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## Cellulose fibers functionalized by metal nanoparticles stabilized in dendrimer for formaldehyde decomposition and antimicrobial activity



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## HIGHLIGHTS

- Dendrimer with metal nanoparticles (5 nm) were chemically bound on cellulose fiber.
- Formaldehyde gas adsorption was 84 times higher on dendrimer site than fiber site.
- Catalytic efficiency of Pt for decomposition of formaldehyde on dendrimer was 65%.
- Silver-loaded fiber revealed excellent biocidal activity against *E. coli*.
- Device is effective for degradation of causative agents of sick building syndromes.

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## G R A P H I C A L A B S T R A C T



## ABSTRACT

Viscose rayon cellulose fiber was selectively oxidized so that carboxylate functional group was introduced on the fiber. Enough dispersed platinum nanoparticles and silver nanoparticles having average sizes of around 5 nm with small size distribution were prepared with capping of amine-terminated fourth generation poly(amido amine) dendrimer and they were immobilized on oxidized fibers through amidation between terminal amine groups of dendrimer and carboxylic acids on oxidized fibers. The fiber containing dendrimer (1 wt%) and platinum (2 wt%) exhibited the 84 times higher adsorption capacity for formaldehyde gas on dendrimer site than on fiber site and the catalytic efficiency (65%) towards decomposition of formaldehyde gas adsorbed on the dendrimer site, and the silver (0.2 wt%)-loaded fiber revealed excellent biocidal activity against *E. coli*. Thus, it can be noted that the immobilization of functional metal nanoparticles protected by dendrimer on cellulose fibers is effective to produce efficient textile products with smart functions like the degradation of causative agents for sick building syndromes. © 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

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Formaldehyde is one of the toxic volatile organic compound gases emitted from wood products such as plywood, pulp, paper, cellulose textiles [1]. Long time exposure of this gas may cause sick building syndromes and diseases like cancer, asthma, skin allergy, etc. [2–4]. Therefore, its presence inside homes and working places

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must be controlled according to World Health Organization guidelines established in 2010. It is established that the exposure of formaldehyde should be within the amount of less than 1 ppm [5]. Many literatures have been reported for control of formaldehyde either through adsorption on different adsorbents like activated carbons [6] and zeolite membranes [7] or through catalytic decomposition reactions on metal oxide catalysts like TiO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> [8] and noble metal particles such as Pt [9], Pt/FeO<sub>3</sub> [10], Pt/TiO<sub>2</sub> [11], Pt/SiO<sub>2</sub> [12], Au/Al<sub>2</sub>O<sub>3</sub> [13], Au/CeO<sub>2</sub> [14], and Ag/ MnOx [15]. These literatures show that the gas removal efficiency is mainly dependent on type of adsorbents, catalysts, substrates, and energy sources (light or heat). Therefore, nowadays people are further working to develop highly effective materials that can eliminate formaldehyde and other toxic indoor gases from the environment. For instance, TiO<sub>2</sub> supported platinum nanoparticles has shown high catalytic efficiency at low temperature despite of extremely low catalyst concentration [9]. Moreover, textile substrates like polyester [16] and cotton [17] were also employed as a support. These supports are easily available at home.

Viscose rayon (VR) fiber is the first man-made textile fiber prepared from a biopolymer called cellulose as a raw material and has been distributed in the textile market since the end of 19th century [18]. The basic process to prepare such fiber is the regeneration of cellulose after chemical treatment of native cellulose to remove non-cellulosic and hemicellulosic components of the raw material [19–21]. Thus, the availability of sustainable cellulose resources and its easy biodegradability have taken the advantage to use VR widely as textile fiber [22]. Hence, in this study, VR textile fibers were used as supports of platinum nanoparticle (PtNP) catalysts and tried to investigate formaldehyde removal/decomposition efficiency. However, one of the limitations of VR fibers is their high moisture uptake capacity, where small organisms could choose to live in and damage the fiber material and/or produce bad odors [23]. To alleviate this problem, we also performed the separate study to investigate antibacterial effect of silver nanoparticles (AgNPs) that were attached on the fiber. In both investigations, polv(amido amine) (PAMAM) dendrimer encapsulated metallic nanoparticles were loaded on chemically modified VR cellulose fiber. Subsequently, the decomposition efficiency of formaldehyde by PtNPs-containing fibers was studied with the confirmation of binding sites for formaldehyde. Meanwhile, AgNPs-containing fibers were studied for their bioactivity against gram negative bacteria, E. coli. In brief, we reported here facile procedures to strongly immobilize PtNPs and AgNPs on the chemically modified VR fibers so that formaldehyde-degradable and self-cleaning fiber materials were prepared. In this situation, the dendrimer plays roles of sizecontroller, protector and stabilizer of small metal nanoparticles like less than 5 nm, which display highly effective catalytic activity, and acts as a reservoir of reactant, which encourages the catalytic efficiency [24,25]. In addition, the dendrimer is the mediator of chemical binding of PtNPs on VR fiber [26], since metal nanoparticles immobilized by only adsorption easy remove from fibers [27].

### 2. Experimental

#### 2.1. Materials and methods

The VR fiber was collected from Formosa Chemicals and Fiber Corp, Taiwan. Consumable chemicals of 2,2,6,6-tetramethyl-1-pip eridinyloxy radical (TEMPO), NaBH<sub>4</sub>, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), and formaldehyde solution (37 wt% in water) were from Acros Organics, USA. An aqueous sodium hypochlorite solution (NaOCl, 12 wt%) was purchased from Shimakyu Pure Chemicals, Japan, and 2,4-pentanedione. Sodium hexachloroplatinate(IV) hexahydrate (NaPtCl<sub>6</sub>·6H<sub>2</sub>O) was from Alfa Aesar, USA. A PAMAM dendrimer (ethylenediamine core, generation 4.0) solution (10 wt % in methanol) and silver nitrate (AgNO<sub>3</sub>) were products from Sigma-Aldrich, USA. Other reagents were commercial grade, and all reagents were used without any pre-treatment. Ultrapure water was used throughout the process.

Characterization was done by using an ultraviolet–visible (UV– visible, JASCO V-670, Japan) spectrophotometer, a Fourier transform infrared (FTIR, NICOLET 6700, Thermo Scientific, USA) spectrophotometer, a thermogravimetric analysis (TGA, TA Q500, USA) instrument, a transmission electron microscope (TEM, JEOL, Japan, 120 kV) and a scanning electron microscope (SEM, JEOL JSM-6390LV, Japan).

#### 2.2. TEMPO-oxidation of viscose rayon (VR) fiber

Oxidation of VR was carried out based on TEMPO-mediated oxidation method [28]. Briefly, fiber (3 g) was soaked in water (300 mL) for 2 h and then TEMPO (137 mg) and NaBr (180 mg) were added in the reaction mixture adjusted at pH 10. Subsequently, an aqueous solution of NaOCl (1:1 M ratio with fiber) was added dropwise. The pH of reaction mixture was constantly maintained at pH 10 by adding 0.5 M NaOH. The oxidized fiber was filtered, washed with water and then dispersed in water (150 mL) for reduction by NaBH<sub>4</sub> for 4 h. The final product was washed, filtered to collect TEMPO-oxidized VR (TOVR) fiber (20 wt% in H<sub>2</sub>O) and then kept in a refrigerator for next process.

## 2.3. Synthesis of nanoparticles

Dendrimer immobilized Pt nanoparticles (DenPtNPs) were synthesized by chemical reduction following a procedure of previous report [29]. Typically, for an ethanol solution (380  $\mu$ L) of PAMAM dendrimer diluted by water (19 mL) and adjusted the pH to below 4, a platinum precursor (16.5 mg) in water (1 mL) and subsequently a reducing agent (NaBH<sub>4</sub>, 1:10 M ratio with precursor) in an aqueous 0.3 M NaOH solution (1 mL) were added dropwise under stirring. Likewise, silver nanoparticles were prepared by following the previous procedure [30]. Briefly, an aqueous AgNO<sub>3</sub> solution (0.75 mM) was mixed with PAMAM dendrimer (10 wt% in methanol) at a molar ratio of 0.01:1 between silver and terminal amino group of dendrimer. NaBH<sub>4</sub> (30 mg) dissolved in a mixed solvent (4 mL, water and methanol in 2:1 vol ratio) was slowly added into the reaction mixture of silver and dendrimer to get silver nanoparticles immobilized in the dendrimer (DenAgNPs).

#### 2.4. Chemical attachment of nanoparticles on TOVR

The binding of DenPtNPs or DenAgNPs on TOVR fibers was done based on amidation reaction [26,31]. An aqueous dispersion of TOVR (1 g, 1 wt%) at pH 10 was mixed with condensation reagents, EDC and NHS (1:1:1 M ratio against carboxylic acid content of the fiber) and kept for 1 h with occasional shaking. Then the dispersion of nanoparticles at 1:1 M proportion of carboxylic acid of TOVR and amino acid of dendrimer was added to the reaction mixture. After 2 h, the suspension was filtered and the products were washed with water thoroughly and dried to obtain TOVR-DenPtNPs or TOVR-DenAgNPs. For the case of TOVR-DenPtNPs, two products containing 1 wt% and 2 wt% of PtNPs in the fiber were prepared as TOVR-DenPtNPs-1 and TOVR-DenPtNPs-2, respectively.

## 2.5. Detection of formaldehyde on TOVR-DenPtNPs

TOVR-DenPtNPs (10 mg) was hanged over an aqueous solution (15 mL) of formaldehyde (2 wt% in water) inside a sealed glass reactor. Then the solution was kept at 50 °C to generate the gas,

and the amount of adsorbed gas on TOVR-DenPtNPs in the reactor was determined by colorimetric technique [32–34]. In detail, formaldehyde adsorbed on TOVR-DenPtNPs was extracted in water (50 mL) at 40 °C for 1 h, and then TOVR-DenPtNPs was filtered out. The filtrate (5 mL) was added to the coloring agent (5 mL), which was prepared by dissolving ammonium acetate (15 g), acetic acid (300  $\mu$ L) and 2,4-pentanedione (200  $\mu$ L) in water (to be total volume of 100 mL). After heated at 40 °C for 30 min, yellowish solution was analyzed by a UV-visible absorption spectrophotometer to determine the concentration of extracted formaldehyde.

## 2.6. Antibacterial activity test on TOVR-DenAgNPs

Bacterial strains and growth conditions were based on the standard biocidal testing technique [35]. *E. coli* (gram-negative bacteria) was aerobically grown in tubes to stationary phase at 37 °C in Luria – Bertani medium. Typically, bacterial cells were diluted to  $4 \times 108$  cfu/mL (cfu: colony forming unit) in a phosphate buffered saline (PBS) solution 1X (PBS 1X) before each 50 µL of a solution was dropped onto the TOVR-DenAgNPs inside 24-well-plate. After the contact of 1 h between cells and TOVR-DenAgNPs, additional PBS (1 mL) was added to the suspension to dilute it. The diluted suspension (100 µL) was spread on the surface of a petri dish covered with Luria – Bertani agar. Then the agar plates were cultivated for 18 h at 37 °C.

## 3. Results and discussion

# 3.1. Chemical immobilization of nanoparticles on TEMPO-oxidized rayon fiber

TEMPO-mediated oxidation reaction using TEMPO/NaBr/NaOCl reagents can selectively oxidize primary alcohol (RCH<sub>2</sub>OH) groups into carboxylate [27,36]. VR is a regenerated cellulose fiber, and carboxylate groups can be introduced on it by selectively oxidizing its primary hydroxyl group at C-6 position of the backbone by using the technique as described above. Although such oxidation reaction could degrade the whole structure, depending on the amount of reagents used [37–40], in this study, the reaction was carried out following the previous report but in mild condition for keeping backbone without degradation [27].

Small sized nanoparticles were synthesized through chemical reduction process of metal ions after complex formation of metal precursor with amino-terminated PAMAM dendrimer. The role of dendrimer was as protector, stabilizer and size-controller, which help to prepare enough dispersed and nano-scaled nanoparticles without aggregation and with narrow size distribution [29,30]. Moreover, the terminal amine in dendrimer was used as a functional group to bind such particles with TOVR fiber through amidation reaction. The formation of enough dispersed PtNPs with small size distribution of around 5 nm in average size was revealed by TEM photograph and size distribution histogram (Fig. 1 (A) and (C)) [29]. Similarly, AgNPs with average size of less than 5 nm were also observed (Fig. 1(B) and (C)). A Plasmon resonance absorption band at 391 nm confirmed the formation of AgNPs [26,30], although PtNPs did not display a defined resonance band (Fig. 1(D) and (E) [41].

The covalent bond formation between amino terminal of dendrimer and carboxylate of TOVR is crucial for guaranteeing the strong immobilization of nanoparticles on cellulose fibers [26]. The procedure was implemented for the effective covalent bond formation between VR fibers and dendrimers encapsulated PtNPs or AgNPs. During the process, carboxylate was activated with condensation reagents to introduce an activated reaction sites [31]. Then dendrimer molecules were attached on the fiber by replacing



**Fig. 1.** TEM images of (A) DenPtNPs and (B) DenAgNPs, (C) a size distribution histogram (black: DenPtNPs, yellow: DenAgNPs) and UV–vis absorption spectra of (D) DenPtNPs and (E) DenAgNPs.

an activated groups on fiber by their amino terminals and forming amide bond.

Characterization of amidation step was confirmed by FTIR analysis, as seen in Fig. 2. The FTIR spectrum of pristine VR fiber showed a characteristic absorption band of OH bending vibration mode at 1643 cm<sup>-1</sup> [42–44]. When VR fiber was oxidized, the produced fiber (TOVR) showed new bands at 1608 and 1420 cm<sup>-1</sup>, which were attributed to COO<sup>-</sup> antisymmetric and symmetric stretching modes, respectively, revealing the introduction of carboxylate group on VR fiber after oxidation. After the amidation reaction with DenPtNPs or DenAgNPs, new absorption bands appeared around at 1650 and 1550 cm<sup>-1</sup> attributed to amide I and II modes of covalently bonded PAMAM dendrimer [26,43,45]. The coexistence of amide bands with carboxylate bands in the products indicates the conversion of limited numbers of carboxylates on TOVR towards covalent attachment of dendrimer on the fiber to produce TOVR-DenPtNPs or TOVR-DenAgNPs. The whole process of the preparation of TOVR-DenMetalNPs is illustrated in Scheme 1.

Fig. 3(A) shows TGA result of pristine VR fiber that showed the loss of adsorbed moisture at temperature up to 110 °C and loss of fiber from onset temperatures at 222 and 450 °C [46,47].



**Fig. 2.** FTIR spectra of (A) pristine fiber (VR), (B) oxidized fiber (TOVR), (C) and (D) amidated fibers (TOVR-DenPtNPs and TOVR-DenAgNPs, respectively).

The oxidized fiber also began the first decomposition at similar onset temperature (220 °C) that supported the loss of common fiber structure (Fig. 3(B)). However, the second decomposition temperature of this material was ended at 700 °C. This elevated decomposition temperature of the oxidized fiber was attributed to the aromatization process of cellulose associated with the creation of inter-fibril hydrogen bonds between carboxylic groups in oxidized fibers to produce well-structured ladder of graphene like aromatic compounds [48].

TOVR-DenPtNPs and TOVR-DenAgNPs (Fig. 3(C–E)) also displayed similar first and second decomposition temperatures same as oxidized fiber, but the whole decomposition of organic component was completed at temperature up to 600 °C, which was lower than that of oxidized fiber due to the partial consumption of carboxyl groups during amidation process and thus the decrease of carboxyl groups responsible for inter-fibril crosslinking *via* hydrogen bond formation.

Additional information obtained from TGA was the amounts of metal nanoparticles loaded. Here, two TOVR-DenPtNPs fibers showed residues of 1.4 wt% and 2.4 wt% even though the calculated amounts from the preparation procedure were 1 wt%



Fig. 3. TGA data of (A) pristine fiber (VR), (B) oxidized fiber (TOVR), (C) TOVR-DenPtNPs-1, (D) TOVR-DenPtNPs-2 and (E) TOVR-DenAgNPs.

and 2 wt% respectively. For AgNPs, around 0.3 wt% was remained, while the calculated Ag amount was 0.2 wt%. These agreements between measured and calculated values indicated that the particles were effectively loaded on VR fibers.

Fig. 4 presents SEM images of VR, TOVR, TOVR-DenPtNPs and TOVR-DenAgNPs. The results displayed that the oxidation process did not significantly affect the fiber morphology: Only swelling of the fiber was observed but no remarkable damage of fiber body like thinning, shortening or depolymerization of cellulose backbone. Although the fiber surface of TOVR-DenPtNPs and TOVR-DenAgNPs displayed roughness, existence of PtNPs and AgNPs was not confirmed from SEM images due to too small size of metal nanoparticles compared to the resolution of SEM and due to too small content of metal nanoparticles compared to TOVR. Alternately, EDX data confirmed the presence of Pt and Ag on the amidated fibers (Fig. 5). Additionally, observed brown color of TOVR-DenPtNPs and pale yellow color of TOVR-DenAgNPs are attributed to loaded nanoparticles on the fibers, although the color depth



Scheme 1. Schematic illustration of immobilization process of metal nanoparticles on VR fiber.



Fig. 4. SEM images of (A) pristine fiber (VR), (B) oxidized fiber (TOVR), and (C) and (D) amidated fibers (TOVR-DenPtNPs and TOVR-DenAgNPs, respectively).



Fig. 5. SEM images ((A) and (C)) and EDX results ((B) and (D)) of DenAgNPs ((A) and (B)) and DenPtNPs-2 ((C) and (D)). Insets indicate photos of fibers. EDX was measured in square region in SEM image.

depended on the loaded amount of particles, that is, the TOVR-DenPtNPs-2 was darker than TOVR-DenPtNPs-1.

The analyses of all experimental data described above confirmed that VR fiber was modified chemically and platinum and silver nanoparticles were loaded on the fiber. The attachment between cellulose fiber and capping agent was so strong that the particles can be held stably on the fiber.

## 3.2. Formaldehyde removal/decomposition effect of TOVR-DenPtNPs

Since PtNPs in TOVR-DenPtNPs have strong catalytic property, the fibers were applied to decompose formaldehyde. The main products of oxidative decomposition of formaldehyde on PtNPs catalyst are  $CO_2$  and  $H_2O$ . The catalytic efficiency of TOVR-DenPtNPs was investigated by determining the amount of remaining formaldehyde on the fiber after the formaldehydedecomposition reaction by using colorimetric technique. The amounts of extracted formaldehyde from control fibers (TOVR and amidated fiber without PtNPs (TOVR-Den)) were compared with those of TOVR-DenPtNPs. Fig. 6(A) indicated that formaldehyde was adsorbed on TOVR due to the dipole interaction between formaldehyde molecules and hydroxyl/carboxylate groups on the fiber. Moreover, voids between each fibrils allowed formaldehyde to be captured inside the fiber [49].

The higher adsorption amount on TOVR-Den can be ascribed to the high adsorption ability of dendrimer molecules immobilized on the cellulose backbone of the fiber. PAMAM dendrimer molecules have shown the effective encapsulation of small molecules into a void volume in their spherical structure [50,51] and the high gas adsorption capacity due to large number of functional groups on



**Fig. 6.** (A) Amount of remaining formaldehyde on (a) TOVR, (b) TOVR-Den, (c) TOVR-DenPtNPs-1 and (d) TOVR-DenPtNPs-2 at different time. (B) Decomposition efficiency of (e) TOVR-DenPtNPs-1 and (f) TOVR-DenPtNPs-2.

their periphery of their spherical structure [52]. Thus, formaldehyde adsorption of almost double amount on TOVR-Den indicates the condensed adsorption of formaldehyde gas on dendrimer moiety of only 1 wt%, namely, the 84 times higher adsorption capacity of dendrimer site than the capacity of TOVR site.

However, in the case of TOVR-DenPtNPs-1 and TOVR-DenPtNPs-2, the detected remaining amount of formaldehyde was decreased compared to that of TOVR-Den due to the existence of PtNPs catalysts that decompose adsorbed formaldehyde molecules [11,29,53,54]. The results also showed that the amount of formaldehyde was lower for TOVR-DenPtNPs-2 than for TOVR-DenPtNPs-1 i.e. the higher Pt content facilitated the more gas decomposition. Since formaldehyde molecules adsorbed on catalyst-encapsulated dendrimer can be decomposed, decomposition efficiency by PtNPs was calculated as formaldehyde amounts decomposed by PtNPs against formaldehyde amounts adsorbed on dendrimer i.e.  $(C_b-C_c \text{ or } C_d)/(C_b-C_a)$ , where  $C_i$  (i = a, b, c, d) is the adsorbed formaldehyde amount plotted in Fig. 6(A). As seen in Fig. 6(B), around 45 and 65% of adsorbed formaldehyde gas on dendrimer site were decomposed on TOVR-DenPtNPs-1 and TOVR-DenPtNPs-2 catalyst systems, respectively, at 120 min reaction. These numerical percentages indicate rather high formaldehyde decomposition efficiency of PtNPs embedded in TOVR and the higher amount of decomposition on high amount PtNPsloaded TOVR-Den. The adsorption and decomposition processes based on these analyses were illustrated in Scheme 2.

#### 3.3. Antibacterial effect of TOVR-DenAgNPs

Antibacterial potency of AgNPs-loaded VR fibers was examined for E. coli and compared to control. While the grown E. coli colonies were clearly visible for the control, the fiber suspension showed the significant antibacterial activity towards E. coli (Fig. 7). AgNPs were expected to diffuse into the saline solution and make a contact with cells. Some studies have reported the effect of AgNPs on cell membrane [55,56]. In all cases the contact between the bacteria cells and antibacterial agents is very important. The significant biocidal result obtained showed that all colonies of E. coli were killed and it was attributed to the effective interaction between AgNPs and surface of bacterial membrane. Thus, structural change, degradation and eventually sterilization of bacteria were resulted in [57]. The possible mechanism of such effect would be due to silver ion (Ag<sup>+</sup>) formed after oxidative dissolution of AgNPs in the presence of oxygen, and subsequently the ion will be attached to cell membrane to cause morphological change. Moreover, the intracellular generation of reactive oxygen species, which was induced by silver nanoparticles, causes the generation of free radicals and then the toxicity to the cell [57].



Scheme 2. Schematic illustration of adsorption/decomposition processes on TOVR-DenPtNPs.



Fig. 7. Images after antibacterial test of control (pristine fiber, VR) and amidated fiber (TOVR-DenAgNPs).

## 4. Conclusions

While some publications were recently used much simple technique [27], we have synthesized PtNPs-loaded VR fibers as flexible catalyst sheet for the removal/decomposition of formaldehyde and similarly AgNPs was also loaded to prepare antimicrobial rayon fibers. The covalent bond formation between metal nanoparticles and VR fibers was crucial to connect particles strongly on the fiber substrate. For this connection, PAMAM dendrimer played a role as an intermediator between metal nanoparticles and VR fibers besides protector (stabilizer) of metal nanoparticles. Another important role of dendrimer was the adsorbent of formaldehyde: The capacity of dendrimer on adsorbent of formaldehyde was 84 times higher than of VR fiber, indicating the selective adsorption of formaldehyde on dendrimer moiety. Similar selective gas capture ability has been reported for CO<sub>2</sub> and NH<sub>3</sub> gas adsorption on PAMAM dendrimer-containing organoclays embedded in cellulose nanofiber films [52]. Gas condensation in PtNPs-loaded dendrimer moiety of VR fibers is advantageous for gas decomposition, since the catalytic reaction occurs at vicinity of the catalyst. In fact, study by using the prepared catalytic composites revealed the decomposition of about 65% of formaldehyde molecules adsorbed in dendrimer moiety in a presence of 2 wt% PtNPs (5 nm size). Additionally, the fiber containing AgNPs (0.2 wt%) with a size of 5 nm showed an excellent biocidal effect against E. coli. In summary, the results of the researches indicate that the present synthesis procedure is applicable to prepare cellulose-based materials with sustainable functionalities such as gas-removal/ decomposition devices, antimicrobial medical equipment and other self-cleaning textiles. The present fiber-based catalytic systems are helpful to prepare household devices/equipment for problem-solving of causative agents for sick building syndromes.

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