<sub>2</sub> (Sigma Aldrich, 200 mg), and the other reaction conditions remained the same as those employed for MnO<sub>2</sub>/CNT. To compare the activation energies of the MnO<sub>2</sub>/CNT (1.0) and the bulk MnO<sub>2</sub>, the H<sub>2</sub>O<sub>2</sub> decomposition reactions were carried out at 15 °C and 35 °C additionally. Subsequently, the activation energy of each catalyst was obtained from the slope of linear line on the Arrhenius plot.

### 5. Iodide Titration

The H<sub>2</sub>O<sub>2</sub> concentration in the reaction was measured via iodide

titration [38]. The process follows two chemical reactions. First, 5 mL of a KI solution (0.1 N) and 5 mL of a H<sub>2</sub>SO<sub>4</sub> solution (0.1 N) were added to a vial. Drops of an ammonium molybdate solution were used as a catalyst for iodide oxidation, and a starch solution (0.5 wt%) was used as an indicator, which turned indigo color by reacting with I<sub>2</sub> (Eq. (1)). The sampled reaction solution from the reactor was added, and a certain amount of I<sub>2</sub> was formed as a function of the H<sub>2</sub>O<sub>2</sub> amount. The indigo solution was titrated with the sodium thiosulfate solution (Fluka) until the solution was colorless (Eq. (2)). Using Eq. (3), we calculated the hydrogen peroxide concentration.



$$\text{H}_2\text{O}_2 \text{ (wt\%)} = \frac{17.007 \times 0.01 \times A}{B \times 1000} \quad (3)$$

A=volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (μL), B=weight of sampled solution (g)

### 6. Hydrogen Peroxide Reaction Rate Constant Calculation

Hydrogen peroxide decomposes into water and oxygen (Eq. (4)), and the reaction follows pseudo first-order kinetics [39,40] as expressed by Eq. (5).



$$\ln\left(\frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0}\right) = -k_d t, \quad k_d = k_{\text{MnO}_2} \times \text{MnO}_2 \text{ weight (g)} \quad (5)$$

(*k<sub>d</sub>*: reaction rate constant, *k<sub>MnO<sub>2</sub></sub>*: reaction rate constant per MnO<sub>2</sub> weight)

The reaction constants (*k<sub>MnO<sub>2</sub></sub>*) of the catalysts were compared to measure the hydrogen peroxide decomposition activity.

### 7. Aeration Time Calculation

Aeration times (*t<sub>aeration</sub>*) were calculated in a 75 m<sup>3</sup> room and at an initial concentration of 1,000 ppm to a final concentration of 1 ppm. The overall process and assumptions made for this calculation are detailed in supplementary material.

## RESULTS AND DISCUSSION

Fig. 1 shows the STEM images of CNT and MnO<sub>2</sub>/CNT (1.0) before and after CTAB removal. A bare CNT has a thickness of approximately 10-12 nm, as shown in Fig. 1(a), and MnO<sub>2</sub>/CNT (1.0) before CTAB removal has a thickness of approximately 20 nm, as shown in Fig. 1(b), which corresponds to Scheme 1-(3). Based on the STEM images, a thin layer of MnO<sub>2</sub> was deposited on CNT. The MnO<sub>2</sub>/CNT structure is a long CNT tube uniformly surrounded by a layer of MnO<sub>2</sub> (bright color). Based on STEM-EDX mapping shown (Fig. 1(d)), the MnO<sub>2</sub> layer was uniformly deposited along the CNT structure. After CTAB removal, the MnO<sub>2</sub> layers were partially irregular on the CNT, as shown in Fig. 1(c), corresponding to Scheme 1-(4). In Fig. 2(a), (b), and (c), the MnO<sub>2</sub>/CNT catalysts exhibited a similar structure with MnO<sub>2</sub>/CNT (1.0). On the other hand, the particle size of bulk MnO<sub>2</sub> was in the 200-300 nm range (Fig. 2(d)).

Fig. 3 shows the XRD patterns for MnO<sub>2</sub>/CNT and bulk MnO<sub>2</sub>.

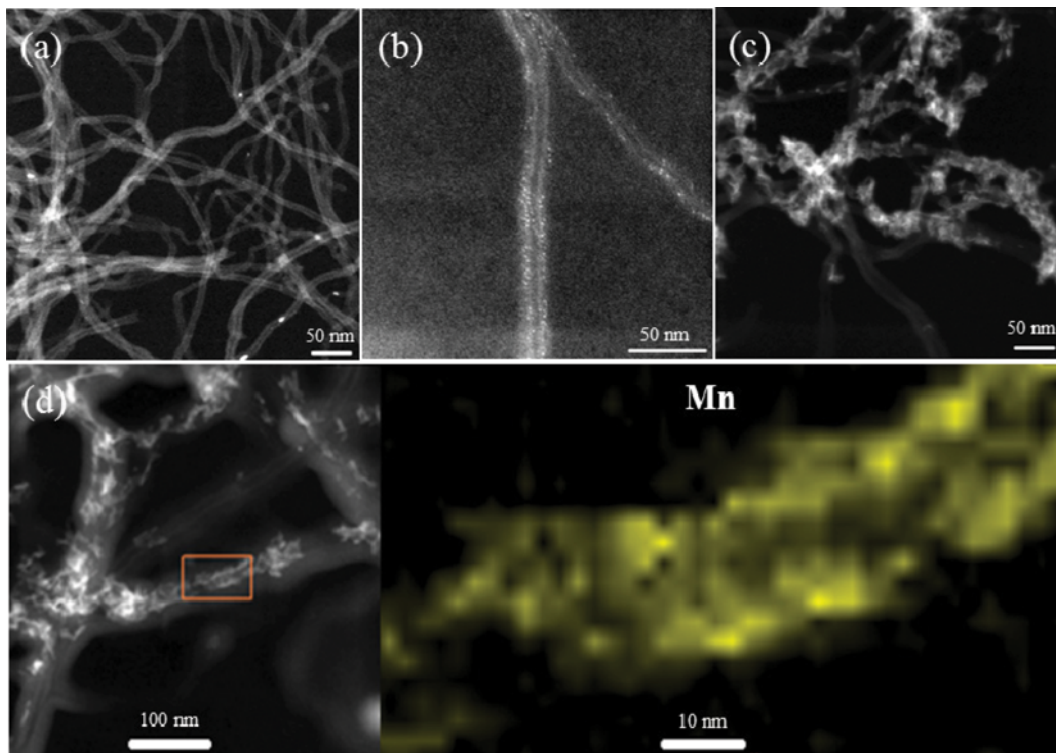


Fig. 1. STEM images of (a) CNT, (b) MnO<sub>2</sub>/CNT (1.0) (before CTAB removal), (c) MnO<sub>2</sub>/CNT (1.0) (after CTAB removal) and (d) STEM EDX of MnO<sub>2</sub>/CNT (1.0).

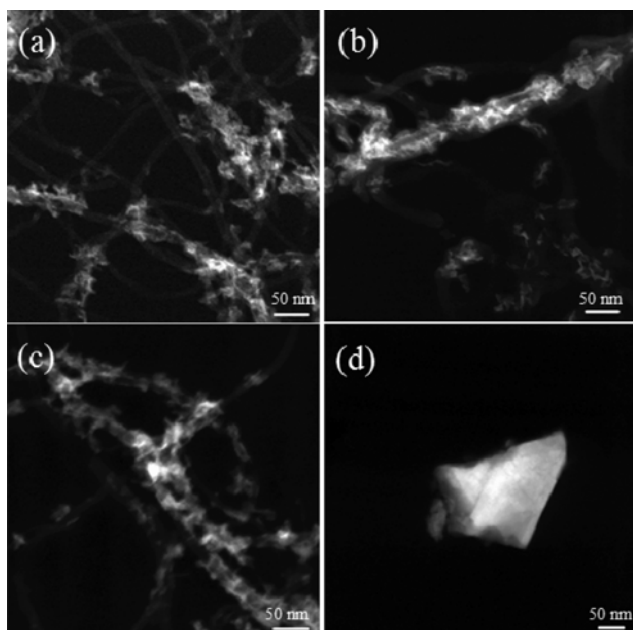


Fig. 2. STEM images of (a) MnO<sub>2</sub>/CNT (0.6), (b) MnO<sub>2</sub>/CNT (0.8), (c) MnO<sub>2</sub>/CNT (1.2) and (d) bulk MnO<sub>2</sub> (Sigma-Aldrich).

In XRD results of MnO<sub>2</sub>/CNT contained three broad peaks at two theta values of 26°, 37°, and 66°. The 26° peak corresponds to the (0 0 2) facet of the CNT structure [41], and the 37° and 66° peaks were due to the (1 1 1) and (0 2 0) facets, respectively, of the manganese oxide monoclinic structure, which was formed by reduc-

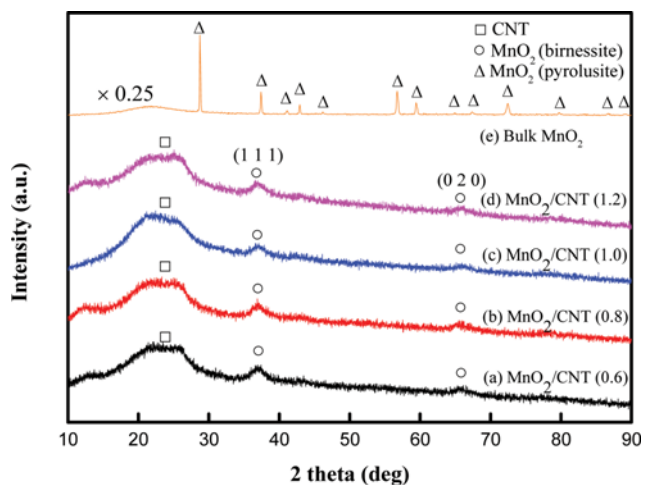


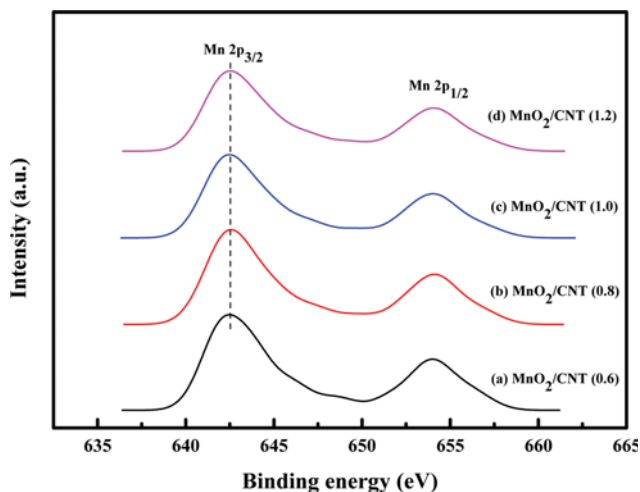
Fig. 3. XRD patterns of the catalysts: (a) MnO<sub>2</sub>/CNT (0.6), (b) MnO<sub>2</sub>/CNT (0.8), (c) MnO<sub>2</sub>/CNT (1.0), (d) MnO<sub>2</sub>/CNT (1.2) and (e) bulk MnO<sub>2</sub> (Sigma).

ing KMnO<sub>4</sub> with ethanol (JCPDS 42-1317). These broad peaks indicate that the MnO<sub>2</sub> layer deposited on the CNT in all of the catalysts had low crystallinity. Using the XRD results, the crystallite size of MnO<sub>2</sub> was calculated with the Scherrer equation. In Table 1, the crystallite sizes of MnO<sub>2</sub> in the synthesized catalysts ranged from 3.4 nm to 4.4 nm, and these values increased as the CTAB template amount decreased. Another study also reported a decrease in the crystallite size of the catalyst as the template amount increased [42]. The bulk MnO<sub>2</sub> (Sigma-Aldrich) crystallite size was approxi-

**Table 1. Crystallite sizes of the catalysts**

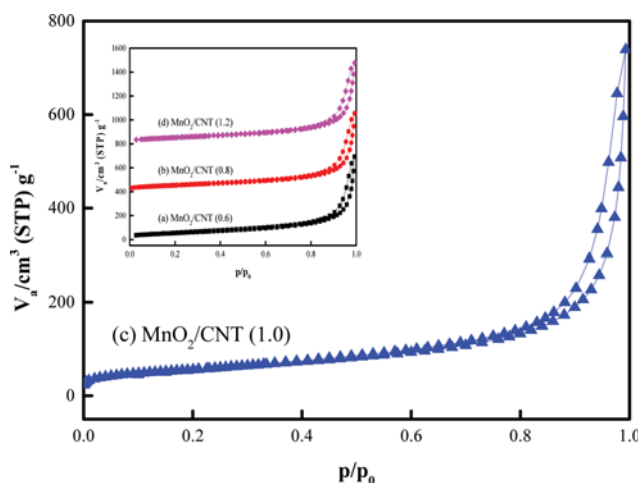
Catalyst	Crystallite size (nm) <sup>a</sup>
MnO <sub>2</sub> /CNT (0.6)	4.4
MnO <sub>2</sub> /CNT (0.8)	4.1
MnO <sub>2</sub> /CNT (1.0)	3.7
MnO <sub>2</sub> /CNT (1.2)	3.4

<sup>a</sup>Crystallite size of the catalyst was calculated from the XRD data

**Fig. 4. Mn 2p XPS of the synthesized catalysts.**

mately 100 nm, which was calculated using the Scherrer equation, and the specific surface area of MnO<sub>2</sub>/CNT is expected to be much larger than that of bulk MnO<sub>2</sub>.

Fig. 4 shows the Mn electronic states of the synthesized catalysts. The oxidation states of the Mn element in the metal oxide are varied, and the binding energies of Mn<sup>2+</sup>, Mn<sup>3+</sup>, and Mn<sup>4+</sup> appear in the region from 640 eV to 643 eV in the Mn 2p<sub>3/2</sub> XPS spectra [43]. The MnO<sub>2</sub>/CNT catalysts showed similar binding

**Fig. 5. N<sub>2</sub> adsorption-desorption isotherms of the catalysts: (a) MnO<sub>2</sub>/CNT (0.6), (b) MnO<sub>2</sub>/CNT (0.8), (c) MnO<sub>2</sub>/CNT (1.0) and (d) MnO<sub>2</sub>/CNT (1.2).****Table 2. Specific surface areas, Mn content and MnO<sub>2</sub> weights of the catalysts**

Catalyst	Specific surface area (m <sup>2</sup> /g) <sup>a</sup>	Mn (wt%) <sup>b</sup>	MnO <sub>2</sub> (wt%) <sup>c</sup>
MnO <sub>2</sub> /CNT (0.6)	197.7	31.1	49.2
MnO <sub>2</sub> /CNT (0.8)	194.2	30.7	48.6
MnO <sub>2</sub> /CNT (1.0)	200.6	29.4	46.5
MnO <sub>2</sub> /CNT (1.2)	190.5	32.2	50.9
Bulk MnO <sub>2</sub>	0.043	-	100

<sup>a</sup>Specific surface area of the catalyst was calculated from the BET equation

<sup>b</sup>Mn weight (%) was confirmed by ICP-OES

<sup>c</sup>MnO<sub>2</sub> weight (%) was calculated from the Mn weight (%) assuming that the Mn composition corresponded to MnO<sub>2</sub> in the catalysts

energies in the XPS spectra, which are confirmed by the dashed line in Fig. 4, where the Mn electronic states are nearly the same as those in the synthesized catalysts.

Fig. 5 shows the N<sub>2</sub> adsorption-desorption isotherms of the MnO<sub>2</sub>/CNT catalysts. At an approximately near-zero relative pressure, a slight increase in the monolayer adsorption of N<sub>2</sub> on the catalyst was observed. The adsorption amount gradually increased in the region from p/p<sub>0</sub> of 0.1 to a p/p<sub>0</sub> of 0.8, and a sharp increase, which may have resulted from the interparticle void space that is due to the catalyst packing, which appeared in the region from a p/p<sub>0</sub> of 0.8 to a p/p<sub>0</sub> of 1.0. Based on these results, the adsorption isotherm can be regarded as Type II [44]. Additionally, a hysteresis loop is present in the isotherm through a wide region (p/p<sub>0</sub> 0.4 to p/p<sub>0</sub> 1.0). The hysteresis under the low pressure seems to be due to the porous structure that is formed by the removal of the CTAB, while the hysteresis under the high pressure appeared to be due to the CNT's entangled structure.

Table 2 lists the specific surface areas, which were calculated from the BET equation and Mn content, which was obtained from ICP-OES analysis. The Mn content ranged from 29.4 wt% to 32.2 wt%, about 30 wt%. The MnO<sub>2</sub>/CNT catalysts exhibited much larger specific surface areas (190-200 m<sup>2</sup>/g) than bulk MnO<sub>2</sub> (0.043 m<sup>2</sup>/g). These large surface areas resulted from the formation of a very thin layer of MnO<sub>2</sub> on the CNT, as confirmed in Fig. 1, and the porous structure of the MnO<sub>2</sub> formed during the CTAB removal. In addition, the specific surface area of the catalysts varied when only the CTAB amount was changed, and the other material quantities were held constant. The largest specific surface area was observed for MnO<sub>2</sub>/CNT (1.0).

The reaction constant ( $k_d$ ) was obtained from the slope of the linear line in Fig. 6, and  $k_{MnO_2}$  of the catalysts determined from  $k_d$  and MnO<sub>2</sub> weights are shown in Table 3. The MnO<sub>2</sub>/CNT catalysts exhibited a 350- to 570-fold improvement in the H<sub>2</sub>O<sub>2</sub> decomposition activity ( $k_{MnO_2}$  = 22.47-35.48 g<sup>-1</sup> min<sup>-1</sup>) compared to that of bulk MnO<sub>2</sub> (0.0625 g<sup>-1</sup> min<sup>-1</sup>). This result confirmed that MnO<sub>2</sub>/CNT exhibited a significant improvement in the catalytic activity for H<sub>2</sub>O<sub>2</sub> decomposition, which originated from the large specific surface area. Aeration times in 75 m<sup>3</sup> (5 m×6 m×2.5 m) system for MnO<sub>2</sub>/CNT (1.0) and bulk MnO<sub>2</sub> were 0.89 hr and 25 hr, respec-

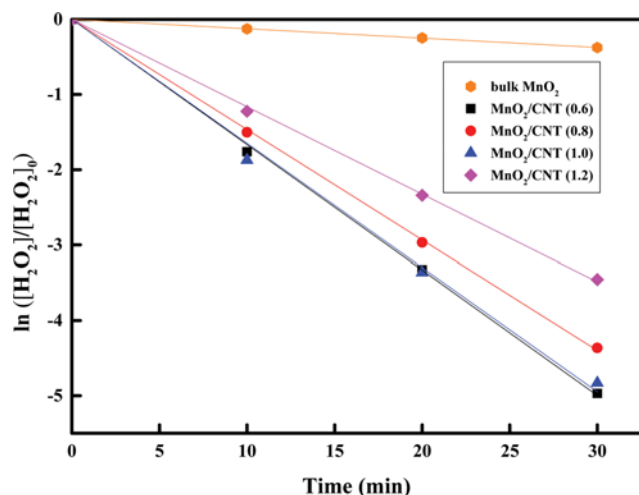


Fig. 6. Hydrogen peroxide decomposition. Test conditions: 25 °C, 1 atm, 10 mg MnO<sub>2</sub>/CNT (bulk MnO<sub>2</sub>, 200 mg), 100 mL water containing [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>, 1,000 ppm, stirring rate 1,200 rpm.

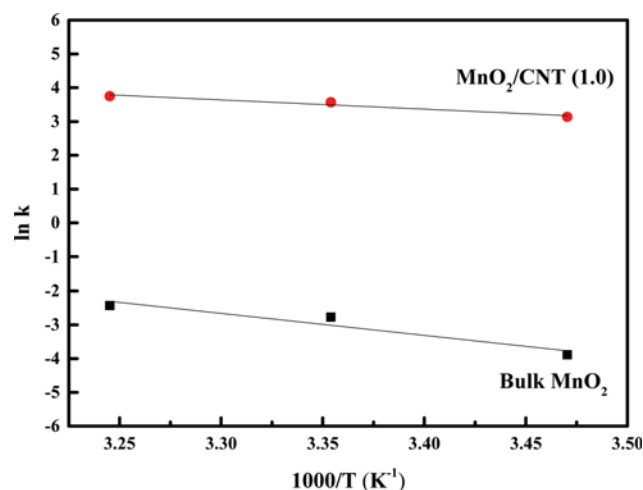


Fig. 7. Arrhenius plot of hydrogen peroxide decomposition.

tively (Supplementary material), which clearly indicates the synthesized catalyst's superior performance for hydrogen peroxide vapor sterilization.

Fig. 7 shows the Arrhenius plots of the MnO<sub>2</sub>/CNT (1.0) and the bulk MnO<sub>2</sub>. From the plot slopes, the activation energies of each catalyst were calculated, and the MnO<sub>2</sub>/CNT activation energy (22.7 kJ/mol) is lower than that of bulk MnO<sub>2</sub> (54.1 kJ/mol). Therefore, the reason that the synthesized catalyst showed the superior

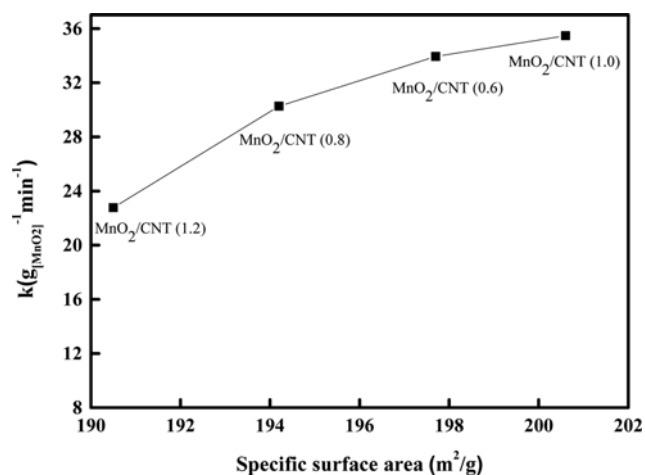


Fig. 8.  $k_{MnO_2}$  of the catalysts (hydrogen peroxide decomposition reaction assumed to follow pseudo first-order kinetics).

H<sub>2</sub>O<sub>2</sub> decomposition activity is the increase of active sites and the reduction of the activation energy compared with the bulk MnO<sub>2</sub>.

Fig. 8 shows a plot  $k_{MnO_2}$  of MnO<sub>2</sub>/CNT (x). The H<sub>2</sub>O<sub>2</sub> decomposition activity is proportional to the specific surface area, which was confirmed by the plot. The difference in CTAB addition amount during catalyst synthesis affected the specific surface area [37] and resulted in changes in the catalytic activity. Although the specific surface area from N<sub>2</sub> adsorption-desorption isotherm analysis does not exactly correspond to the specific surface of MnO<sub>2</sub> in the catalyst, we can assume that the MnO<sub>2</sub> surface area is most likely proportional to the MnO<sub>2</sub>/CNT catalyst specific surface area because the MnO<sub>2</sub> layer nearly covers the CNT [35]. Therefore, the H<sub>2</sub>O<sub>2</sub> decomposition activity is correlated with the MnO<sub>2</sub> surface area of the catalyst.

## CONCLUSIONS

MnO<sub>2</sub>/CNT catalysts synthesized using a soft template method exhibited improvement in catalytic activity for hydrogen peroxide decomposition compared to that of bulk MnO<sub>2</sub> due to the increased specific surface area and reduced activation energy in the hydrogen peroxide decomposition. The template amount was varied to determine the optimal mass ratio between the catalyst and the support, and the specific surface area of the catalyst was identified as a factor in determining the catalytic activity. The largest specific surface area was observed for MnO<sub>2</sub>/CNT (1.0), which exhibited the highest activity among the synthesized catalysts. In a

Table 3. Reaction rate constants ( $k_d$  and  $k_{MnO_2}$ ) of the catalysts

Catalyst	[H <sub>2</sub> O <sub>2</sub> ] <sub>0</sub> (t=0, ppm)	[H <sub>2</sub> O <sub>2</sub> ] (t=30 min, ppm)	$k_d$ (min <sup>-1</sup> )	$k_{MnO_2}$ (g <sup>-1</sup> ·min <sup>-1</sup> )
MnO <sub>2</sub> /CNT (0.6)	1065	7.4	0.167	33.94
MnO <sub>2</sub> /CNT (0.8)	1100	14	0.147	30.27
MnO <sub>2</sub> /CNT (1.0)	1040	8.3	0.165	35.48
MnO <sub>2</sub> /CNT (1.2)	1040	32.8	0.116	22.77
Bulk MnO <sub>2</sub>	1045	718	0.0125	0.0625

vapor sterilization system, aeration times for bulk MnO<sub>2</sub> (Sigma-Aldrich) and MnO<sub>2</sub>/CNT (1.0) were calculated, and the times were shortened from 25 hr (bulk MnO<sub>2</sub>) to 0.89 hr (MnO<sub>2</sub>/CNT (1.0)). The synthesis is easily carried out in mild conditions without the need for hydrothermal setting and calcination. Therefore, the utilization of MnO<sub>2</sub>/CNT as a decomposition catalyst in hydrogen peroxide sterilization provides a good approach for enhancing the efficiency of the hydrogen peroxide sterilization system.

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#### SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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## Supporting Information

### Porous MnO<sub>2</sub>/CNT catalysts with a large specific surface area for the decomposition of hydrogen peroxide

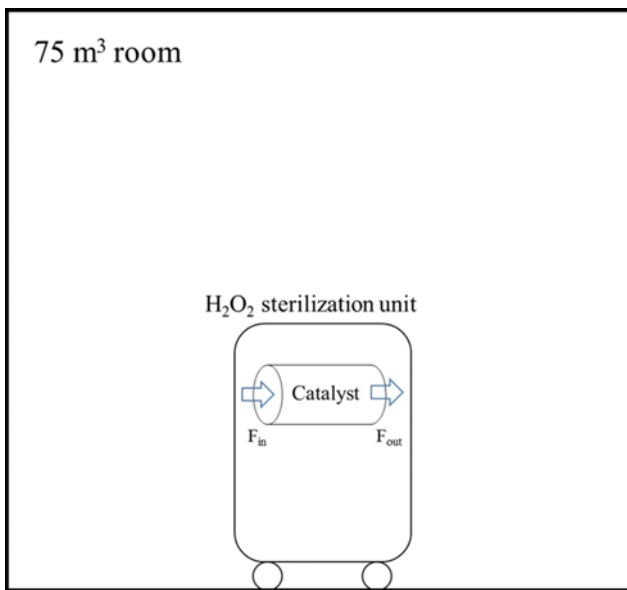
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#### Assumption in this calculation for aeration time

1. Space volume (V): 75 m<sup>3</sup>, Aeration flow rate (u): 1,000 m<sup>3</sup>/hr
  2. H<sub>2</sub>O<sub>2</sub> concentration (N<sub>A</sub>): 1,000 ppm (N<sub>A0</sub>) to 1 ppm (N<sub>Af</sub>)
  3. There is no pressure drop and conversion (X) in catalyst layer is constant
  4. Catalyst layer: 4 inch diameter and 20 cm length (V<sub>c</sub>=1,620 cm<sup>3</sup>)
  5. N<sub>A</sub> only depends on time
  6. H<sub>2</sub>O<sub>2</sub> decomposition is first order reaction in catalyst and it can be calculated as plug flow reactor (PFR)
- Mass balance for H<sub>2</sub>O<sub>2</sub> in 75 m<sup>3</sup> room

$$-F_{in} + F_{out} = \frac{dN_A}{dt} \quad (1)$$

$$(N_A = C_A \times V, F_{in} = C_A \times u, F_{out} = C_A \times (1-X) \times u)$$

Integrating Eq. (1),

$$\ln \frac{N_{Af}}{N_{A0}} = -\frac{Xu}{V} \times t_{aeration} \quad (2)$$

H<sub>2</sub>O<sub>2</sub> decomposition (1<sup>st</sup> order reaction) in catalyst (PFR)

$$k\tau = -\ln(1-X) \quad (3)$$

$$\left( \tau = \frac{V_c}{u}, k = [\text{MnO}_2 \text{ weight}] \times k_{\text{MnO}_2} \right)$$

$\tau$  is (min) from V<sub>c</sub> and u in this system.

#### 1. Bulk MnO<sub>2</sub> (Sigma-Aldrich)

4 inch diameter and 20 cm length of catalyst layer, bulk MnO<sub>2</sub> amount is 8,100 g (density of MnO<sub>2</sub>=5 g/cm<sup>3</sup>).

k=0.0625 (g<sup>-1</sup>·min<sup>-1</sup>)×8100 g=506.7 (min<sup>-1</sup>) and X=2.06×10<sup>-2</sup> is obtained from Eq. (3).

With X and Eq. (2), t<sub>aeration</sub> (bulk MnO<sub>2</sub>)=25 hr is determined.

#### 2. MnO<sub>2</sub>/CNT (1.0)

3 inch diameter and 15 cm length of catalyst layer, MnO<sub>2</sub>/CNT (1.0) amount is 1,296 g (density of catalyst=0.8 g/cm<sup>3</sup>), 602 g MnO<sub>2</sub> is included in this catalyst (from ICP analysis). ( $\tau$  is assumed as 4.11×10<sup>-5</sup> (min), which is equal to bulk MnO<sub>2</sub> catalyst system)

k=35.48 (g<sup>-1</sup>·min<sup>-1</sup>)×602 g=21360 (min<sup>-1</sup>) and X=0.584 is obtained from Eq. (3).

With X and Eq. (2), t<sub>aeration</sub> (MnO<sub>2</sub>/CNT (1.0))=0.89 hr (53 min) is determined.