Multifunctional Thin Film Optically Graded Flexible Absorber

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Abstract: Flexible near perfect optical absorbers have many applications in the field of photovoltaic, energy harvesting and defence technologies. Even though flexible absorber coatings can be easily applied on the curved surfaces with complex geometry, the experimental realization of such absorbers having high absorption capacity in the broadband range is a challenging task. Here, we report the design and fabrication of a polydimethylsiloxane (PDMS) based optically graded thin (total thickness - 750 ȝm) assembly which shows near perfect absorption (95%) in the wavelength range of 300 to 2000 nm. The observed high absorbing capacity may be attributed to the presence of multiscale feature size in optically graded assembly which leads to efficient light trapping and multiple scattering of incident beam. The multilayer assembly comprises layers of PDMS reinforced with iron, zinc oxide (ZnO) and carbon nanotubes (CNTs). In addition to this, detailed fracture mechanism of fabricated absorber is studied. Moreover, contact angle study of fabricated thin film structure reveals that it is not only a near perfect absorber but also hydrophobic in nature. The ease of fabrication process combined with the excellent properties shown by the multilayer flexible assembly makes it an attractive option for industrial applications.

Introduction: “Stray Light” is the unwanted light which enters in the optical system and decrease the efficiency of system [1]. Stray light is a big concern for space satellites as it causes reduction in performance of devices which leads to magnitude errors in positioning systems (radiometer measurements) [2]. In addition to this stray light deteriorate signal quality or generate false one, as noise is so high it can also cause the burning of detector and fragile optical components [3,4].

Stray light can be reduced by proper designing mechanical systems or with the use of a black coatings in optical systems. A black coating can be developed which can absorbed light in broadband wavelength range independent of incident angle. Commonly used materials for producing these ultra-black coatings is vertically aligned carbon nanotubes (VACNTs) and graphene [5–7]. However, it is difficult to fabricate VACNTs and graphene at large scale, also it requires unique fabrication facilities which leads to high cost. Moreover, recently Ghai et al. has shown that ultra-high absorption of more than 99.98 % is possible in UV-Vis-NIR...
wavelength region using flower carbon nanotubes (FCNTs) [8]. Even though the absorption of FCNTs is highest reported till date but these absorbers possess the problem of rigidity. Due to this problems, a new material with flexible ultra-black surface at a broadband wavelength range is required. Polymer based nanocomposites having a property of flexibility and durability are in demand as they can be applied on variety of surfaces and to different curvatures or contours [9–13]. These nanocomposites pave the way for future material applications (e.g. flexible electronics or photonics) [14–18].

In this study, we have demonstrated optical gradation scheme to fabricate an optical absorber with ultra-high absorption capacity in a broader wavelength range. CNTs, Zinc oxide (ZnO) and Iron nanoparticles are used as a filler materials in Polydimethylsiloxane (PDMS) polymer matrix. Effect of optical gradation in light trapping capacity (absorption) is studied for broadband wavelength range of 300 to 2000 nm. In addition to this tensile strength along with its failure mechanism is studied.

**Material and Method:** Flexible ultra-black nanocomposite was fabricated using gradation scheme [19–21]. For the design of optically graded flexible absorber PDMS was used as a base material along with 1 wt. % of each filler (CNTs, ZnO and Fe nanoparticles). Detailed synthesis of filler materials and base material used can be found in our previous study [13]. Flexible absorber was fabricated by coating thin films (250 µm) of PDMS+Fe followed by PDMS+ZnO and PDMS+CNTs on a glass slide which after curing is peeled off.

For the characterization of fabricated absorber scanning electron microscopy (SEM) (Jeol 6610LV, Japan) was conducted which shows the morphology of optical graded assembly while energy dispersive X-Ray analysis (EDX) (Oxford INC A X, ACT, United Kingdom) confirms presence of different fillers in the fabricated composite. Moreover, absorption capacity of fabricated absorber was calculated using \( A = 1 - T - R \), where total reflectance (both specular and diffusive) and transmittance was captured using spectrometer (PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer, USA). In addition to this, ellipsometric measurements were performed using Woollam Spectroscopic Ellipsometer (M 2000-F, USA). A universal testing machine (Tinius-Olsen H50KS, USA) was used for tensile testing. Whereas, the contact angle study was performed on a goniometer (First Ten Angstroms, USA).

**Results and Discussion:** Elemental mapping on flexible optically graded assembly with a total thickness of 750 µm is performed to confirm the presence of fillers in PDMS. EDX performed on the assembly (Figure 1a) shows the presence of C, Si, Fe, O and Zn in the PDMS. Moreover, EDX of individual layers containing fillers is also studied as shown in Figure 1b to 1e. Moreover, surface morphology of fabricated graded absorber shows the presence of multiple lengths scales as shown in Figure 1f. The zoomed view of Figure 1f reveals an interesting observation that all the fillers added are uniformly distributed in the PDMS.

Light trapping capacity of fabricated graded assembly and the role of individual fillers and base material in enhancing the average absorption capacity is studied. It is observed that 250 µm thick pure PDMS layer average absorption is nearly 10 %. With the addition of fillers absorption improves significantly to around 18 % PDMS+ZnO, 30 % for PDMS+Fe, and 85 % for PDMS+CNT in 300-2000 nm wavelength range as shown in Figure 2a. Moreover, the absorption spectra of PDMS+Fe layer is flat in entire UV to NIR region as show in Figure 2a. While the absorption decrease in case of ZnO (38 % in UV region to 25 % in NIR) and CNTs 92 % in UV region to 82 % in NIR). This implies that addition of Fe particles is critical to maintain the stable absorption of light in the whole UV-Vis-NIR region. Moreover, it is worth
noting that the combine effect of fillers in graded assembly having multilayer as shown in Figure 2b is having the absorption capacity of more than 95 % in broader wavelength range. This increase in absorption is of twofold: (1) Due to better optical impedance matching between different interfaces present in the assembly. As the refractive index of air is ~1, most of the incident light travels from air to PDMS+CNTs layer ($n = 1.17$) this does not allow any reflections from the interface. Similarly, the light keeps on entering the assembly due to better impedance matching between each layer having refractive index of 1.28 (PDMS+ZnO) and 1.39 (PDMS+Fe). (2) Due to presence of multiscale features with CNTs (length ~ 400 µm, diameter - 120 nm), ZnO (diameter - 150 nm, aspect ratio - 4.6) and Fe particles (diameter - 0.5 µm) are having different size scale in the polymer matrix. These variation of size from fillers added an additional advantage of multiple scattering of incident beam. Moreover, the increase in multiple scattering in the assembly with the addition of fillers leads in increase of optical path length of incident light. A remarkable increase in the absorption capacity is observed with the combined effect of different filler layers forming a graded assembly finds huge potential for many real life applications.

Figure 1. Elemental mapping and SEM study (a) elemental mapping of flexible graded assembly from top view (b) PDMS+CNT layer (c) Pure PDMS (d) PDMS+Fe (e) PDMS+ZnO (f) SEM image of graded assembly showing presence of multiscale features.
Figure 2. (a) Absorption spectra of individual layers and graded assembly (b) schematic of optical graded assembly fabricated using PDMS and different fillers with a total thickness of 750 µm.

Tensile Study: A flexible absorbers undergo tensile force when applied on different curvatures and contours of solar cells, wearable devices and stray light attenuators for space telescopes. Optical absorber will fracture when applied tension force is greater than that of the material fracture point. To determine the strength and stretchability limit of optical absorber tensile test is performed.

Figure 3. Study of tensile strength of individual filler materials and graded assembly in PDMS.

To understand contribution of each filler material on the tensile properties, tensile test is performed on pure PDMS, PDMS+ZnO, PDMS+CNT, and PDMS+Fe composites separately and studied under SEM and optical microscope. It can be observed from Figure 3 that PDMS+Fe composite has highest modulus, tensile strength, and elongation, which can be attributed to better dispersion and interaction of iron particle with PDMS elastomer matrix. To support this further, SEM images of fractured surfaces after tensile test of individual filler materials of pure PDMS (Figure 4a), PDMS+Fe (Figure 4b), PDMS+CNT (Figure 4c), and
PDMS+ZnO (Figure 4d) have been captured. It is observed from the surface comparison of PDMS+Fe with PDMS+ZnO, and PDMS+CNT that the PDMS+Fe has no agglomeration of Fe nanoparticle in the fractured surface and also there are no embedded Fe particles onto the fractured surface of elastomer matrix. This indicates towards a stronger interfacial adhesion between Fe and PDMS matrix (Figure 3b). Whereas, PDMS+ZnO composite shows a relatively lower value of elongation and tensile strength as compared to the other composites (Figure 3). This can be explained from the SEM image of fractured surface of PDMS+ZnO, which shows high agglomeration of ZnO causing early nucleation of micro-voids and lowering the strength and elongation (Figure 4d). PDMS+CNT composites have smaller nucleation sites compared to PDMS+ZnO (Figure 4c). This indicate that PDMS+CNT has smaller agglomerate compared to PDMS+ZnO hence higher tensile strength compared to PDMS+ZnO. However, the graded assembly has higher strength than pure PDMS, PDMS+ZnO, PDMS+CNT, and PDMS+Fe indicating a good bonding at the interface of different compositions as shown in Figure 3.

Figure 4. SEM image of fractured surface Top Row: Microscopic image of fracture surface Bottom Row: SEM image of same (a) Pure PDMS (b) PDMS+Fe (c) PDMS+CNT and (d) PDMS+ZnO (e) contact angle of water droplet resting on fabricated graded assembly.

In addition to this, the contact angle of fabricated assembly with water is studied and found to be hydrophobic in nature with a contact angle of ~122± 3° as shown in Figure 4e. Fabricated absorber being a water hating surface signifies that it will able to resist the environmental degradation due to moisture.

Conclusion: In summary, we have demonstrated that with optical gradation scheme ultra-high light trapping is possible in a broader wavelength range. The graded assembly is fabricated using layer by layer deposition of different filler materials (Fe, ZnO, CNTs) in PDMS having ordered refractive index. The graded assembly with an absorption capacity of more than 95 % is achieved in entire UV-Vis-NIR wavelength region. The ultra-high absorption is found to be
due to the addition of multiscale features and better impedance matching. Moreover, the tensile strength and fracture mechanism of fabricated graded assembly is studied. It is observed that the graded assembly is having higher strength compared to the individual strength of fillers in PDMS. In addition to this, contact angle of fabricated assembly (122°) shows that the designed absorber is not only having ultra-high absorption capacity but also is hydrophobic in nature.

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