

Fabrication of Air Filter Using Nanoparticle/polyelectrolyte Layer-by-Layer Sequentially Adsorbed Thin Films

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Abstract: In recent years many air cleaners are developed by the improvement of the air tightness around life spaces and by the needs for comfortable space free from toxic gas. We developed an extremely high performance air filter for trimethylamine and acetic acid gas by forming metal-oxide nanoparticle/polyelectrolyte hybrid thin film by layer-by-layer self-assembled technique on porous alumina substrate. Titanium dioxide and magnesium oxide were used for metal-oxide nanoparticle and poly phosphoric acid was used as polyelectrolyte. Since electronegativity of titanium dioxide is large and that of magnesium oxide is small, titanium dioxide work as acid and magnesium oxide work as base. We found that there is a saturation point in the relationship between filter efficiency and number of bilayers. A remarkable high performance filter for removing trimethylamine and acetic acid gas was developed by forming organic polyelectrolyte/inorganic metal-oxide nanoparticle layer-by-layer sequentially adsorbed thin films

Key words: Filter, Honeycomb alumina plate, Layer-by-layer self-assembled film, Trimethylamine and Acetic acid

1. INTRODUCTION

In recent years many air cleaners are developed by the improvement of the air tightness around life spaces and by the needs for comfortable space free from bad gas. There are two types in air cleaner. One is to adsorb gas molecules and the other is to decompose gas molecules. One of the representatives of the former is activated carbon; main adsorption mechanism of this is physisorption to the pore of the substrate [1][2][3][4]. It is low-cost but there is problem in adsorption efficiency and permanence. One of the representatives of the latter are plasma discharging method and photo-catalysis; main adsorption mechanism of them is free radical that have very high oxidation power, and the free radical decompose gas molecules. In this case, there is no problem in permanence, but there is a problem that the equipment becomes big size and requires high voltage [5].

In this study we made air filter for trimethylamine and acetic acid gas fabricated metal-oxide nanoparticle/polyelectrolyte thin films by layer-by-layer self-assembled technique [6][7] on honeycomb alumina plate. Gas molecules physically and chemically adsorbed to the filter to the pore of

substrate and the thin films.

2. EXPERIMENTAL SECTION

2-1 Materials

Metal oxides are classified as acidic, amphoteric or basic [8][9]. Experimentally, this classification corresponds to the adsorption of probe molecules. Amine groups are base probe molecules that react with the electron deficient metal atoms (Lewis acid) or the protons adsorbed on the hydrated surface. According to this classification, TiO_2 belongs to the amphoteric species and MgO to the base species. Magnesium is more electropositive than titanium (1.23 vs. 1.32 according to Allred [10][11]); it followed that Mg cations are less acidic than Ti cations; the LUMO of Ti^{4+} is lower than that of Mg^{2+} and the electron affinity of the ions are 4.32 and 15.0 eV, respectively. It also follows that MgO is more ionic than TiO_2 , increasing the basicity of the surface oxygen atoms [8].

TiO_2 was obtained from Ishihara Sangyo Kaisha, Ltd (7nm diameter), MgO was obtained from Wako (10nm diameter) and poly phosphoric acid (PPA) was obtained from Aldrich. TiO_2 and MgO of 1wt. % and PPA solution of 0.01M (based

on the repeat unit molecular unit) were made from 18M Ω Millipore water. When fabricate TiO₂/PPA multilayer film, the pH of TiO₂ dispersion and PPA solution were 2.3 or 1.5 adjusted with HCl. And when fabricate MgO/PPA multilayer film, the pH of MgO dispersion and PPA solution were 11.4 by using NaOH. The pH of rinse bathes was same of adsorption solutions. Honeycomb alumina plate was used as substrate.

2-2 Film fabrications

The layer-by-layer self-assembled technique involves the repeated sequential dipping of a substrate into metal oxide nanoparticle dispersion and polycation solution with rinsing between each deposition step. Because the process only involves adsorption from solution, there are in principle no restrictions with respect to substrate size and topology [12]. In this study, the layer-by-layer deposition process was carried out via the use of an automatic dipping machine in the form of a programmable slide stainer (HMS programmable slide stainer from Zeiss Inc.). Dipping time in the metal-oxide nanoparticle dispersion, polyanion solution and rinse solution was 300, 300 and 60 sec.

2-3 Evaluation in closed system

A closed system (325 \times 550 \times 315mm, made from acrylic resin) which has a fan with filter for air cleaning and a fan for diffusion. Soon after gas was introduced in the system, two fans were started to work. Then the gas concentration was measured by gas detector tube every 15 minutes. This method was repeated until filter was broken through. Schematic Fig of the experimental system is shown in Fig. 1.

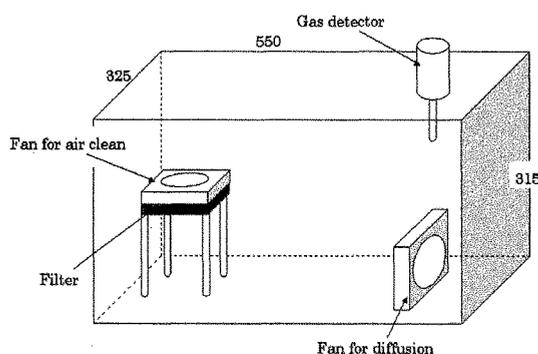


Fig.1 Experimental setup for the evaluation of the gas adsorption into the fabricated filter

3. RESULTS AND DISCUSSIONS

3-1 Film fabrication

FE-SEM images of (TiO₂/PPA)₃₀ deposited on Si wafer were shown in Fig.2. This figure 2 clearly shows that TiO₂/PPA self-assembled film was very uniform and dense.

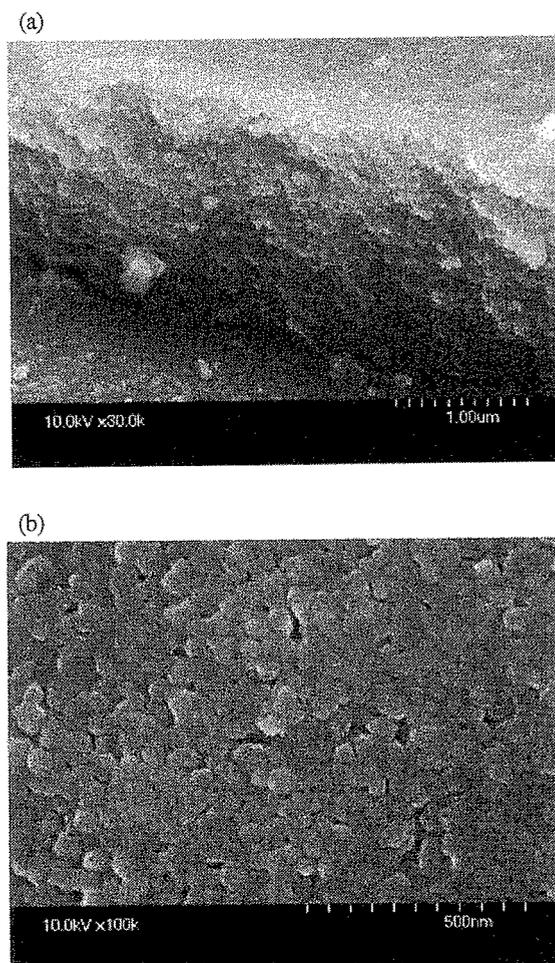


Fig.2 FE-SEM images of (TiO₂/PPA)₃₀ deposited on Si substrate.

(a) cross-sectional view , (b) surface view

3-2 Change of filter efficiency by deposited bilayers

The gas weight adsorbed to filter until filter was broken through was shown in Figs.3 and 4. Figures 3 and 4 show filter efficiency for trimethylamine (TMA) gas by (TiO₂/PPA)_n and for acetic acid (AA) gas by (MgO/PPA)_n, respectively.

Although the trimethylamine gas weight adsorbed to filter until filter was broken through was increasing as increase of the number of deposited bilayers until 50 bilayers, it was saturated when 100 bilayers are deposited. To search the reason of the saturation of filter efficiency bound of 50 bilayers, we examined the specific surface area of honeycomb alumina plate with (TiO₂/PPA)_n (n=0,10,30,50,100) by adsorption of

nitrogen gas.

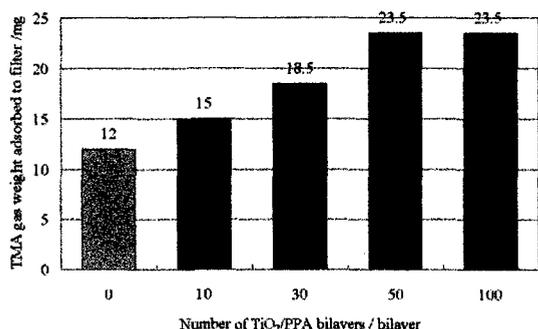


Fig.3 Change of trimethylamine gas weight adsorbed to filter until filter was broken through as the increase of number of TiO₂/PPA bilayers

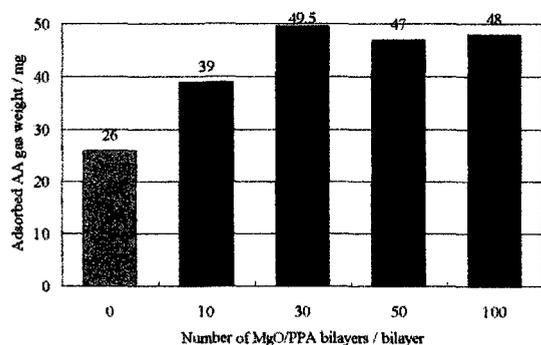


Fig.4 Change of acetic acid gas weight adsorbed to filter until filter was broken through as the increase of number of MgO/PPA bilayers

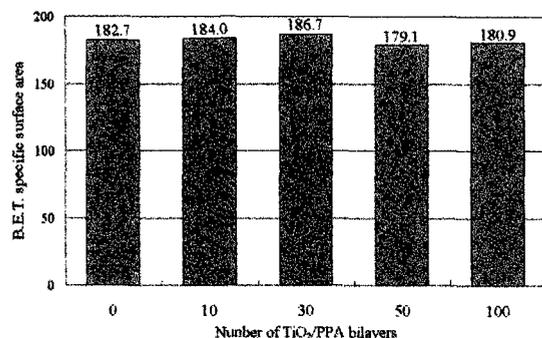


Fig.5 Change of B.E.T. specific surface area as the increase of number of TiO₂/PPA bilayers

Since any drastic change was not observed in B.E.T. specific surface area and pore radius distribution by deposition of TiO₂/PPA multiplayer on honeycomb alumina plate, we

conclude that the change of filter efficiency originates from the film thickness. Gas cannot penetrate over the certain TiO₂/PPA multilayer film thickness. The change of filter efficiency for acetic acid gas by deposited MgO/PPA bilayers is the same reason.

3-3 Change of filter efficiency by pH of deposited solution

The change of filter efficiency for trimethylamine gas by the pH of dipping solution at the fabrication of TiO₂/PPA multilayer film was shown in Fig.6.

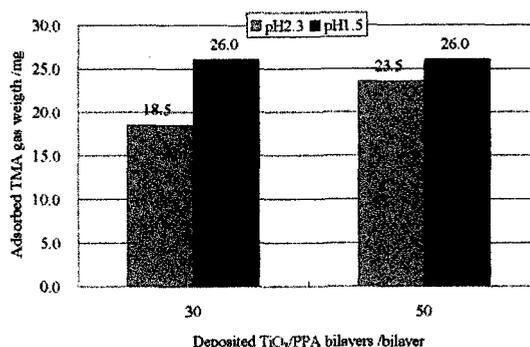


Fig.6 Change of filter efficiency for trimethylamine gas by pH of dipping solution

Being an oxide, TiO₂ has H⁺ and OH⁻ ions as its potential determining ions, and hence the pH of aqueous medium has a substantial effect on the absolute surface potential (ζ potential) of TiO₂ nanoparticle. Since the ζ potential of TiO₂ nanoparticle at pH1.5 is higher than at pH2.3, more TiO₂ nanoparticle was taken into TiO₂/PPA multilayer film. So, the filter fabricated at pH1.5 solutions showed higher performance than the filter fabricated at pH2.3 solutions.

3-4 Filter efficiency of (TiO₂/PPA)₂₀/(MgO/PPA)₂₀

The adsorbed gas weight until the filter was broken through was shown in Tables I and II for several types of filters.

(Table I: for trimethylamine gas, Table II: for acetic acid gas) From Tables I and II, the (TiO₂/PPA)₂₀/(MgO/PPA)₂₀ deposited filter showed high performance for both trimethylamine and acetic acid gas. For trimethylamine gas, the (TiO₂/PPA)₂₀/(MgO/PPA)₂₀ deposited filter showed the same removal effect of the (TiO₂/PPA)₃₀ deposited filter. Trimethylamine gas is adsorbed to both TiO₂ and PPA. Though the amount of TiO₂ in the latter film was larger than in the former film, the amount of PPA in the former film was larger than the latter film. So the two filters showed the same filter efficiency for trimethylamine

gas.

Table I Adsorbed trimethylamine gas weight until the filter was broken through

Type of filter	Adsorbed trimethylamine gas weight /mg
Bare honeycomb alumina plate	12.0
(TiO ₂ /PPA) ₁₀ deposited	15.0
(TiO ₂ /PPA) ₃₀ deposited	18.5
(TiO ₂ /PPA) ₅₀ deposited	23.0
(TiO ₂ /PPA) ₂₀ /(MgO/PPA) ₂₀ deposited	18.5

Table II Adsorbed acetic acid gas weight until the filter was broken through

Type of filter	Adsorbed trimethylamine gas weight /mg
Bare honeycomb alumina plate	26.0
(MgO/PPA) ₁₀ deposited	39.0
(MgO/PPA) ₃₀ deposited	49.5
(TiO ₂ /PPA) ₂₀ /(MgO/PPA) ₂₀ deposited	48.5

4. CONCLUSION

An extremely high performance air filter for trimethylamine and acetic acid gas was fabricated by forming TiO₂/PPA (for trimethylamine gas) and MgO/PPA (for acetic acid gas) layer-by-layer self-assembled film on porous honeycomb alumina plate. For each gas, optimal number of deposited bilayers was existed. This change of filter efficiency by the number of deposited bilayers is related strongly with the film thickness. By forming (TiO₂/PPA)₂₀/(MgO/PPA)₂₀ multilayer film, this filter remove both trimethylamine gas and acetic acid gas efficiently.

By taking more materials which have high activities to toxic gas into layer-by-layer self-assembled filter, higher performance filter which simultaneously adsorb various toxic gases can be developed.

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