Multilayerization of Organophotocatalyst Films that Efficiently Utilize Natural Sunlight in a One-Pass-Flow Water Purification System

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S *Supporting Information*

ABSTRACT: A full-spectrum visible-light-responsive organo-photocatalyst membrane array is designed and employed for a one-pass-flow water purification system. Whereas previous photocatalyst systems required strong light source, the present design manages with natural sunlight intensity, owing to multilayerization of a newly optimized low-absorbance organophotocatalyst. The design of the system is to utilize natural-sunlight-equivalent visible light with 1 m^2 of irradiation area to process 1 ton/day of water. A 1/3300 scale module of the system was constructed and experimentally demonstrated its viability. The reactor part of the flow system contains 24 stacked layers of organic-semiconductor-laminated Nafion film. The organic semiconductor is a bilayer of metal-free phthalocyanine (H_2Pc, p-type semiconductor) and 3,4,9,10-perylenetertacarboxylic-bisbenzimidazole (PTCBI, n-type semiconductor). Transparent Nafion functions as mechanical support and absorbent of trimethylamine, which was chosen as a typical contaminant of underground water in coastal areas. The reactor was irradiated for only 1 h/day by visible light (10 mW/cm^2). The light intensity at the bottom layer was estimated to be 0.1 mW/cm^2, which was sufficient intensity (internal quantum efficiency was 0.15.) for the photocatalytic reaction, due to the optimized absorbance and photocatalytic quantum efficiency of each layer. The inlet TMA concentration was 3 ppm, while that of the outlet was less than 0.03 ppm for the first day of the operation of the system with and without the bilayer. Without the bilayer, the TMA concentration of the outlet flow increased after 20 days. With the bilayer, the TMA concentration of the outlet flow remained at less than 0.03 ppm for the 40-day experimental period due to its photocatalysis. The turnover number of photocatalytic reaction was calculated to be 1.8×10^4.

KEYWORDS: *Visible light photocatalyst, p/n junction, Phthalocyanine, Perylene, Water purification, Trimethylamine, Solar cell*
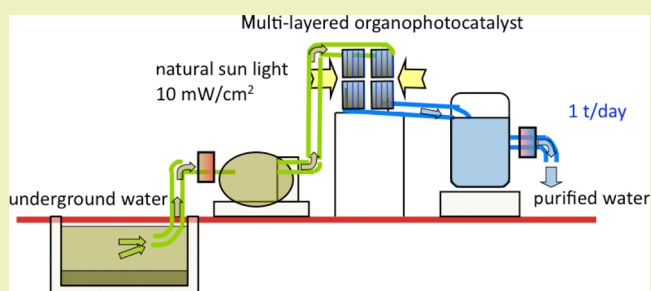
INTRODUCTION

Water consumption for human activities is increasing in both developing and industrialized countries. High throughput, low-cost, and robust methods to disinfect and decontaminate waters are needed from source to point-of-use, without further stressing the environment or endangering human health by the treatment method itself.[1,2]

In order to remove impurities, water purification processes generally involve large inputs of chemicals, sand filter, adsorbent area, and volume, etc., which correspond to energetic and economic input.[3] Photocatalytic water purification has been investigated as a means to address those problems, but practical TiO_2 photocatalyst is activated only by UV light.[4−12] The following problems have been pointed out: (1) The use of sunlight is low efficiency because visible light was not utilized. (2) The reaction rate on a photocatalyst surface in water phase is limited by the diffusion rate of the pollutant, which is much lower than that in gas phase. Furthermore large-scale photocatalytic degradation of pollutants requires correspondingly large photocatalyst quantity and its reactor size. Here, we introduce a compact system design for the practical use of sunlight in order to overcome these difficulties. The design utilizes natural sunlight, minimizes the irradiation area and system volume, and utilizes a recently identified organo-photocatalyst film.[13]

Organic semiconductor p/n junction has the potential to expand the active spectrum of photoenergy conversion and has provided photovoltaic cells such as 3,4,9,10-perylenetertacar-boxylic-bisbenzimidazole (Figure 1c, PTCBI) of n-type semiconductor and phthalocyanine (Figure 1b, H_2Pc) of p-type semiconductor.[14−18] Though the use of the p/n bilayer, a photoinduced reflectance device was fabricated through

(a)

-(CF_2-CF)_m-(CF_2-CF_2)_n-

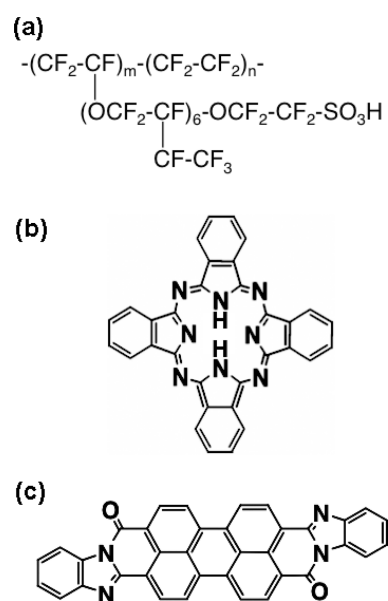(OCF_2-CF)_6-OCF_2-CF_2-SO_3H

CF-CF_3

(b)

(c)

Figure 1. Chemical structures of (a) Nafion (absorbent), (b) phthalocyanine (H_2Pc) (p-type semiconductor), (c) 3,4,9,10-perylenetetracarboxylic-bisbenzimidazole (PTCBI) (n-type semiconductor).

photoinduced charge separation and free electron accumulation in the n-type semiconductor.[19−21] Furthermore, the p/n bilayer exhibited photooxidation and photoreduction on the p- and n-type semiconductor surfaces, respectively.[22−32] On the basis of these results, we developed a full-spectrum visible light (<780 nm) responsive photocatalyst composed of the organic p/n bilayers with Nafion, which showed photocatalytic activity to decompose trimethylamine (TMA) almost completely into CO_2 for gas and water phases.[33,34] The mechanism of the photocatalytic cycle is similar to that of the photovoltaic devices; i.e., successive processes of light absorption, exciton diffusion, charge separation at p/n junction, carrier conduction, and carrier collection. The different part is that the final carrier collection is the redox in the photocatalyst. Nafion film functions as a mechanical support and absorbent of TMA. The

Nafion/H_2Pc/PTCBI trilayer film offers another benefit of being metal-free, whereas many visible-light responsive photocatalysts contain heavy metals[35−41] that must be avoided for the purpose of providing potable water.

For the second problem (the limited photocatalysis rate due to the slow diffusion in water and consequent large photocatalyst area), the layered photocatalyst design provides a large reaction surface area relative to the system footprint, however, light attenuation is increased at the bottom layers. The transparency of Nafion and low absorbances of H_2Pc/PTCBI are attractive in overcoming the dilemma of retaining the layered structure while achieving sufficient light intensity for the bottom layer. Furthermore, a one-path flow system is preferable to minimize the time and space required to purify the water.

We chose organic amine as a typical water pollutant contaminant, which is sometimes found in anaerobic groundwaters in the coastal regions, agriculturally polluted water, etc. One of the leading methods of removing organic amine is the use of chlorine as an oxidizing agent; however, the use of chlorine is regulated because the products contain aldehyde, monochloramine, etc.[42,43] Photocatalytic removal can provide an alternative means of removing amine. The TMA was decomposed quantitatively to CO_2 for the vapor phase and aqueous phase without the use of chlorine. On the basis of these merits, we design a one-pass flow system with the layered photocatalyst reactor to remove an organic amine in water with compactness, −1 m² area for 1 t/day, which is as three times as the daily life water per a person in Japan (305 L/day).[44] A 1/3300 module of the design was constructed and experimentally demonstrated for more than 40-days use.

■ EXPERIMENTAL SECTION

Materials. PTCBI was synthesized[45] and purified[46] according to the previously described procedure. Commercially available H_2Pc (Tokyo Kasei Co., Ltd.) was purified by sublimation prior to use (cf., thermal control was conducted for the exterior of the vessel at 510 °C). Nafion 112 membrane (Figure 1a) was purchased from SIGMA-Aldrich Corp. The Nafion/H_2Pc/PTCBI trilayer film used as a photocatalyst was prepared by vapor deposition at 5×10^{-4} Pa, with a deposition rate of 0.03 nm s^{-1} (H_2Pc and PTCBI were coated as the
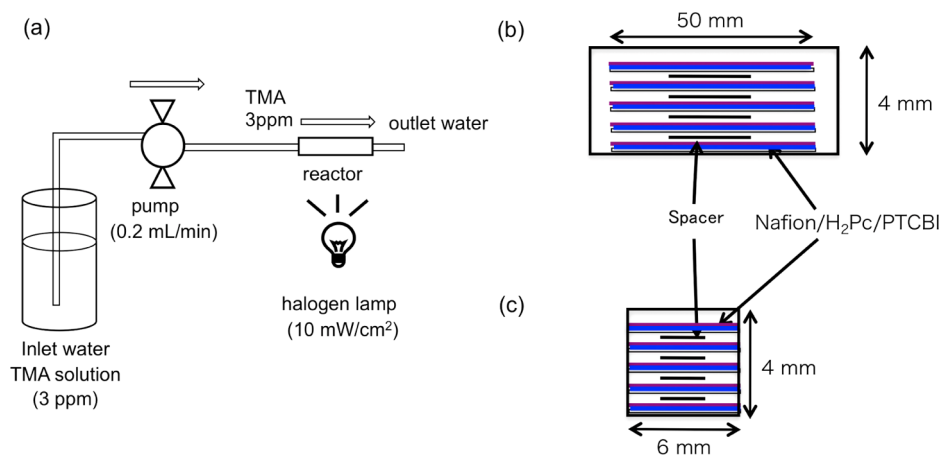
Figure 2. (a) Schematic view of the present one-pass flow system. The Tigon tube was used for liquid transfer. TMA was supplied from a closed container and the flow rate was controlled by a pump. The source of white light was a halogen lamp (10 mW/cm², spectrum shown in Figure 3). The TMA concentration of the outlet solution from the reactor was measured by GC. Schematic cross-sectional view of the reactor from (b) side view of flow and (c) cross-section view from the upper stream. The reactor contains 24 layers of Nafion/H_2Pc/PTCBI film with 0.11-mm-thick plastic spacers of 2 mm × 20 mm between each film. H_2Pc and PTCBI were deposited with a 10 nm thickness each on 6 mm × 50 mm of Nafion film (50 μm).

first and the second layer, respectively.). The deposited thin H_2Pc/PTCBI layer showed an imperfect layer structure, as seen in the SEM image (Hitachi SU8020, 0.5 kV) of the surface of Nafion/H_2Pc/PTCBI is shown in Figure S1. Since the additivity of the absorption coefficients is considered to hold on the visible absorption spectrum of the trilayer films, the average thickness of each layer was estimated by solving simultaneous equations for the absorbance at two distinct wavelengths. The absorption spectrum was measured with a Hitachi U-2010 spectrophotometer. TMA, the reactive substrate here, was purchased from Tokyo Kasei Kogyo Co., Ltd. and was diluted to 3 ppm using Millipore water.

Photocatalysis Activity Test. The p/n bliayer-coated Nafion was kept at the bottom of the closed container and light was irradiated from the bottom. The film size, container volume, and water volume were 5×5 mm^2, 3 mL, and 2 mL, respectively. The light illumination was started after 7.2×10^3 s after the injection of TMA (1.5×10^{-7} mol). Amounts of photocatalytically generated CO_2 were estimated using a gas chromatograph.[33]

Setup for the Water Purification Reaction and Monitoring of the Photocatalytic Activity. Figure 2 shows a schematic view of the one-path water flow system. The Nafion/H_2Pc/PTCBI parallel-multilayered reactor has a stacked structure of 24 layers of organophotocatalyst film, Nafion(50 μm)/H_2Pc(10 nm)/PTCBI(10 nm), with 24 spacers (thickness 0.11 mm). The size of each organophotocatalyst films was 6 mm $\times$ 50 mm. The parallel-multilayered reactor was connected to the TMA solution by a plastic tube (Hishi tube UGEB3050, Mitsubishi Plastics Industries Ltd.) with transmittance of 90% at 580 nm.

The TMA solution (3 ppm) was supplied to the reactor at a continuous flow rate of 0.2 mL/min (24 h/day). Visible light from a filtered halogen lamp (400−750 nm) was used to irradiate to the reactor and was aligned normally to the organophotocatalyst films. The spectrum of the irradiation light agrees well with the action spectrum for the photocatalysis in the visible region as shown in Figure 3. The light intensity was 10 mW/cm^2. The concentration of TMA
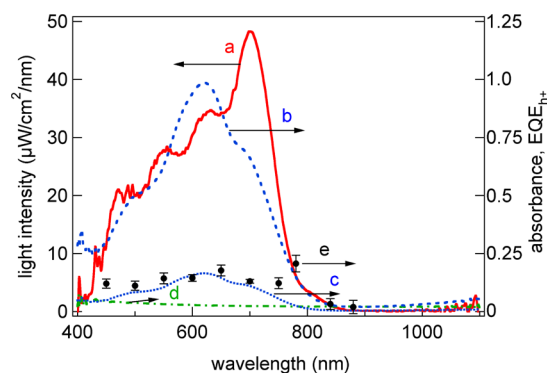

Figure 3. (a) Luminescence spectrum of the present light source, which is an 800-nm filtered halogen lamp light, and absorption spectrum of Nafion/H_2Pc/PTCBI (b: 50 μm/50 nm/200 nm, c: 50 μm/10 nm/10 nm) and 50 μm Nafion (d). For the Nafion/H_2Pc/PTCBI (50 μm/50 nm/200 nm), action spectrum of external quantum efficiency of the photocatalysis is shown as plots (e) estimated from eq (2) (EQE_{h+}) based on the data in ref 33.

was monitored at a distance of 1 cm from the end of the reactor using a gas chromatograph (GC) (GC-2014, Shimadzu), equipped with a Thermon 3000+KOH 5 + 1% Sumpak-A column (Shinwa Chemical Industries Ltd.) at 140 °C and a flame ionization detector (FID), where the retention time of TMA was 3.0 min.

■ RESULTS AND DISUCSSION

Design of Multilayered Organophotocatalyst. *Optimization of Reactor Flow Length, Area, and Layer Number to Remove TMA.* In order to satisfy quick removal of TMA

during the flow path of water, the reactor scale is optimized here. The first parameter is absorbent area which must provide sufficient contact to absorb TMA in the flow solution. A monolayered Nafion film of 33×60 mm^2 in a cylinder path, (ϕ 20 mm) absorbed only 11% of 3 ppm TMA at a flow rate of 20 mL/min, which was less than that of multilayered Nafion films. As shown in the Table 1, TMA absorption increased with additional film layers to 38% when using 24 layers of 6×10 mm^2 with 0.11 mm spacers in which the sectional area of the flow was 42 mm^2.

Table 1. Removal Ratio of TMA for its 3 ppm Solution According to Number of Nafion Layers Using the Flow System Shown in Figure 2 except the Absorber Structure[a]

| gap between Nafion films (mm)	number of layers	nafion area (mm^2)	cross sectional area of flow (mm^2)	removal of TMA for its 3 ppm (%)
	1	33×60	314	11
1	8	6×10	46.5	18
0.11	24	6×10	42	38

[a]The results indicate that removal ratio increases with more layers.

The second parameter is the flow rate, which was measured for 24-layered absorber films. Only 41% of 3-ppm TMA was absorbed at flow rate of 20 mL/min. As shown in Supporting Information Figure S2, TMA absorption increased with slower flow rate, reaching 75% at 0.2 mL/min flow rate.

Third, the absorber length along the flow path was optimized. The cross-section of the flow was fixed to be 6 mm $\times$ 6 mm. When the absorber length was 10 mm, absorption was 72% for 3 ppm TMA. For absorber lengths of 20 and 50 mm, TMA absorption increased to 77% and 99%, respectively, as shown in Supporting Information Figure S3. The absorber length was chosen to be 50 mm in this study.

Estimation of Organic Semiconductor Thickness. In the one-path flow system described above, we optimized the number of Nafion layers to be 24. When the photocatalyst layers were coated on Nafion, light intensity at the bottom layer decreased with the addition of more layers. In layered structures with flow paths, it is necessary to achieve a low proportion of light absorbance at each layer in order to ensure sufficient light intensity is supplied to the bottom photocatalytic membrane.

The photocatalytic activity for the TMA oxidation as in eq 1 was quantitatively confirmed about carbon product (CO_2) in the aerobic condition.[33] As a nitrogen product, N_2 was significantly observed (data is not shown).

$$(CH_3)_3N \xrightarrow{h\nu} 3CO_2 + 1/2N_2, \tag{1}$$
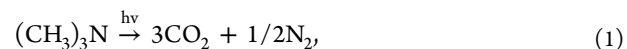
On the basis of the amount of the product, CO_2, external quantum efficiency (EQE_{h+})[33] was appropriately evaluated in eq 2,

$$EQE_{h+} = nM_{CO2}N_A/(3IS\tau/E_{h\nu}) \tag{2}$$

where M_{CO2}, N_A, n, I, S, τ, and $E_{h\nu}$ represent the molar number of generated CO_2 (mol), Avogadro's number, number of consumed holes for TMA oxidation ($n = 1$ in the present case), incident light intensity (W/cm^2), irradiation area (cm^2), irradiation time, and photon energy (J), respectively. The number 3 corresponds to the number of CO_2 molecules generated from one molecule of TMA as shown in eq 1. Examples showed linear relationships between τ and M as seen

in examples as shown in Supporting Information Figure S5. Equation 2 is based on the assumption that only one hole is consumed for TMA oxidation to TMA$^+$ (eq 3).

$$(CH_3)_3N \xrightarrow{h\nu} (CH_3)_3N^+ \qquad (3)$$

The three CO_2 molecules are evolved due to autoxidation following one-electron oxidation:

$$(CH_3)_3N^+ \xrightarrow{O_2} 3CO_2 \qquad (4)$$

For the light intensity of 360 $\mu W/cm^2$, the EQE$_{h+}$ was estimated to be 0.14,[33] which is similar to the IPCE values for the photoelectrochemical oxidation (0.10 at 600 nm) and EQE for a photovoltaic cell (0.14).[18] In comparison with other electron number (n) oxidation, for example 21-hole oxidation shown in eq 5, the present estimation is reasonable, because the calculations gave n-times EQE as the present EQE$_{h+}$ value. [31]

$$(CH_3)_3N + 6H_2O + 21h^+ \xrightarrow{h\nu} 3CO_2 + 1/2N_2 + 21H^+ \qquad (5)$$
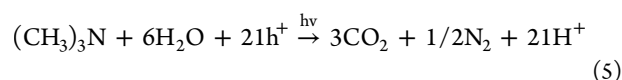
For the present design, EQE$_{h+}$ values are required to be evaluated for the thin p/n bilayer and for light intensities less than that of solar light. The evaluation is shown in Table 2. In

Table 2. External and Internal Quantum Efficiency (EQE and IQE) for the Decomposition of TMA to CO_2 in the Closed Container Using Nafion/H$_2$Pc/PTCBI, Depending on the Bilayer Thickness and Light Intensity^a

photocatalyst structure	EQE$_{h+}$	IQE$_{h+}$	light intensity	light wavelength
Nafion/H$_2$Pc (50 nm)/PTCBI (200 nm)^b	0.12	0.14	360 $\mu W/cm^2$	600 nm
Nafion/H$_2$Pc (50 nm)/PTCBI (200 nm)^b	0.16	0.25	300 $\mu W/cm^2$	740 nm
Nafion/H$_2$Pc (50 nm)/PTCBI (200 nm)	0.05	0.06	3.5 mW/cm^2	600 nm
Nafion/H$_2$Pc (10 nm)/PTCBI (10 nm)	0.05	0.15	150 $\mu W/cm^2$	600 nm
Nafion/H$_2$Pc (10 nm)/PTCBI (10 nm)	0.024	0.07	350 $\mu W/cm^2$	600 nm
Nafion/H$_2$Pc (10 nm)/PTCBI (10 nm)	0.012	0.04	3.5 mW/cm^2	600 nm

^{a}On the basis of eq 3, one-electron oxidation and the following autoxidation process are assumed for the calculation: $(CH_3)_3N \xrightarrow{h\nu} (CH_3)_3N^+ \xrightarrow{O_2} 3CO_2$ (3) and (4). ^{b}Previously reported.[33]

both the (H$_2$Pc (50 nm)/PTCBI (200 nm)) cases and cases of thin (H$_2$Pc (10 nm)/PTCBI (10 nm)) p/n bilayer, the low intensity gave higher EQE$_{h+}$ than high intensity did. This phenomenon is similar to that reported for organic thin solar cells,[15,18] dye-sensitized solar cells,[47] and TiO$_2$ photocatalyst.[48] The mechanism to explain the phenomenon is widely received as the charge recombination path which increases with more carriers not to be consumed by the carrier collection process. The thick layer gave larger EQE than the thin ones did. Interestingly, internal quantum efficiency (IQE), in which EQE is devided by the absorbed photon number, is of the same order (50−66%) for the thin pn bilayer as the thick one.

$$IQE_{h+} = EQE_{h+}/(1 - 10^{-abs}) \qquad (6)$$

where IQE$_{h+}$ and abs are IQE for one-electron oxidation, as in eq 3, and absorbance, respectively. The same order IQE$_{h+}$ means the charge separation and redox efficiency is not strongly

dependent on thickness and the thickness is not essential for the processes after light absorption. The lower IQE$_{h+}$ for the thin p/n bilayer would be due to the imperfect p/n junction layer formation due to the comparable crystal size of the H$_2$Pc and PTCBI to the average thickness (Supporting Information Figure S1).

The IQE$_{h+}$ values were 0.04−0.15 at 3.5−150 $\mu W/cm^2$, respectively; therefore, the allowable thickness of 10 nm/10 nm (= H$_2$Pc/PTCBI), with corresponding maximun absorbance is 0.18 at 630 nm. When external light intensity is 10 mW/cm^2, which is typical of a cloudy day, the 24 layers give the darkest condition with 11 upper layers for incident light from both sides of the reactor. The sum of the absorbance of 11 layers is 2.0 (= 0.18 × 11), and the darkest intensity is 0.1 mW/cm^2 (= 10 mW/cm^2 × 10^{-2}).

To summarize, the present organophotocatalyst is active at low light intensity, for example, EQE$_{h+}$ = 0.05, IQE$_{h+}$ = 0.15 at 150 $\mu W/cm^2$ of 600-nm light. Therefore, sufficient light intensity can be supplied throughout the layered photocatalyst structure. The optimized organophotocatalyst structure to remove TMA solution (3 ppm) is 24 layers of Nafion/H$_2$Pc (10 nm)/PTCBI (10 nm) of 6 mm (width) × 50 mm (length) area with spacer thickness of 0.11 mm. At a solution flow rate of 0.2 mL/min, the system can remove 99% of TMA at 3 ppm and more than 90% at 100 ppm, as shown in Supporting Information Figure S4. The required intensity is 10 mW/cm^2 for irradiation at both sides.

Removal of TMA Using One-Pass Flow Organophotocatalyst Reactor. Figure 4 shows the concentration
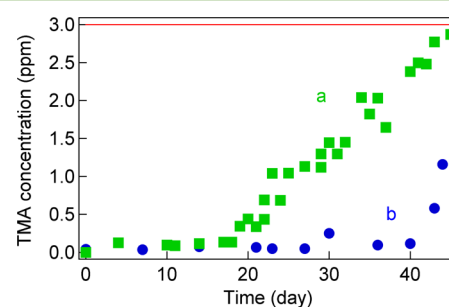

Figure 4. TMA concentrations estimated using GC after passing through the one-pass-flow water purification system with Nafion/H$_2$Pc/PTCBI (●) and Nafion (■), as shown in Figure 2. Initial TMA concentration was 3 ppm. The photocatalyst was irradiated by visible light (10 mW/cm^2), only 1 h/day. The absorbability of Nafion for TMA decreased after the 20 day, while that with H$_2$Pc/PTCBI maintained absorption for 40 days.

of TMA after passing of 3-ppm TMA solution through the present one-pass flow system each day. The reactor was irradiated with visible light (10 mW/cm^2) for 1 h per a day. In both the presence and absence of H$_2$Pc/PTCBI, the outlet flow showed TMA concentration <0.03 ppm for the first day. In the absence of H$_2$Pc/PTCBI, the TMA concentration remained at <0.03 ppm for 20 days, after which it gradually increased due to saturation of absorption.

In the presence of H$_2$Pc/PTCBI, the TMA concentration of the outlet flow remained at <0.03 ppm for 40 days, which was longer than that without H$_2$Pc/PTCBI. After 40 days, the TMA concentration of the outlet flow increased even when using Nafion/H$_2$Pc/PTCBI trilayer film. It is concluded that the longer duration of low TMA concentration at the outlet was due to the photocatalytic decomposition of TMA. After 47

days, the visible absorption of Nafion/H$_2$Pc/PTCBI trilayer film was similar to the virgin one, in which the absorbance value at 600 nm was the same as that after the use. This finding indicates that there was no degradation of H$_2$Pc/PTCBI. A possible reason for the TMA absorption declining after the 40th day is a change in morphology of the hydrophilic cluster, which is the channel by which TMA accesses the H$_2$Pc/Nafion interface. Such morphological change was reported to decrease of the hydration radius of Nafion induced by TMA.[49] We also observed lower water content in the Nafion after TMA contact.

Photocatalytic Properties and Nafion Absorbability of TMA. Figure 5 shows the integral value of TMA removed by
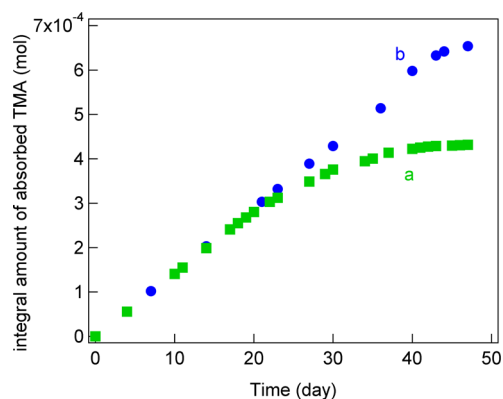

Figure 5. Integral of absorbed TMA onto Nafion/H$_2$Pc/PTCBI trilayer film (●) and only Nafion (■) in the flow system shown in Figure 2. Data were estimated from Figure 4.

Nafion/H$_2$Pc/PTCBI and Nafion without H$_2$Pc/PTCBI. After the 20th day, the integral value for Nafion with H$_2$Pc/PTCBI increased at the same rate, while that for Nafion without H$_2$Pc/PTCBI saturated to 4.2×10^{-4} mol. The difference between two cases shown in Figure 5 was the effect of the photocatalyst.

This difference must represent the photocatalytic decomposition of TMA, denoted as M_{TMA} value (2.4×10^{-4} mol). From the M_{TMA} value, the photocatalytic turnover number (TON) of this flow system is estimated as follows:

$$\text{TON} = M_{TMA}/P \tag{7}$$

where P is the amount of photocatalyst molecules (H$_2$Pc) at the surface (1.3×10^{-8} mol) in the flow reactor, which was calculated from the single molecule area (0.9 nm^2) of H$_2$Pc and the area of Nafion/H$_2$Pc/PTCBI trilayer films (300 mm$^2 \times 24$ layers).[23] Then the TON value was estimated to be 1.8×10^4, indicating that the reaction proceeded catalytically.

Because TMA being almost completely absorbed may be due to sulfonic groups in Nafion, herein, we discuss the saturation of the integral in relation to the acid capacity of Nafion. The saturation of integral amount of TMA in the absence of the bilayer (4.2×10^{-4} mol) can be converted to the density of TMA per volume to be 1.2×10^{-3} mol/cm^3 based on the total volume of the total Nafion films [$= 24 \times 0.6 \times 5.0 \times (5 \times 10^{-3})$ cm^3]. The molar concentration of $-SO_3H$ group into Nafion is estimated to be 1.6×10^{-3} mol/cm^3 from the density of Nafion 112 (1.98 g/cm^3) and weight of sulfur in the element analysis (2.1%).[50] The TMA density at the saturation is as 75% [$= (1.2 \times 10^{-3})/(1.6 \times 10^{-3})$] as the concentration of -SO$_3$H group. The smaller but the same order volume as the expected value from acid capacity would be due to the imperfect network of the hydrophilic (cluster) network of Nafion,[51] the accessibility

due to percolation to the sulfonic groups is not perfect for example 40−80%.[52] The present case of 75% is relatively high within the range.

On the other hand, the saturation of integral of TMA in Nafion with H$_2$Pc/PTCBI was 1.9×10^{-3} mol/cm^3 (calculated from the integral of TMA from Figure 5 and the Nafion volume of the trilayer films), which is 120% of the concentration of $-SO_3H$ group 1.6×10^{-3} mol/cm^3 of Nafion 112. This result is higher than unity, and it is consistent with the regeneration of the absorbability of TMA due to photocatalytic decomposition of TMA.

We can estimate the efficiency of the photocatalyst system, as the average external quantum efficiency (Φ_{ave}) as follows:

$$\Phi_{ave} = nM_{TMA}N_A/(IS\tau/E_p) \tag{8}$$

where $M_{TMA} = 2.4 \times 10^{-4}$ mol, $I = 10$ mW/cm^2, $S = 3.0$ cm$^2 \times 2$, $\tau = 1.72 \times 10^5$ s. E_p can be chosen as the average photon energy (2.8×10^{-19} J for 700 nm). We again assume $n = 1$, based on eqs 3 and 4. The Φ value was estimated to be 0.004, which is one order less than the optimized monolayer (0.05 for 3.5 mW/cm^2), while the present one-path-flow system can purify 700 mL water per 3.0 cm^2 of compact reactor area and is efficient for practical use. Multiple modular units, for example, 3.3×10^3 pieces of the present unit can be installed on a plane of 1 m^2, for which 1 t of water can be purified per day.

■ SUMMARY

A 1 t/day one-pass water purification system was designed with a multilayered photocatalytic reactor composed of 24 Nafion/H$_2$Pc/PTCBI trilayer films of 1-m^2 irradiation area. This Nafion/H$_2$Pc/PTCBI trilayer film responds to sunlight of <780 nm with thin organic semiconductor of H$_2$Pc/PTCBI = 10 nm/10 nm with light absorbance of 0.18 at 630 nm. Owing to the low absorption with sufficient EQE, reaction density with 24-layered photocatalyst films can be used for pollutant absorption. A 1/3300 module of the design was experimentally demonstrated using 10 mW/cm^2 visible light illumination for 1 h/day. The absorbability of Nafion was recovered photocatalytically; The removal efficiency of TMA was maintained for more than 46 days, compared with 20 days when using Nafion without H$_2$Pc/PTCBI. The TON of photocatalytic reaction was calculated to be 1.8×10^4.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Figures of a SEM image of the surface of Nafion/H$_2$Pc/PTCBI, removal ratio of TMA depending on various flow conditions, and the photocatalysis behavior. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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