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Carbon–polydimethylsiloxane-based integratable optical technology for spectroscopic analysis

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ABSTRACT

A polydimethylsiloxane (PDMS)-based optical system has been demonstrated. To suppress intense background radiation due to multiple internal scatting in a transparent material, a composite structure of a carbon–PDMS compound and PDMS was proposed. The index matching of the real part of the refractive index can suppress internal scattering, and an absorption of 99–99.7% was attained by using carbon micro particles and carbon nano tubes. The black-PDMS light channel functions as a light filter for straight pass, and an optical density of 5 was obtained by bending the filter.

1. Introduction

Traditionally, an optical system configures optical components in a space [1,2]. It means that the optical path through the components as robust path and the spaces as flexible path. This robust/flexible combination was very useful to attain the tunability and stability of the system simultaneously. The tunability was guaranteed by the flexible path and tuning mechanisms of the components, and the stability was guaranteed by the robustness of the components and a fundamental base. Therefore, the fundamental bases with black optical covers generally render optical systems heavy, hard, and expensive. Since robust material is preferred for optical component, the robust path is generally the path filled with transparent and solid-state medium. We term it "filled path" in this paper as an opposite word of empty traditional path such as a space.

Some of advanced and integrated optical systems (TIRF, SPR, lab on a chip and so on) reported the replacement of the spaces with transparent solids partially in its optical path [3–5]. This replacement increased stability and decreased tunability. Furthermore, it became the system more compact due to the reducing fundamental base. On this view point, an optical fiber based system [6] proposes an important conceptual advancement. Though an optical fiber is filled path, it can simultaneously provide longitudinal robustness and transverse flexibility due to its small cross section. Thus, waveguide technology such as WDM has been studied [7].

Recently, many research groups have studied optical detection in the "lab on a chip" concept [8]. A very simple optical system such as an absorption cell was integrated in the flow-injection system consisting of glass, and a severe internally scattered background was observed in the filled optical path of glass. Thus, external components such as optical filters must be included for sensitive measurement. If a complicated optical system is designed with the filled optical path, multiple internal scattering causes severe background noise in optical detection. However, the use of the filled optical path provides the possibility of constructing an optical system using soft materials such as polydimethylsiloxane (PDMS), if internal stray light can be reduced. In this study, we propose a novel concept for a compact optical system using the soft and flexible material, PDMS, as the optical system based on filled path scheme. To suppress intense background radiation due to multiple internal scatting in a transparent material, a core/clad structure of a carbon–PDMS compound (clad) and a PDMS (core) was proposed. The refractive index matching of the core and the clad can suppress internal scattering, and an absorption of 99–99.7% was attained by using carbon micro particles and carbon nano tubes.

2. PDMS-based optical system

PDMS has suitable optical properties, which are listed as follows:

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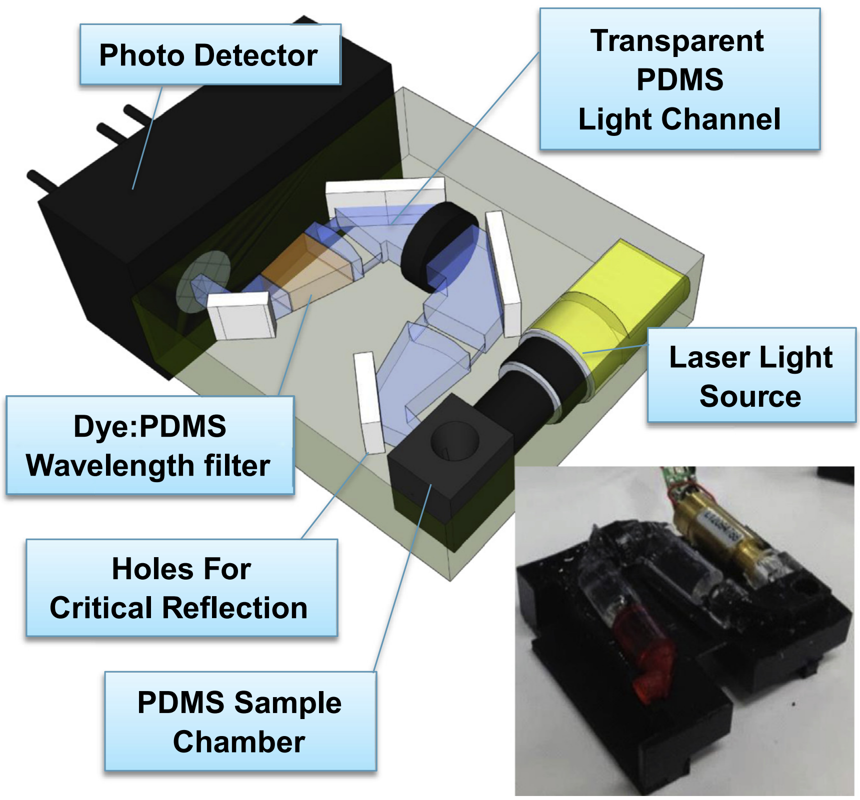

Fig. 1. Schematic of PDMS/Carbon–PDMS module for laser induced fluorescence detection. All optical component is covered black-PDMS molding. Right bottom image is the photo image of the assembled components for the pumping at 532 nm and measuring at 600 nm without covering black-PDMS.

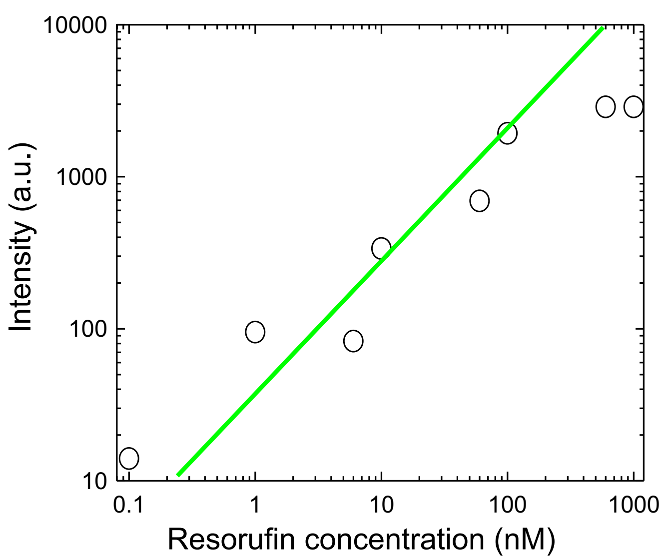

Fig. 2. An example of calibration curve of the Resorufin fluorescence detection using the PDMS module.

- Low fluorescence
- High chemical stability
- Transparency in the UV region.

Fig. 1 shows a schematic of an example of the proposed laser-induced fluorescence (LIF) system for a small sampling tube (such as a PCR: polymerase chain reaction tube) [9,10]. The filled optical path was constructed with transparent PDMS, and it was covered with a similar PDMS material in which absorption particles are diffused. The PDMS material with absorption particles diffused is termed black-PDMS in this article. A mixture of a carbon-particle compound (Shinetsu, KE-COLOR-BL) and room temperature curable PDMS (Shinetsu, SIM-360) was adopted.

A pumping laser was coupled with a PCR chamber consisting of black-PDMS with PDMS windows. LIF was collected 90° relative to the laser-beam axis and propagated in the PDMS light channel. The light channel was folded four times by critical reflection with rectangular parallelepiped holes. Furthermore, two holes with spherical surfaces were used to construct a spatial filter. The PDMS channel was also covered with black-PDMS to reduce unexpected light propagation. The scattered laser beam was trapped by a black-PDMS chamber, laser-blocking filter, and absorbing PDMS channel containing dye and an integrated spatial filter. Finally, the filtered LIF was observed using a photodetector. As a first demonstration, module for pumping at 532 nm and observing at 600 nm was developed. A battery driven diode pumped solid state green laser (DPSS green laser, Lightvision, JSM-6-M, Nd:YVO_4, 532 nm, 1 mW) was used as the pumping laser unit. The mixture of carbon particle compound and PDMS was used as the black-PDMS, and Sudan-II dye was adopted for absorbing dye:PDMS part. The laser blocking filter (Edmund #86-120, OD6@532 nm) was also adopted. The photodetector was a photomultiplier-tube module (Hamamatsu, H10721).

Fig. 2 shows an example for fluorescence detection in a water solution of 7-hydroxy-3H-phenoxazin-3-one (Resorufin) dye in a 50-μL PCR tube. The three data samples were averaged without re-entry. The blank signal corresponds to 150–300 a.u., and the detection limit can be approximated as 2–3 nM. A dynamic range over 1–100 nM was also confirmed.

3. Evaluation of scattering trap performance

The low blank signal level seemed to be due to the trapping effect of scattered light at the boundary between black-PDMS and

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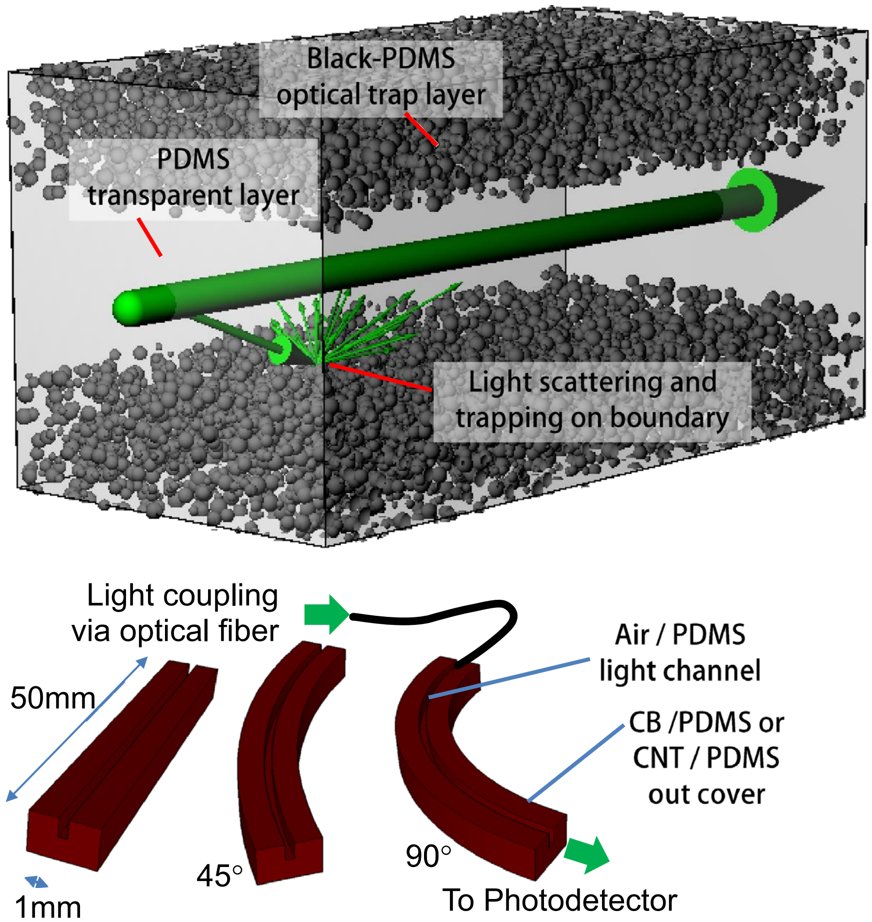

Fig. 3. Schematics of a PDMS/black-PDMS light channel and light propagation between the boundary structures (top) and schematics of bent light channels without covering black-PDMS for the trapping investigation (bottom).

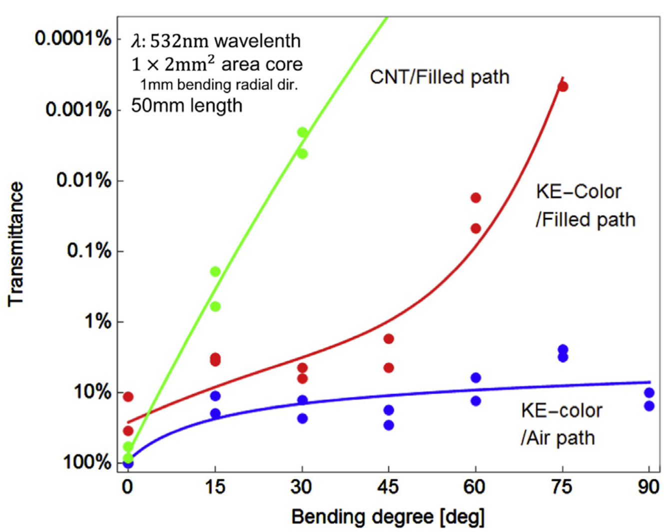

Fig. 4. Experimental transmittance of the flexible black-PDMS/PDMS light channel as a function of the bending angle. Blue indicates air channel (hole) in CB:PDMS cover, red indicates PDMS channel covered with CB:PDMS, and green indicates PDMS channel covered with CNT:PDMS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

PDMS. With the light channel shown Fig. 3, the light that is not propagating along the transparency channel can be absorbed at the scattering point of the diffused black particles in the black-PDMS region. As no Fresnel reflection occurred, the PDMS-filled light channel can work as a particular spatial filter that can pass only the light propagating along the channel's axis. It can also prevent the unexpected off-axis pass through a dielectric filter such as the notch filter. In the module described in Fig. 1, the light path has 4 reflections to reduce the unexpected stray light from the photodetector. Furthermore, the external light was also blocked by the black-PDMS coating over the module. The flexible PDMS can remove the air gap from the boundary between the DPSS laser, the hard optics, and the photodetector. Consequently, the gap-free interface can block the intrusion of the external light.

To evaluate the trap performance of the spatial filter, straight light guides (cross section of 1×2 mm^2, length of 50 mm) were prepared. The light propagation channel was filled with PDMS or air, and it was covered with a PDMS compound diffused with carbon black (CB) particles (concentration of 10 wt%) or with multiwall carbon nano tubes (CNTs, Cnano Flotube9000, 0.83 wt-%). The cladding thickness was greater than 5 mm. The light guide can be expected to function as a straight filter that can pass only the light propagating along its axis. A laser beam propagating in an optical fiber (1 mmφ, 532 nm) was coupled to an end of the channel, and the output from the other end was measured. The filters were bent according a curved flame to emulate the multiple scattering to trap the incident light. The transmittance was calculated from normalization by using the output of the straight air-channel filter, and it is plotted as a function of the bending curvature in Fig. 4. Although the transmittance was approximately 10% even with 90° bending for the air-channel filter, the filled channel in CB showed an optical density (OD) > 5.3 at 75°. Furthermore, the filled channel in CNTs showed OD > 4.3 at 30°. As the minimum number of reflections m to pass the light channel

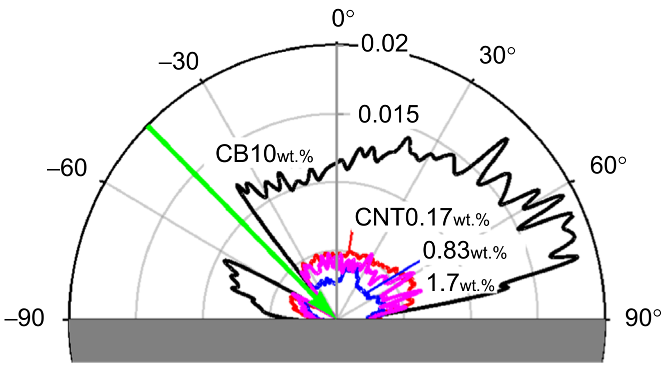

Fig. 5. Polar-plotted scattering intensity from the boundary of PDMS/black-PDMS. Black line indicates CB:PDMS of carbon black concentration of 10 wt%, magenta, blue and red lines indicate CNT:PDMS of carbon nano tube concentration of 1.7, 0.83 and 0.17 wt%, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

can be given by $m=\theta/(2\cos^{-1}((\frac{L}{\theta}-w/2)/(L/\theta+w/2))$, where θ is bending angle and L and w are the length and width of the channel, respectively. Therefore, $m>2$ and $m>3$ correspond to $\theta>40^\circ$ and $>80^\circ$, respectively. Consequently, an OD of approximately 5 can be attained with more than 3 (for CB) and 2 (for CNT) reflections. The absorption coefficient of the CB:PDMS film was also measured. An absorption coefficient of $7.2\times10^{2}\mathrm{cm}^{-1}$ was obtained at a wavelength of 532 nm. This number corresponds to an OD of 6 with a 0.19-mm-thick film; therefore, the external background was well reduced by coating the 10 wt% CB:PDMS. On the other hand, as the CNT:PDMS concentration was limited to <2 wt%, the thickness of CNT:PDMS should be 10–20 times the above value.

To analyze the trapping principle, single scattering at the black-PDMS/PDMS interface was investigated. We prepared cylindrical PDMS samples by dispersing the black particles in the half region divided by the diameter. A DPSS green laser beam was incident at an angle of 45° relative to the interface, and the angular intensity distribution of the scattered light was measured. Fig. 5 shows the angular distributions for 10 wt% CB:PDMS and 0.17, 0.83, and 1.7 wt% CNT:PDMS. Firstly, CB:PDMS shows intense scattering and a complicated angular distribution. The scattering intensity in CNT:PDMS is 1/2–1/3 times that in CB:PDMS. The reason why a relatively complicated angular distribution was observed for 10 wt% CB seems to be the blockage of the incident light by the dense CB blocks just on the surface of the back-PDMS region, because of which the scattering profile seems to be close to the Mie scattering profile. In comparison with the Mie scattering model for a sphere, the experimental profile seems close to the scattering profile that superimposed Mie profile of spherical diameter 0.5–2 μm. The scattering in 10 wt% CB was predominantly caused by the single Mie scattering of a CB particle at the interface. On the other hand, lower concentrations such as 0.83 and 0.17 wt% CNT show homogeneous scattering profiles, which imply that multiple Mie scattering had become dominant owing to the penetration of light. The intensity of scattering is decreased to 1/3 times on changing the black particle from CB to CNT. For 0.83 wt% CNT, the scattering intensity was minimum, total reflection was as low as 0.3% of the irradiated beam, and absorption was as high as 99.7%. This result can explain the very low transmittance in Fig. 4.

Finally, Fig. 6 shows scanning electron microscope images of 10 wt% CB:PDMS and 0.19 wt% CNT:PDMS. The cut surface of the PDMS is not smooth, but we could confirm the particle size of the diffused CB, which ranged from 0.5 to 3 μm. We also confirmed that the aggregation size increased when the concentration exceeded 10 wt%. On the other hand, even with 0.19 wt% CNT, some aggregated particles were observed. Although the aggregated

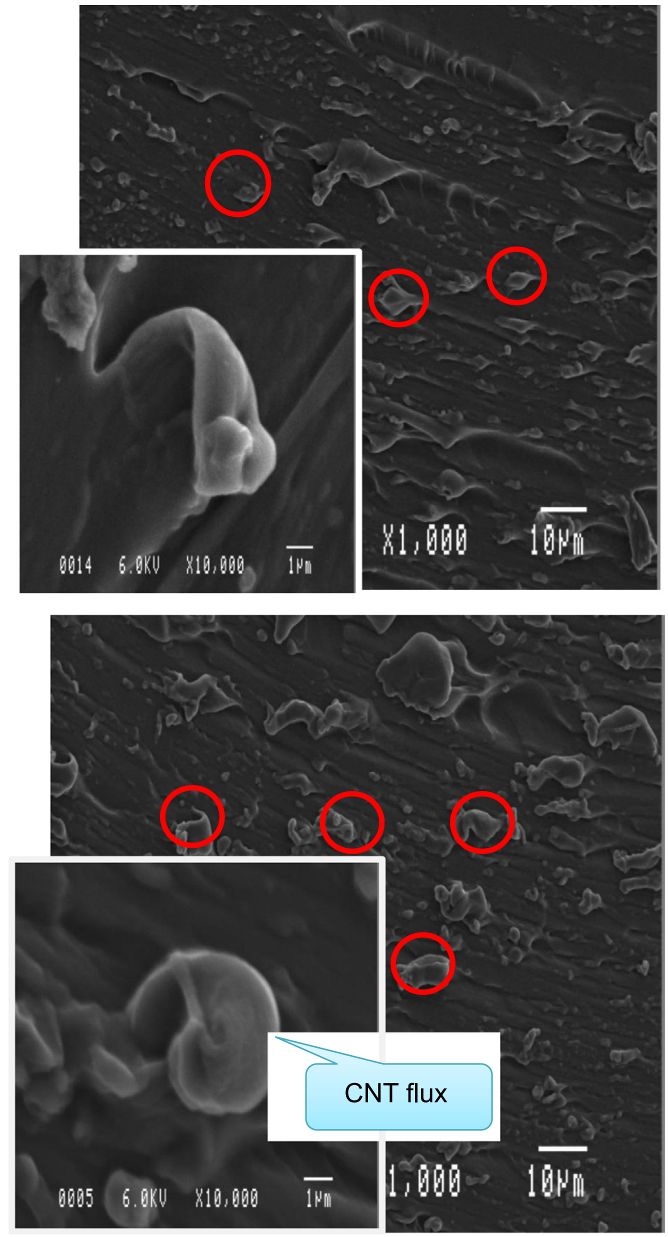

Fig. 6. Scanning Electronic Microscope image of the cut-surface of the black-PDMS. Above image is from CB:PDMS of carbon black concentration of 10 wt%, and below image is from CNT:PDMS of carbon nano tube concentration of 0.19 wt%. Red circles indicate the aggregated black particle due to the high concentration diffusing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

particle size is large as 10 μm, the CNT flux structure was also confirmed.

4. Summary

We proposed a novel integrated optical system based on a polydimethylsiloxane composite with diffused black particles. A laser fluorescence detection module was demonstrated with a folded optical path containing a spatial filter. The PDMS/black-PDMS interface results in absorption greater than 99% per scattering at 532 nm. CNT of concentration 0.83 wt% showed an absorption of 99.7%. The black-PDMS light channel functions as a light filter for straight pass, and an optical density of 5 was obtained by bending the filter.

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