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Photosensitizer Dye Nanoparticle-coated Membranes for Singlet Oxygen Generation under Atmospheric Conditions

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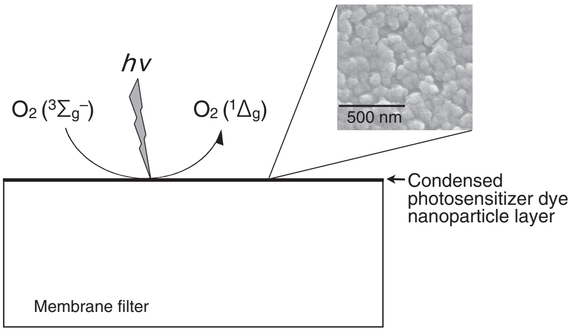
A simple and easily controllable immobilization method for photosensitizer dyes and the resulting photosensitizer dye nanoparticle-coated membranes (PDNMs) that generate singlet oxygen ($^1O_2$) under atmospheric conditions were demonstrated. A 100% porphyrin nanoparticles layer that is less than 1 µm thick on a membrane filter caused quantitative $^1O_2$ production under illumination. The thin layer promotes effective light absorption as well as significantly slowed deactivation of $^1O_2$ by supporting materials. Moreover, the PDNMs were highly resistant to photobleaching of dye itself.

Facile and highly efficient production of $^1O_2$ is widely known to proceed in the presence of a photosensitizer dye by low-energy illumination. $^1O_2(^1\Delta_g)$ is a long-lived reactive oxygen species resulting from spin-forbidden transition from $^1\Delta_g$ to ground state ($^3\Sigma_g{}^-$), in particular the lifetime in the gas phase is longer than that in the liquid phase. The observed lifetimes of $^1O_2(^1\Delta_g)$ in the gas phase at 0.6 torr[1] and in dry oxygen at 1 atm[2] are reported to be 7 s and 124 ms, respectively. In the liquid phase, there have been many applications of $^1O_2$, including photodynamic therapy (PDT),[3] disinfection,[4] lithography,[5] photochemical degradation of harmful pollutants,[6] and oxidation in organic synthesis.[7] However, in the gas phase, the utilization of $^1O_2$ has been unexplored due to technical problems in immobilization and light stability of photosensitizers. The fixation of a photosensitizer on a solid support has been attempted by conventional impregnation based on physical adsorption to porous or fibrous materials,[8] covalent bonding or ionic bonding to organic polymers[9] or metal alloy,[10] sol–gel method,[11] and electrospanning process.[12] However, there are a lot of difficulties, such that insufficient and uncontrollable loading on the solid support, strong deactivation of $^1O_2$ by supporting materials, and high gas flow of O_2 are required for sufficient production of $^1O_2$.[13] In addition, serious photobleaching of the photosensitizer dyes during light illumination[14] has restricted the application of $^1O_2$ to atmospheric conditions.[8]



Scheme 1. A conceptual rendering of photosensitized $O_2(^1\Delta_g)$ production by photosensitizer dye nanoparticle-coated membrane.

Here we propose a technically feasible and highly reproducible immobilization method of a photosensitizer dye and a new photosensitizer dye nanoparticle-coated membrane (PDNM) for photosensitized $^1O_2$ production under atmospheric conditions. As shown in Scheme 1, PDNM has a distinctively thin layer on the top surface of the membrane filter, where 100% photosensitizer nanoparticles are condensed. The fabrication method of PDNM is similar to that we previously reported for metal ion detection,[15] which is simple and feasible for mostly hydrophobic dyes. A nanodispersion of a hydrophobic dye prepared by reprecipitation[16] is simply filtered through a finely woven membrane filter to form the condensed photosensitizer layer. The amount of loading photosensitizer dye and the layer thickness is easily controllable only by regulating the volume of the nanodispersion. In this article, two porphyrins, tetraphenylporphyrin (TPP, $\Phi_\Delta = 0.80$ in benzene[17]) and protoporphyrin IX (PpIX, $\Phi_\Delta = 0.56$ in an aqueous Triton X-100 solution[18]) are demonstrated as a hydrophobic photosensitizer.

TPP and PpIX nanodispersions were prepared by injecting 100 µL of 2 mM TPP or 1 mL of 0.2 mM PpIX in tetrahydrofuran (THF) into 10 mL of vigorously stirred water. The sizes of the TPP and PpIX nanoparticles were estimated by both dynamic light scattering (DLS) measurement and scanning electron microscopy (SEM) observation to be 50–300 nm in diameter with an average diameter of 150 nm. The PDNMs were fabricated by passing the dispersion solution through a 170 µm thick nylon membrane filter with 0.22 µm pores and an effective area of 9.6 cm^2 (Millipore Co.). A 99.74% portion of TPP nanoparticles was coated uniformly and firmly on the membrane with no additive and the surface density was calculated to be 2.07×10^{-8} mol cm^{-2}. Cross-sectional photographs of PpIX PDNM (Figure 1) indicate that the PpIX nanoparticles adhere to each other and stick to the fibers of superior surface of the nylon membrane. In fact, photosensitizer dye nanoparticles were not peeled from the supporting membrane even by rubbing with a finger or by twisting the PDNMs. Pencil hardness tests demonstrated that the layer's mechanical strength of TPP and PpIX are higher than 3H grade. The top surface of the membrane is not microscopically flat as shown in Figure 1b, therefore, a probable thickness of PpIX nanoparticles layer was estimated to be less than 1 µm.

Figure 2 shows a comparison of the PDNM and a conventionally impregnated membrane under same loading dose of PpIX. In the case of the PpIX PDNM all the PpIX molecules are located on the filter surface, while in case of the PpIX-impregnated membrane the molecules are distributed all over the filter. Taking into account depth profiles of both membranes, if

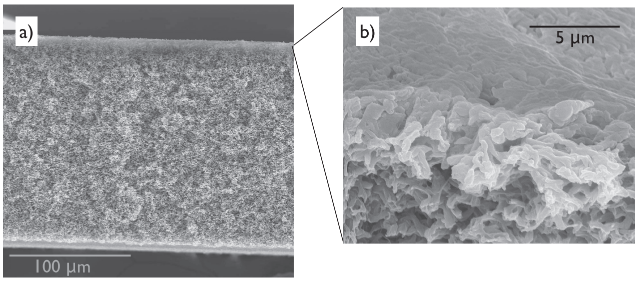


Figure 1. Cross-sections of protoporphyrin IX nanoparticles-coated membrane. a) A full view of the membrane and b) an enlarged view of the top surface of the membrane filter to where the nanoparticles adhere firmly.

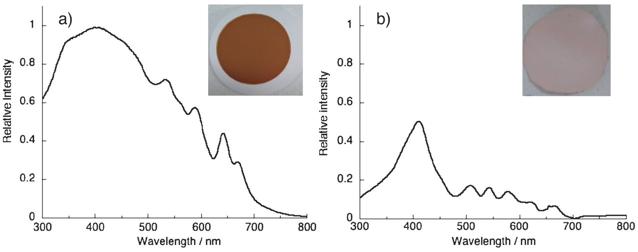


Figure 2. Reflection–absorption spectra and photographs of a) PpIX PDNM and b) PpIX-impregnated membrane. Both membranes contain 2.0×10^{-7} mol of PpIX.

illumination light reaches within 2 µm deep from the surface there are a large difference in the amount of effective PpIX that can trigger photosensitized $^1O_2$ production between on the PDNM and in the impregnated membrane (2.0×10^{-7} and 2.35×10^{-9} mol, respectively). Characteristically, the reflection–absorption spectra of TPP and PpIX PDNMs were significantly different from the absorption spectra of the corresponding THF solutions. As shown in Figure 2, the Soret and Q bands of PpIX on PDNMs were shifted and extensively broadened, which is mainly attributed to the strong interactions in the aggregated porphyrins and the coexistence of J- and H-aggregates of the porphyrins.[19] The reflection–absorption intensities of the Q bands of both PDNMs were relatively higher than those of impregnated membranes, and this spectral feature is likely to encourage the highly efficient generation of $^1O_2$.

Figure 3 shows near infrared (NIR) luminescence measurements of the TPP PDNM and TPP-impregnated membrane obtained using a Nd:YAG pulse laser at 532 nm, a monochromator, and a photomultiplier. Although the same amount of TPP was loaded on each membrane, the luminescence intensity of $^1O_2$ on the TPP PDNM was remarkably higher, which implies that the thin layer structure composed of 100% photosensitizer nanoparticles promoted more effective use of light energy and resulted in more efficient $^1O_2$ production. It is noteworthy that aggregated photosensitizers were able to generate $^1O_2$ quantitatively, despite being reported to diminish the $^1O_2$ generating capacity because of the strong π–π interactions between porphyrins that affect the Frank–Condon factor.[20] Moreover, deactivation of $^1O_2$ by the base nylon membrane is kept to a minimum due to minimal contact between the photosensitizer dye and the base membrane. The major components generated from $^1O_2$ deactivation in air are N_2, O_2, and H_2O (humidity). According to the calculation based on the Einstein–Smoluchowski equation using the deactivation rate constants of these quenchers[21] and the estimated coefficient of diffusion at 298 K,[22] the lifetime of $^1O_2$ is expected to be 59–68 ms at 1 atm and 298 K for 30–60% relative humidity. The decay curve of the NIR luminescence at 1270 nm (Figure 3, inset) exhibits complex multiexponential components, because the summation of the NIR luminescence of $^1O_2$ molecules under various conditions such as surface adsorption and inside infiltration was observed. A rough estimation of the lifetime of $^1O_2$ was less than 130 µs, which was considerably shorter than the expected one, most likely because desorbed $^1O_2$ molecules from the PDNM are undetectable by the NIR luminescence measurement.

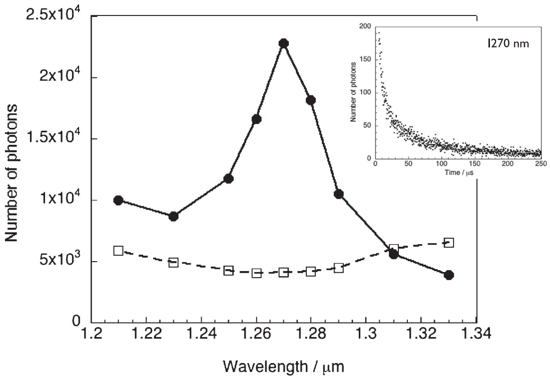


Figure 3. NIR luminescence spectra of TPP nanoparticles-coated membrane (–●–) and TPP-impregnated membrane (–□–).

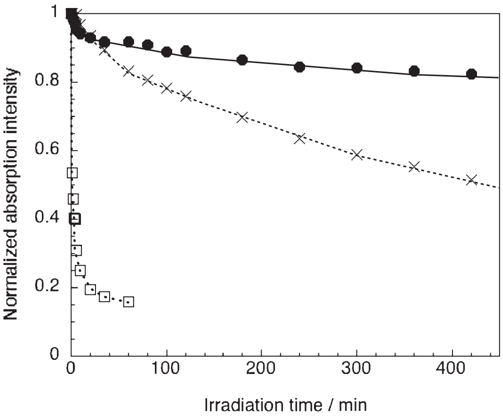


Figure 4. Photobleaching test of protoporphyrin IX nanoparticle-coated membrane (–●–), protoporphyrin IX-impregnated membrane (–□–), and protoporphyrin IX THF solution (– × –).

Photobleaching of photosensitizer itself was investigated using PpIX and shown in Figure 4. The comparative experiments of the PDNM, the impregnated membrane, and the THF solution with an equimolar amount of PpIX were performed by the time course of reflection or absorption intensity of the Soret band under illumination with a 500 W tungsten lamp. The signal intensity of the PDNM was nearly unchanged after 7 h illumination with a 17% decrease compared to 84% decrease for the impregnated membrane and 48% decrease for the THF solution. More surprisingly, the TPP PDNM was more tolerant to photobleaching, the intensities of the Soret and Q bands were decreased after 7 h illumination by 0% at 413 nm and 4.7% at 517 nm, respectively. It is clear that photosensitizers in an aggregation state significantly increase their stability against photoinduced oxidation including self-produced $^1O_2$. At present, one possible reason for the relatively high light-resistance is that close packing structure composed of planar TPP or PpIX molecules suppresses the O_2 penetration inside the particles. The other is that significantly reduced T_1 states of some TPP and PpIX in aggregation states quench $^1O_2$ and protect the nanoparticles against oxidative damage by $^1O_2$. As shown in Figure 2, the aggregated PpIX and TPP showed relatively more intense long-wavelength absorption over 600–800 nm than the monomeric ones, therefore, triplet states of some molecules are expected to be lower due to strong π–π stacking interactions. Actually, it has been reported that monomers of phthalocyanines and naphthalocyanines having intense far-red absorption bands serve not only as efficient photosensitizers but also as active quenchers of $^1O_2$ in aerobic solutions based on the energy transfer from $^1O_2$ to their low-lying T_1 states.[23] The high resistance of the PDNMs against light will promote more effective use of photosensitizer dyes for environmental detoxifications and medical applications with $^1O_2$ under atmospheric conditions.

In conclusion, the PDNMs were easily fabricated by the simple filtration of nanodispersion of hydrophobic photosensitizer dyes through a membrane filter, and almost all dyes were coated uniformly and firmly on the top surface of the filter. The condensed photosensitizer nanoparticle layer having thickness of less than 1 µm was particularly advantageous for the efficient utilization of light energy and the minimization of $^1O_2$ deactivation by the supporting material. The stability of the photosensitizer dye is notably increased due to the aggregated structure formed on the PDNM. The PDNMs were demonstrated to be promising photocatalyst materials for the generation of $^1O_2$ under atmospheric conditions.

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