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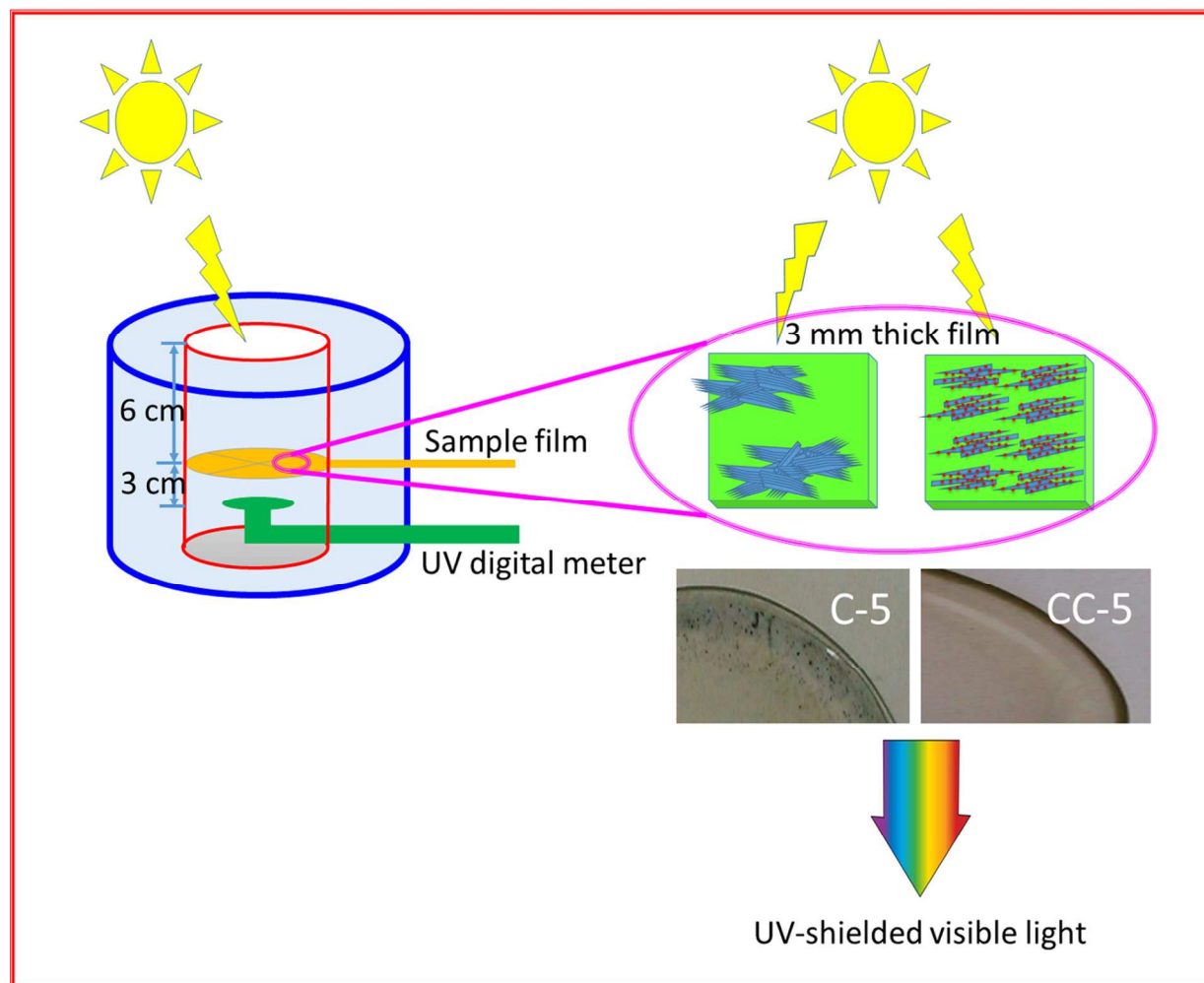
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Carbon quantum dots decorated leaf-like CuO nanosheets were prepared by a simple method and successfully dispersed in the polymer film to improve UV-shielding property.



Journal Name

COMMUNICATION

Carbon quantum dots decorated leaf-like CuO nanosheets and their improved dispersion for an excellent UV-shielding property in polymer film

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Periyayya Uthirakumar,^{a,b,*} S. Muthulingam,^a Rizwan Khan,^a Van-Dung Dao,^b Van-Huong Tran,^b and In-Hwan Lee^{b,*}

We report a simple method for synthesizing the carbon quantum dots (CQDs) decorated leaf-like CuO nanosheets. The CQDs not only relay to improve the dispersion of CuO but also offering a higher UV-shielding property. An excellent UV-shielding property was witnessed in a polymer film containing 0.5 wt% of CQD/CuO nanocomposites.

The intensity of ultraviolet (UV) rays on the earth's surface has been enormously increased due to the thinning of the ozone layer in the past few decades [1]. Numerous reports predicted that the overexposure of UV radiation could cause severe negative effects on the biosphere, human eyes, skin, immune system and biological genomes [2,3]. In this context, UV-shielding materials have gained a special attention in the recent decades, particularly for developing a simple method to fabricate the polymer films containing UV-shielding materials, which could effectively block the UV-rays without disturbing the transparency in the visible region [4]. Hence, many research groups have focused to develop the UV-shielding materials such as TiO₂, ZnO, CuO and CeO₂ dispersed transparent polymeric film, as the protective UV coatings [5-7]. Although, the majority of transition metal oxides showing a good UV-shielding property, it also exhibits a photocatalytic property upon UV light absorption. Nevertheless, CuO has been scarcely employed as a photocatalyst due to its inability to produce good amount of radicals [8]. Hence, low photocatalytic activity of CuO is more preferable to use as a UV-shielding material to avoid the degradation of polymeric matrix [9]. The CuO, a well-known p-type semiconductor material with a narrow band gap (1.2-1.5 eV) has received a

particular interest over other metal oxide for its low cost, good stability, low toxicity, abundant resources, higher UV absorption, and easy preparation with diverse shapes [10].

The development of polymer film with UV-shielding materials has focused a great deal of research in recent years. The physical properties of polymer films are certainly affected by several factors including size, degree of dispersion, and contents [11]. Demir *et al.* reported the ZnO dispersed PMMA composite films with strong UV absorption and a better light transmittance in visible region [12]. Similarly, a strong UV-absorbance of ZnO/PS nanocomposite films without losing transparency at low ZnO content was reported by Chae *et al.* [13]. The major drawback of these films are losing their transparency at high concentration because of aggregation of nanoparticles. We demonstrated the maximum of 66% of UV light absorption by the CuO/PMMA nanocomposites film at lower CuO content [7]. However, to improve further, a similar problem of the particle aggregation is inevitable at high content of CuO. Therefore, a suitable modification is essential to avoid the particle aggregation. Hence, the carbon quantum dots (CQDs) were preferred to decorate on the surface of the CuO to facilitate the high level of dispersion in the polymer matrix [14]. Here, carbon based materials offer not only to improve the dispersion but also to increase UV-shielding property together with non-toxic, low cost, heavy metal-free and eco-friendly in nature [15]. Herein, we report the preparation of CQDs decorated leaf-like CuO (CQD/CuO) nanocomposites and their improved dispersion in polymer film for an excellent UV-shielding characteristics.

The primary information on preparation and characterization of leaf-like CQD/CuO nanocomposites are discussed in electronic supplementary information file. The surface morphology of leaf-like CQD/CuO nanocomposites was examined by FESEM analysis. The high-magnification FESEM image shows the leaf-like CuO nanosheets were uniformly distributed, as shown in Fig. 1a. The average width, length and

^a Nanoscience Center for Optoelectronic and Energy Devices, Department of Chemistry, Sona College of Technology, Salem 636 005, Tamilnadu, India

^b School of Advanced Materials Engineering and Research Center of Advanced Materials Development, Chonbuk National University, Jeonju 561-756, South Korea

* E-mails: uthirakumar@gmail.com (P. Uthirakumar) and ihlee@jbnu.ac.kr (In-Hwan Lee)

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

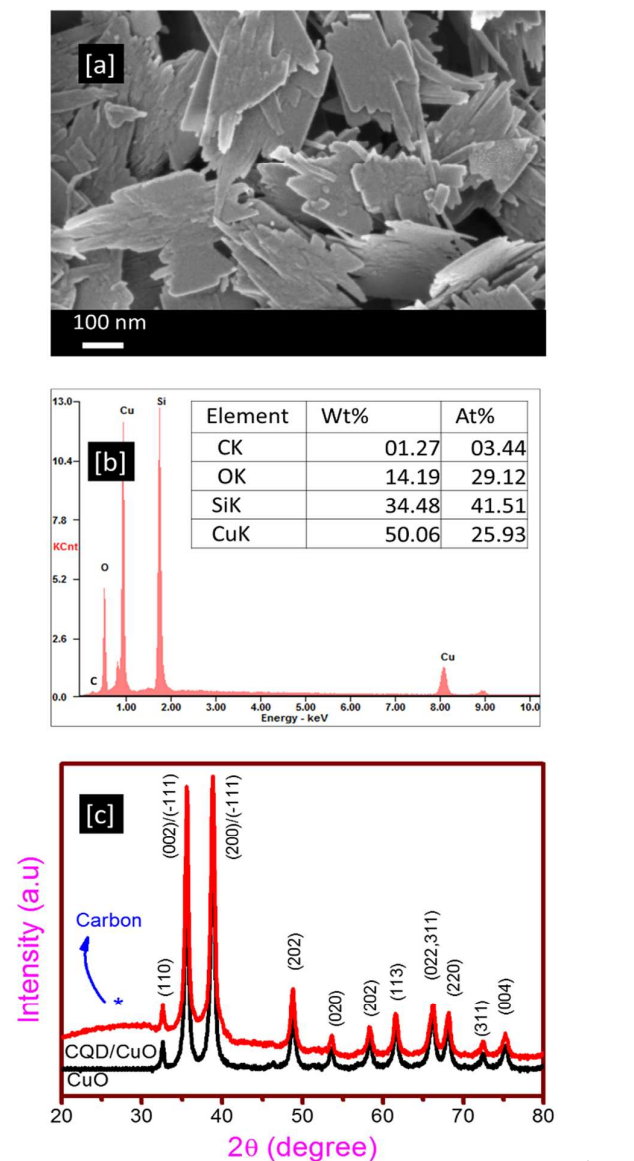


Fig. 1.

(a) FESEM image, (b) EDX results and (c) XRD patterns of leaf-like CQD/CuO nanocomposites. [Inset: Elemental analysis report]

thickness of an individual CuO nanosheet are found to be ~ 500 nm, ~ 700 nm and ~ 20 – 30 nm, respectively. It was very hard to visualize the CQDs on the surface of the CuO nanosheets by FESEM images before and after CQDs decoration. Hence, EDX spectroscopy was used to calculate the elemental analysis of CQD/CuO nanocomposites. Fig. 1b shows the EDX spectrum of CQD/CuO nanocomposites and the corresponding elemental analysis report is displayed, as an inset. The EDX result reveals the existence of copper, oxygen, and carbon that strongly confirms the presence of CQD in leaf-like CQD/CuO nanocomposites. The FESEM image of leaf-like CuO nanosheets is displayed in electronic supplementary information file, Fig. S1.

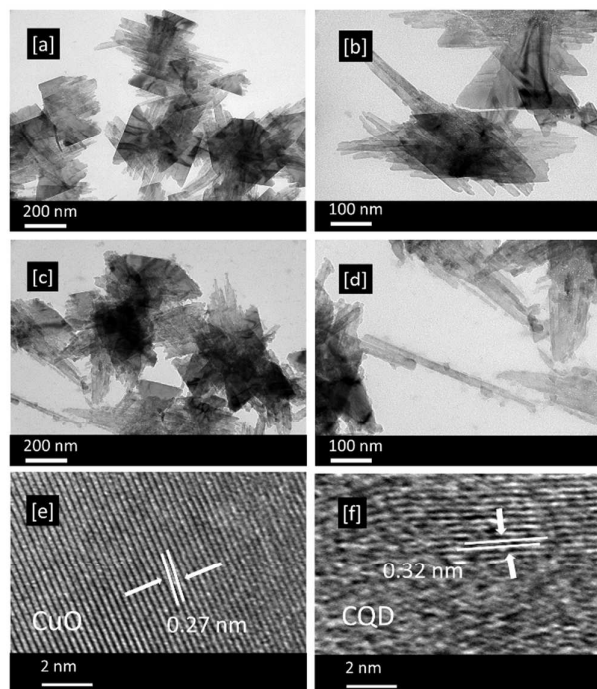


Fig. 2. Low and high magnification TEM images of (a-b) leaf-like CuO nanosheets, (c-d) leaf-like CQD/CuO nanocomposites. The HRTEM images (e-f) of leaf-like CQD/CuO nanocomposites.

Fig. 1c shows the X-ray diffraction patterns of leaf-like CuO nanosheets and the CQD/CuO nanocomposites. The sharp X-ray diffraction peaks suggest the formation of high crystalline CuO primary crystals. The diffraction peaks along the (110), (002), (111), (202), (113), (311) and (220) planes confirm the monoclinic structure of CuO and were well-matched with the standard data (JCPDS No. 05-0661) [11]. In addition, no other crystal phases of Cu_2O and $\text{Cu}(\text{OH})_2$ were observed beyond the characteristic CuO diffraction peaks, indicating the formation of pure and high crystalline leaf-like CuO nanosheets [16]. Besides, particularly, a broader diffraction peak, highlighted with a star mark, was observed at 26° related to the graphitic (002) peak confirming the presence of CQD in leaf-like CQD/CuO nanocomposite [17]. The zoomed XRD patterns of CuO/CuO nanocomposites are given in electronic supplementary file (Fig. S2) to elucidate the clear difference in the diffraction patterns to specify the graphitic (002) peak appeared at 26° .

Furthermore, the existence of both phase of CQDs and CuO was substantiated with TEM images. Fig. 2 displays the low and high magnification TEM images and HRTEM images of leaf-like CuO nanosheets and CQD/CuO nanocomposites. The thickness of an individual CuO nanosheet was measured to be ~ 22 nm and ~ 700 nm in length, which was in good agreement with FESEM images. Besides, randomly decorated CQDs were clearly visualized on the surface of the leaf-like CuO nanosheets at high magnified TEM image, as shown in Fig. 2d. This observation strongly confirms the formation of CQDs decorated leaf-like CQD/CuO nanocomposites. In addition, the

HRTEM images of CQD/CuO nanocomposites in Fig. 2(e-f), the lattice spacing was

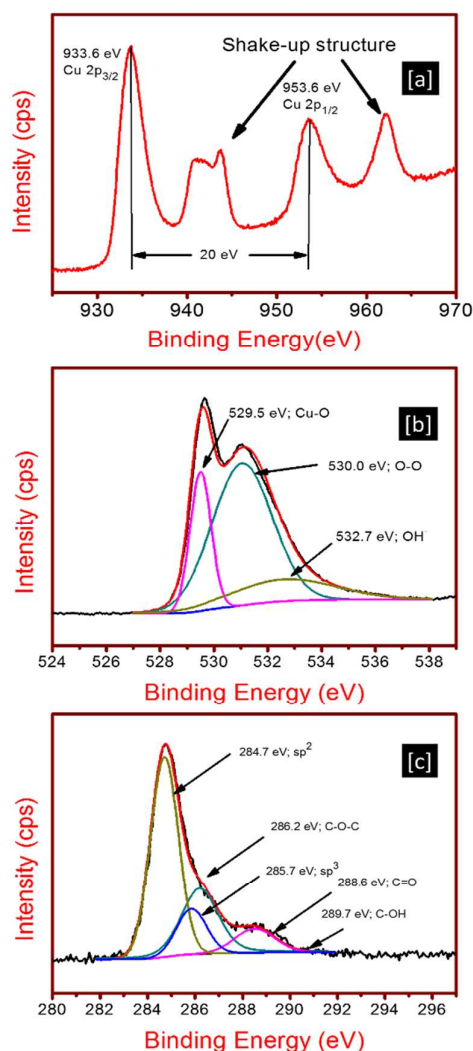


Fig. 3. The high resolution core level (a) Cu 2p, (b) O 1s, and (c) C 1s XPS spectra of leaf-like CQD/CuO nanocomposites.

valued to be ~ 0.27 nm, which corresponds to the [110] lattice fringe of the monoclinic CuO [18] and ~ 0.32 nm for carbon [17]. Based on these results, it was concluded that the decoration of CQDs was successful.

The oxidation state and the stoichiometry of leaf-like CQD/CuO nanocomposites was investigated by XPS technique. High-resolution XPS spectra of core level Cu 2p, O 1s, C 1s are displayed in Fig. 3. The full survey spectrum (Fig. S2) demonstrates that the occurrence of main elements of Cu, O, and C in the CQD/CuO nanocomposites. Fig. 3a shows the high-resolution core level Cu 2p XPS spectrum illustrates the spin-orbit split peaks located at 933.6 and 953.6 eV correspond to Cu 2p_{3/2} and Cu 2p_{1/2} bands, respectively. The distance between the two peaks was found to be ~ 20 eV, which were characteristic of Cu²⁺ compounds [19, 20]. In addition to the Cu

2p_{3/2} and Cu 2p_{1/2} bands, two shake-up satellite peaks were evident and diagnostic of an open 3d⁹ shell, corresponding to Cu²⁺ state appear at binding energies of 943.4 and 963.5 eV.

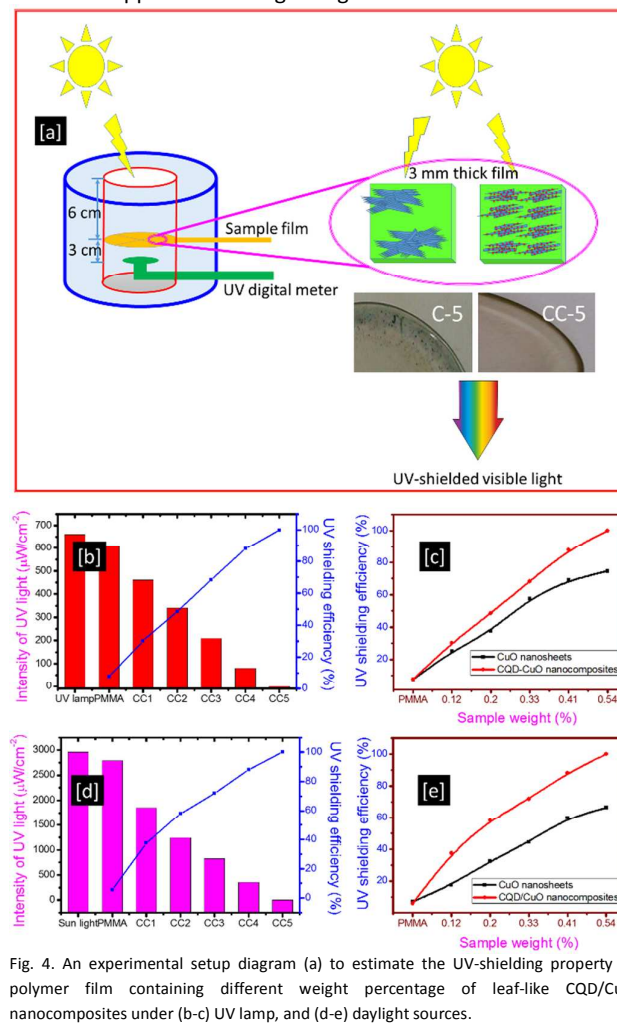


Fig. 4. An experimental setup diagram (a) to estimate the UV-shielding property of polymer film containing different weight percentage of leaf-like CQD/CuO nanocomposites under (b-c) UV lamp, and (d-e) daylight sources.

The de-convoluted high-resolution core level O 1s XPS spectrum of leaf-like CQD/CuO nanocomposite consists of three peaks, as shown in Fig. 3b. The main peak at the lower binding energy of 529.47 eV was attributed to Cu–O [21]. The other oxygen binding energies at 530 eV and 532.7 eV were assigned to the adsorbed oxygen, mainly the –OH groups and the adsorbed H₂O molecules. Meanwhile, the peak observed at 530 eV corresponds to the O 1s band, suggesting the nano-leaflet structured CuO [22]. Fig. 3c reveals the high-resolution core level C 1s XPS spectrum of leaf-like CQD/CuO nanocomposites. A main peak appeared at 284.7 eV after deconvolution of C 1s spectrum was attributed to the sp² hybridized C–C orbital. The other peaks at different binding energies at 285.7 eV, 286.2 eV, 288.6 eV, and 289.7 eV were assigned to the sp³ hybridized carbons, C–O–C, C=O, and C–OH, respectively [23]. Notably, the intensity of C–OH peak at 289.7 eV was weakened, which indicates the oxygenic functional groups were reacted with the surface-adsorbed oxygen of CuO via the dehydration reaction [24]. Thus, it was

confirmed that leaf-like CQD/CuO nanocomposite consists of both phases of CuO and CQDs.

A few weight percentage of leaf-like CQD/CuO nanocomposites were dispersed in PMMA with the help of acetone, an organic solvent to prepare the transparent polymer film. For measuring the UV-shielding property of the polymer film, we made-up a simple experimental setup to measure the UV-shielding capability of the polymer film, as shown in Fig. 4a. Briefly, a polymer film holder and a UV digital meter were placed in a hollow wooden cylinder with the distance of 6 and 9 cm from the top, respectively. In this lab, the maximum UV absorbing capability of 66% with the 0.8 mm thick CuO/PMMA film was reported [7]. Further to improve the UV-shielding capability of the polymer film, the higher loading of leaf-like CuO nanosheets is inevitable. On the other hand, no significant improvement in UV-shielding capability was observed upon increasing the content of CuO nanosheets, due to the particle aggregation. The main reason behind the particle aggregation is due to incompatibility of leaf-like CuO nanosheets in polymer matrix. Thus, in continuation, the CQDs were chosen to introduce onto the surface of the leaf-like CuO nanosheets to improve the degree of dispersion in polymer matrix to avoid particle aggregation at higher loading. In specific, the CQD enables a good interaction and compatibility between CQDs and a wide range of polymers with the assistance of oxygenated functional groups [25, 26].

A 3.0 mm thick polymer film was prepared to investigate the UV-shielding property with different concentration of leaf-like CQD/CuO nanocomposites. Five samples of polymer films (CC-1 to CC-5) were prepared with increasing the concentration of leaf-like CQD/CuO nanocomposites from 0.1 to 0.5 wt%. The pure polymer film was obtained for reference. Similarly, other sequence of polymer films (C-1 to C-5) were prepared with leaf-like CuO nanosheets, for comparison. Fig. 4(b-c) shows the UV-shielding property of polymer films with respect to the different weight percentage of CQD/CuO nanocomposites under UV lamp (18 W). The UV-shielding property of pure polymer was noticed to be ~7% ($610 \mu\text{W}/\text{cm}^2$) and the initial UV light intensity of UV lamp was $660 \mu\text{W}/\text{cm}^2$. Whereas, the sample CC-1 with just 0.1 wt% and CC-5 with 0.5 wt% of leaf-like CQD/CuO nanocomposites were shielded 30% ($460 \mu\text{W}/\text{cm}^2$) and 100% ($0 \mu\text{W}/\text{cm}^2$) of UV light, respectively. However, in case of pure leaf-like CuO nanosheets dispersed polymer films, C-1 and C-5 containing 0.1 wt% and 0.5 wt% were measured to be 25% ($495 \mu\text{W}/\text{cm}^2$) and 74% ($168 \mu\text{W}/\text{cm}^2$), respectively (Fig. 4c). The detailed UV-shielding property of C-1 to C-5 can be seen in Fig. S3. Therefore, ~0.5 wt% of leaf-like CQD/CuO nanocomposites is quite enough to remove an entire UV light, while, ~74% of UV light can be shielded by the leaf-like CuO nanosheets, under UV light.

In order to re-evaluate the UV-shielding property of CQD/CuO nanocomposites, a similar testing was conceded under direct daylight, as shown in Fig. 4(d-e). The UV light intensity of the direct daylight source was recorded to be $2960 \mu\text{W}/\text{cm}^2$, and the pure polymer film itself absorbed ~7% ($2740 \mu\text{W}/\text{cm}^2$) of UV light from the daylight source. The polymer

film CC-1 containing 0.1 wt% of leaf-like CQD/CuO nanocomposites absorbed to the level of ~37% ($1850 \mu\text{W}/\text{cm}^2$) of UV light.

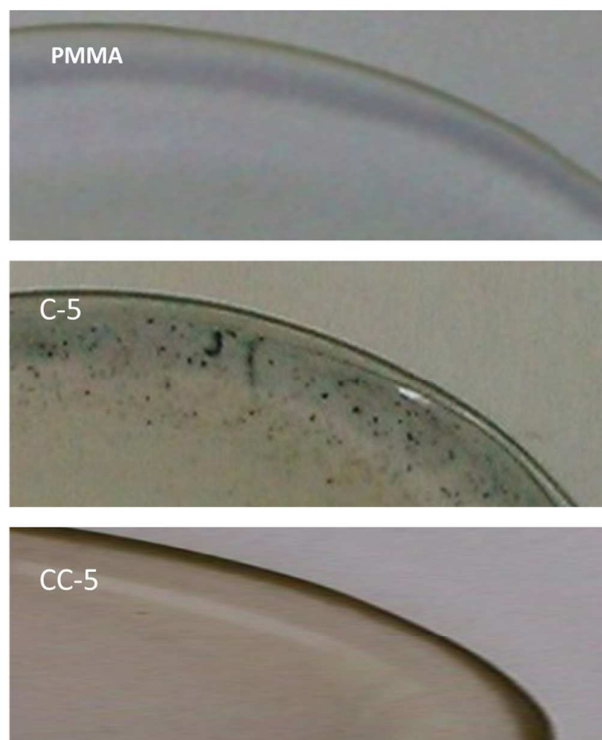


Fig. 5. The photographs of pure PMMA, C-5 and CC-5 polymer films.

Accordingly, the UV-shielding property was increased by increasing the concentration of leaf-like CQD/CuO nanocomposites. For instant, around 58% ($\mu\text{W}/\text{cm}^2$), 72% ($830 \mu\text{W}/\text{cm}^2$), and 88% ($350 \mu\text{W}/\text{cm}^2$) of UV light were absorbed by the sample CC-2, CC-3, and CC-4, respectively. Finally, an entire UV light was shielded by the polymer film consisting of 0.5 wt% of CQD/CuO nanocomposites in CC-5, as shown in Fig. 4d. In contrary, in case of leaf-like CuO nanosheets, the maximum UV-shielding property 66% ($995 \mu\text{W}/\text{cm}^2$) was observed with a polymer film, C-5 containing 0.5 wt% of leaf-like CuO nanosheets, under daylight, as shown in Fig. S3. The extent of UV-shielding capability of other polymer films, C-1 (17%), C-2 (32%), C-3 (44%), and C-4 (60%) were noticed in Fig. 4e.

To authenticate this result, the UV-vis absorption spectra of polymer films were measured (Fig. S4). The UV absorption spectrum of CC-5 film shows the appearance of strong UV-light absorption shoulder with increasing the content of leaf-like CQD/CuO nanocomposites, when compared to C-5 film. This result indicates the possibility of high level of UV light absorption by the decorated CQDs. Similarly, as far as particle dispersion is concerned, the photographs of pure polymer, C-5, and CC-5 films were taken and displayed in Fig 5. Here, the plenty of aggregated CuO particles were clearly seen in C-5 film, while, very hard to trace any aggregated particles in CC-5

film. In addition, confocal laser scanning microscope (CLSM) was performed at an excitation wavelength of 488 nm (Argon/2 laser) with the 505-575 nm filter to support the particle distribution in the polymer film, as shown in Fig. S6. It was found that an improved dispersion of CQD/CuO nanocomposites in polymer film when compared to leaf-like CuO nanosheets. These results strongly confirm that the role of CQDs in the polymer film is not only to improve the degree of dispersion but also to facilitate an excellent UV light absorption.

In conclusion, we have prepared CQDs decorated leaf-like CuO nanosheets by a simple method and successfully dispersed in a polymer film. An excellent UV-shielding property was observed in a polymer film containing 0.5 wt% of CQD/CuO nanocomposites under UV lamp and the results are compatible with daylight. Therefore, it can be foreseen that leaf-like CQD/CuO nanocomposites is one of the potential candidates to be used as a UV filter.

Acknowledgement

This research was encouraged by the Sona College of Technology and supported by National Research Foundation of Korea (NRF) funded by Ministry of Science, ICT & Future Planning (2013R1A2A2A07067688, 2010-0019626).

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