

# Development of New Carbon Nanomaterials for Photodynamic Therapy and Investigation of Their Photophysical Properties

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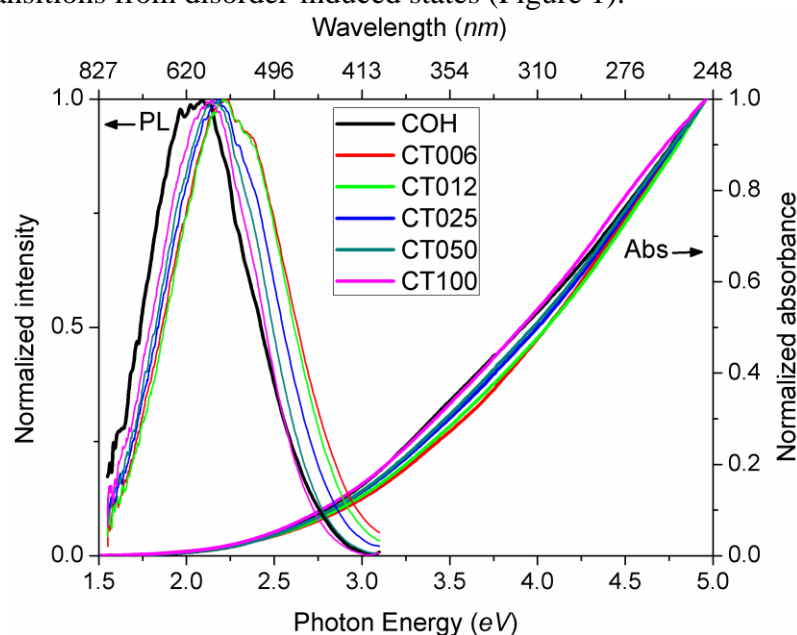
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Since its discovery in 1985, buckminsterfullerene ( $C_{60}$ ) has stimulated a large body of research due to its unique photophysical properties [1, 2]. Chemical modification allows  $C_{60}$  to luminesce [2]. In general, certain carbon nanomaterials exhibit optical emission due to quantum confinement effects [3]. In this way, nano-sized carbon materials have attracted much attention since they are expected to replace conventional cadmium-based quantum dots.

Recently, highly water-soluble fullerene nanoparticles ( $C_{60}$ -TEGs) were prepared by conjugating with tetraethylene glycol (TEG) using lithium hydroxide as a catalyst [4]. Here, we studied the photophysical properties of the  $C_{60}$ -TEGs by combining various experimental approaches of continuous-wave and time-resolved spectroscopy. In presented fullerene nanoparticles broad emission band arising from a wide-range of excitation energies was mainly attributed to optical transitions from disorder-induced states (Figure 1).



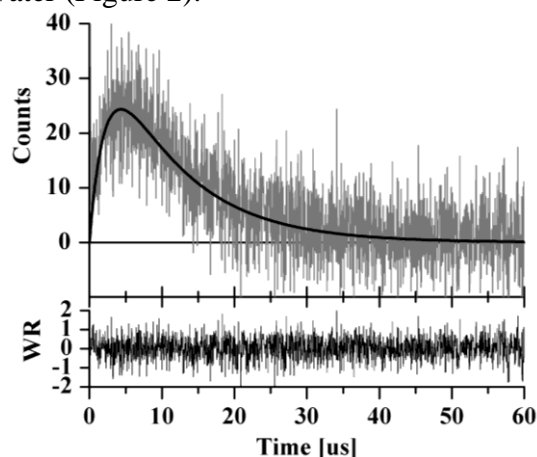
**Figure 1** – Normalized photoluminescence and absorption spectra of the  $C_{60}(OH)_n$  and  $C_{60}$ TEGs water solutions. The luminescent spectra were obtained for excitation at 350 nm (3.5 eV).

Triplet state properties of modified  $C_{60}$  should also be promising, since pristine fullerene readily generates singlet oxygen ( $^1O_2$ ) and other reactive oxygen species by illuminating ultraviolet or visible light [5]. Energy transfer from the excited triplet state of fullerene to the ground state of oxygen gives rise to  $^1O_2$  as illustrated in the following triple-step scheme: (1) fullerene +  $h\nu \rightarrow ^1\text{fullerene}^*$ ; (2)  $^1\text{fullerene}^* \rightarrow ^3\text{fullerene}^*$ ; (3)  $^3\text{fullerene}^* + ^3O_2 \rightarrow \text{fullerene} + ^1O_2$ .

Singlet oxygen is able to irreversibly cause various cell damage including mitochondria, lipid, and nucleus, thus leading to damage of target diseased cells or tissue [6]. However, due to its extremely low solubility in water monomeric  $C_{60}$  does not show a significant photodynamic effect in aqueous systems. To overcome the drawback, many efforts have been explored to develop the

water-soluble C<sub>60</sub> by various approaches including reaction with hydrophilic moieties, grafting polymers, and applying surfactants [7]. As a rule, such modification of C<sub>60</sub> significantly affects its photophysical properties. For example, fullerol (C<sub>60</sub>(OH)<sub>24</sub>), a representative water-soluble fullerene, is known to have low activity of <sup>1</sup>O<sub>2</sub> generation compared to that of pristine fullerene [8]. Therefore, it is a challenge to synthesize water-soluble fullerene derivatives with sufficient photosensitizing activity.

Using highly sensitive kinetic spectrometer [9], for the first time the <sup>1</sup>O<sub>2</sub> kinetic luminescence signals produced by polyhydroxylfullerene (C<sub>60</sub>(OH)<sub>n</sub>) and C<sub>60</sub>-TEGs nanoparticles were detected and described in water (Figure 2).



**Figure 2** – Kinetics of CT050-photosensitized luminescence of singlet oxygen in water at excitation wavelength 355 nm. A solid line is the two-exponential curve fitting. <sup>1</sup>O<sub>2</sub> luminescence rise and decay times were found to be  $2.3 \pm 0.5 \mu\text{s}$  and  $10.3 \pm 1.8 \mu\text{s}$ , respectively. WR are the weighted residuals

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