

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

¹Alexander S. Stasheuski, e-mail: a.stasheuski@ifanbel.bas-net.by

²Jinyoung Jeong, ¹Victor A. Galievsky

¹Boris M. Dzhagarov, e-mail: bmd@imaph.bas-net.by

²Bong Hyun Chung, e-mail: chungbh@kribb.re.kr

¹*B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk, Belarus*

²*BioNanotechnology Research Center, Korea Research Institute of Bioscience and Biotechnology, Daejeon, Korea*

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).

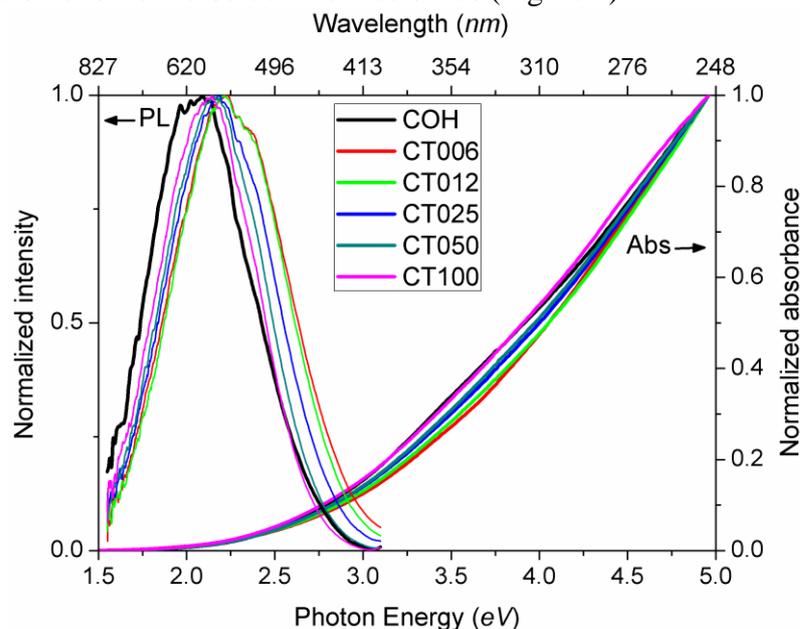


Figure 1 – Normalized photoluminescence and absorption spectra of the $C_{60}(OH)_n$ and C_{60} TEGs water solutions. The luminescent spectra were obtained for excitation at 350 nm (3.5 eV).

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 C₆₀ by various approaches including reaction with hydrophilic moieties, grafting polymers, and applying surfactants [7]. As a rule, such modification of C₆₀ significantly affects its photophysical properties. For example, fullerol (C₆₀(OH)₂₄), a representative water-soluble fullerene, is known to have low activity of ¹O₂ 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 ¹O₂ kinetic luminescence signals produced by polyhydroxylfullerene (C₆₀(OH)_n) and C₆₀-TEGs nanoparticles were detected and described in water (Figure 2).

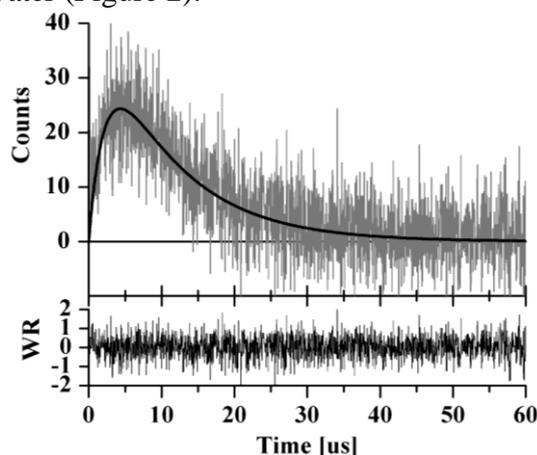


Figure 2 – Kinetics of CT050-photosensitized luminescence of singlet oxygen in water at excitation wavelength 355 nm. A solid line is the two-exponential curve fitting. ¹O₂ luminescence rise and decay times were found to be $2.3 \pm 0.5 \mu\text{s}$ and $10.3 \pm 1.8 \mu\text{s}$, respectively. WR are the weighted residuals

Acknowledgements

This work was supported by Belarusian Republican Foundation for Fundamental Research (grant Ph12KOR-002) and National Research Foundation of Korea (grant 2012K2A1-A2033135).

References

- [1] J.W. Arbogast *et al.*, Photophysical properties of C₆₀, *J. Phys. Chem.* 95 (1991) 11-12.
- [2] G. Accorsi, N. Armaroli, Taking Advantage of the Electronic Excited States of [60]-Fullerenes, *J. Phys. Chem. C* 114 (2010) 1385–1403
- [3] L. Liu *et al.*, Graphene oxidation: Thickness-dependent etching and strong chemical doping. *Nano Lett.* 8 (2008) 1965–1970.
- [4] J. Jeong, J. Jung, M. Choi, J.W. Kim, S.J. Chung, S. Lim, H. Lee, B.H. Chung, Color tunable photoluminescent fullerene nanoparticles, *Adv. Mater.* 24 (2012) 1999-2003.
- [5] P. Mroz, G.P. Tegos, H. Gali, T. Wharton, T. Sarna, M.R. Hamblin, Photodynamic therapy with fullerenes, *Photochem. Photobiol. Sci.* 6 (2007) 1139-1149.
- [6] M.J. Ochsner, Photophysical and photobiological processes in photodynamic therapy of tumors, *J. Photochem. Photobiol., B* 39 (1997) 1–18.
- [7] Z. Markovic, V. Trajkovic, Biomedical potential of the reactive oxygen species generation and quenching by fullerene (C₆₀), *Biomaterials* 29 (2008) 3561-3573.
- [8] B. Zhao, Y.-Y. He, P.J. Bilski, C.F. Chignell, Pristine (C₆₀) and hydroxylated [C₆₀(OH)₂₄] fullerene phototoxicity towards HaCaT keratinocytes: type I vs type II mechanisms, *Chem. Res. Toxicol.* 21 (2008) 1056–1063.
- [9] V.A. Galievsky *et al.*, Laser NIR lifetime spectrometer with nanosecond time resolution, *Instrum. Exp. Tech.* 53 (2010) 568–574.