CHEMICAL TRANSFORMATION OF CARBONACEOUS NANOMATERIALS IN NATURAL AND ENGINEERED ENVIRONMENT

JAEHONG KIM, PH.D.
ASSOCIATE PROFESSOR
SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY
POSSIBLE NANOPARTICLE MODIFICATIONS IN THE ENVIRONMENT

ALVAREZ, P.J., COLVIN V., LEAD, J., STONE, V. (2009) ACS NANO
RESEARCH PRIORITIES TO ADVANCE ECO-RESPONSIBLE NANOTECHNOLOGY
VARIOUS FORMS OF C₆₀ IN THE AQUEOUS PHASE

1. AGGREGATE FORMATION

WATER STABLE COLLOIDS OF UNDERIVATIZED C₆₀ LOST MOST OF INTRINSIC C₆₀ MOLECULAR PROPERTIES

2. SURFACE ENCAPSULATION (SURFACTANT)

CLOSE TO MOLECULAR C₆₀ IN PHOTOCHEMICAL AND CHEMICAL REACTIVITY

3. HYDROPHILIC FUNCTIONALIZATION

MOLECULARLY DISPERSED OR SMALL AGGREGATES VARYING CHEMICAL AND PHOTOCHEMICAL PROPERTIES

STRONG PHOTOSENSITIZER
HIGH RADICAL REACTIVITY

THREE KNOWN PATHWAYS TO STABILIZE IN WATER
VARIOUS FORMS OF $\text{nC}_60$

**AQUA/\text{nC}_60**
Mixing dry $\text{C}_60$ with water for extended period.

**SON/\text{nC}_60**
Sonicating binary mixture of $\text{C}_60$/toluene and water.

**THF/\text{nC}_60**
Exchanging organic solvent (THF) with water.

Antibacterial activity of fullerene water suspensions: effects of preparation method and particle size.
C₆₀ AGGREGATES IN WATER: BRIEF REVIEW

nC₆₀ CAN BE PREPARED VIA VARIOUS METHODS
nC₆₀ IS COMPRISED OF PRIMARILY OF UNDERIVATIZED C₆₀
DIFFRACTION ANALYSES INDICATE CRYSTALLINE NATURE
NEGATIVELY CHARGED SURFACE (ξ POTENTIAL = - 36 mV)

nC₆₀ IS STABLE AT LOW IONIC STRENGTH
ENVIRONMENTALLY RELEVANT REACTIONS AND CHEMICAL TRANSFORMATIONS

PHOTOSENSITIZATION (ROS PRODUCTION)
HYDROXYL RADICAL
ELECTRON REDUCTION/ABSORPTION (REDOX)
OZONATION (CHLORINATION)
PHOTOLYSIS (UV AND VISIBLE)
BIODEGRADATION
COMPARING PHOTOACTIVITY OF VARIOUS C\textsubscript{60} SAMPLES

\[ ^1\text{C}_{60} \xrightarrow{h\nu} ^1\text{C}_{60}^* \xrightarrow{3\text{O}_2} ^3\text{C}_{60}^* \xrightarrow{} ^1\text{O}_2 \]

PHOTOCHEMICAL PRODUCTION OF REACTIVE OXYGEN SPECIES BY C\textsubscript{60} IN THE AQUEOUS PHASE DURING UV IRRADIATION
C₆₀ AS AN ELECTRON ACCEPTOR

NANOSECOND TRANSIENT SPECTROSCOPY

C₆₀ RADICAL ANION WAS DETECTED ONLY WHEN DISPERSED VIA SURFACTANT MICELLES (TX100 APPLIED ABOVE C.M.C.)

C₆₀ RADICAL ANION WITH ANY DETECTABLE LIFE-TIME WAS NOT DETECTED FOR OTHER C₆₀ SAMPLES

MECHANISM OF C₆₀ PHOTOREACTIVITY IN WATER: FATE OF TRIPLET STATE AND RADICAL ANION AND PRODUCTION OF REACTIVE OXYGEN SPECIES
RADICAL REACTIVITY OF C₆₀ AGGREGATE

PULSE AND GAMMA RADIOLYSIS

UNDER N₂-SATURATED CONDITION

\[ e_{aq}^- + A \rightarrow A^- \]

\[ (CH₃)_2CHOH + •OH \rightarrow (CH₃)_2C•OH + H₂O \]

\[ (CH₃)_2CHOH + H• \rightarrow (CH₃)_2C•OH + H₂ \]

UNDER N₂O-SATURATED CONDITION

\[ e_{aq}^- + N₂O + H₂O \rightarrow N₂ + OH^- + •OH \]

\[ H• + N₂O \rightarrow N₂ + •OH \]
REACTIVITY OF nC$_{60}$ WITH OH RADICAL

\[ C_{60} + OH^\cdot \xrightarrow{k_5} intermediate \]

\[ SCN^- + OH^\cdot (+ SCN^-) \xrightarrow[k_6]{1.05 \times 10^{10} \text{M}^{-1}\text{s}^{-1}} OH^- + (SCN)_2\cdot^- \text{(MONITORED AT 472 nm)} \]

SECOND-ORDER RATE CONSTANT = $7.34 \pm 0.31 \times 10^9 \text{M}^{-1}\text{s}^{-1}$. 

\[
\frac{[(SCN)]_0}{[(SCN)]} = 1 + \frac{K_5[C_{60}]}{K_6[SCN^-]} 
\]
REACTIVITY OF $nC_{60}$ WITH HYDRATED ELECTRONS

DIRECTLY MONITORING OF THE DECAY KINETICS OF HYDRATED ELECTRON AT 700 nm IN THE PRESENCE OF $nC_{60}$ AT DIFFERENT CONCENTRATIONS.

SECOND-ORDER RATE CONSTANT = $2.34 \pm 0.02 \times 10^{10}$ M$^{-1}$s$^{-1}$
**γ-RADIOLYSIS STUDY**

**N₂O SATURATED**
Correspond to 11 and 22 mM of *OH

**N₂ SATURATED**
Correspond to 5.4 and 11.8 mM of eₐq⁻
XPS ANALYSIS RESULT

ON $\gamma$-RADIOLYSIS PRODUCT

N$_2$O SATURATED CONDITION
1. UNDERIVATIZED CARBON: 64.2%
2. MONOOXIDIZED CARBON: 35.8%

N$_2$ SATURATED CONDITION
1. REDUCED CARBON: 41.6%
2. UNDERIVATIZED CARBON: 53.6%
3. MONO-OXIDIZED CARBON: 4.75%
QUANTUM MECHANICAL INVESTIGATION

SINGLE $C_{60}$ MOLECULE

DENSITY FUNCTIONAL THEORY
LOCAL DENSITY APPROXIMATION (LDA) PERDEW-WANG CORRELATION (PWC) FUNCTIONAL WITH DOUBLE-NUMERICAL (DN) QUALITY BASIS SET

$C_{60}$ (SINGLET) •OH (DOUBLET) •$C_{60}$–OH (DOUBLET)

HOMO = -9.345 eV
LUMO = -7.770 eV

$-2263.053334$ Ha

HOMO = -6.683 eV
LUMO = -0.599 eV

$-75.140423$ Ha

HOMO = -8.565 eV
LUMO = -8.252 eV

$-2338.26528$ Ha

$\Delta E_{binding} = E_{\cdot C_{60}-OH} - (E_{C_{60}} + E_{\cdot OH})$

$= -44.88$ kcal/mol
MODELING C_{60} CLUSTERS

1-INFINITE LAYER
\[ \Delta E_{\text{binding}} = -44.72 \text{ kcal/mol} \]

2-INFINITE LAYER
\[ \Delta E_{\text{binding}} = -17.23 \text{ kcal/mol} \]

3-INFINITE LAYER
\[ \Delta E_{\text{binding}} = 51.37 \text{ kcal/mol} \]
REACTION WITH O$_3$ IN THE AQUEOUS PHASE

FORTNER ET AL. (2007). ENVIRON. SCI. TECHNOL
REACTION OF WATER-STABLE C$_{60}$ AGGREGATES WITH OZONE
PRODUCT CHARACTERIZATION

MS

\[ C_60 + O_3 \text{ product} \]

\[ C_60(OH)_{22} (MER) \]

\[ C=O \]

\[ C=\cdot O\cdot C \]

\[ C=\cdot C \]

\[ O\cdot C\cdot O \]

FTIR

XPS

\[ \text{ABS (A.U.)} \]

\[ \text{Counts / s} \]

\[ \text{C(1s) Binding Energy (eV)} \]
PHOTOCHEMICAL TRANSFORMATION IN SUNLIGHT

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>0</th>
<th>10</th>
<th>30</th>
<th>65</th>
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<tbody>
<tr>
<td>[nC₆₀] (mg/L)</td>
<td>65</td>
<td>19.5</td>
<td>2.6</td>
<td>0.47</td>
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<tr>
<td>Color</td>
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<tr>
<td>TEM image*</td>
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<tr>
<td>Mean diameter** (nm)</td>
<td>500</td>
<td>320</td>
<td>250</td>
<td>160</td>
</tr>
<tr>
<td>After centrifugation***</td>
<td></td>
<td></td>
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</table>

PHOTOCHEMICAL TRANSFORMATION OF AQUEOUS C₆₀ CLUSTERS IN SUNLIGHT
PHOTODEGRADATION OF nC_{60} 
BY UV\textsubscript{254} IRRADIATION

LEE ET AL. (2009). \textit{ENVIRON. SCI. TECHNOL.}
TRANSFORMATION OF AGGREGATED C\textsubscript{60} IN THE AQUEOUS PHASE BY UV IRRADIATION
PRODUCT CHARACTERIZATION: FTIR AND XPS

Transformation of aggregated C\textsubscript{60} in the aqueous phase by UV irradiation.
MULTIPLE PEAKS WITH 24 M/Z INTERVALS BELOW THE PARENT COMPOUND PEAK

C\textsubscript{60} WITH STEPWISE LOSS OF C2 FRAGMENTS DURING LDI

C\textsubscript{60} OXIDE WITH ETHER OR EPOXIDE FUNCTIONAL GROUPS

LEE ET AL. (2009). ENVIRON. SCI. TECHNOL.
TRANSFORMATION OF AGGREGATED C\textsubscript{60} IN THE AQUEOUS PHASE BY UV IRRADIATION
VARIOUS FORMS OF C$_{60}$ IN THE AQUEOUS PHASE

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THREE KNOWN PATHWAYS TO STABILIZE IN WATER
C$_{60}$ POROUS MEDIA TRANSPORT

LABORATORY ASSESSMENT OF THE MOBILITY OF NANOMATERIALS IN POROUS MEDIA
BIOLOGICAL DECOMPOSITION OF C₆₀

WHITE-ROT BASIDIOMYCETE-MEDIATED DECOMPOSITION OF C₆₀ FULLEROL
THESE WHITE ROT BASIDIOMYCETE FUNGI (*TRAMETES VERSICOLOR*, *PHLEBIA TREMELLOSA*) ARE CAPABLE OF INCORPORATING THE FULLEROL CARBON INTO FUNGAL BIOMASS, ALTHOUGH ONLY TO A SMALL DEGREE.

OXIDIZING SOME OF C$_{60}$ CAGE CARBON TO CO$_2$
OZONATED C₆₀: INTERACTION WITH E. COLI

OZONATED C₆₀ INACTIVATES E. COLI ONLY IN THE PRESENCE OF O₂ AND LIGHT

ESCHERICHIA COLI INACTIVATION BY WATER-SOLUBLE, OZONATED C₆₀ DERIVATIVE: KINETICS AND MECHANISMS
MECHANISM OF *E. COLI* INACTIVATION

EXTRACTED PROTEIN ASSAY USING SDS-PAGE AFTER 1 LOG INACTIVATION

- **M**: MARKER
- **P**: POSITIVE CONTROL
  - $O_3 + \text{EXCESS } H_2O_2$
- **N**: OZONATED nC$_{60}$
  - NITROGEN PURGING
- **O**: OZONATED nC$_{60}$

DEGRADATION OF INTRACELLULAR ENZYME

$\beta$-D-galactosidase (%)

WITH t-BuOH

WITHOUT t-BuOH

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<tr>
<th>Time (min)</th>
<th>0</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
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<tbody>
<tr>
<td>WITH t-BuOH</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WITHOUT t-BuOH</td>
<td>80</td>
<td>60</td>
<td>40</td>
<td>20</td>
<td>0</td>
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ESCHERICHIA COLI INACTIVATION BY WATER-SOLUBLE, OZONATED C$_{60}$ DERIVATIVE: KINETICS AND MECHANISMS
The minimal inhibitory concentrations of parent \( nC_{60} \) and the UV photolysis products for \( E. coli \)

<table>
<thead>
<tr>
<th>Concentration of ( C_{60} ) cluster (or UV-treated products) (mg/L)</th>
<th>UV illumination time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
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<tr>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>1</td>
<td>+</td>
</tr>
<tr>
<td>2</td>
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<td>4</td>
<td>-</td>
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<tr>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
</tr>
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</table>

Transformation of aggregated \( C_{60} \) in the aqueous phase by UV irradiation.
INTERACTION WITH VIRUS

MS2 INACTIVATION WITH PHOTOACTIVATED FULLEROL

\[ y = (-0.071 \pm 0.002)x \]
\[ R = 0.99 \]

Time (min)

\[ \log (N/N_0) \]

PHOTOSENSITIZATION PATHWAYS

INACTIVATION OF BACTERIOPHAGES VIA PHOTOSENSITIZATION OF FULLEROL NANOPARTICLES
# C$_{60}$ Derivative Application

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Abbreviation</th>
<th>$R'$</th>
<th>$R''$</th>
<th>Charge at pH 7</th>
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<tbody>
<tr>
<td>HC1</td>
<td>-CO$_2$H</td>
<td>-CO$_2$H</td>
<td>anionic</td>
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</tr>
<tr>
<td>HC2</td>
<td>-CO$_2$H</td>
<td></td>
<td>anionic</td>
<td></td>
</tr>
<tr>
<td>HC3</td>
<td>NHCH(CH$_2$OH)$_2$</td>
<td>NHCH(CH$_2$OH)$_2$</td>
<td>neutral</td>
<td></td>
</tr>
<tr>
<td>HC4</td>
<td>-CO$_2$(CH$_2$)$_2$NH$_3^+$CF$_3$CO$_2^-$</td>
<td>-CO$_2$(CH$_2$)$_2$NH$_3^+$CF$_3$CO$_2^-$</td>
<td>cationic</td>
<td></td>
</tr>
</tbody>
</table>


Photochemical and antimicrobial properties of novel C$_{60}$ derivatives in aqueous systems.
C_{60} DERIVATIVE APPLICATION

**E. coli Inactivation**

![Graph](image)

**MS2 Phage Inactivation**

![Graph](image)


Photochemical and antimicrobial properties of novel C_{60} derivatives in aqueous systems
QUANTUM DOTS WITH INTACT SURFACE COATINGS DECREASED GROWTH RATES OF B. SUBTILIS AND E. COLI BUT WERE NOT BACTERICIDAL.

WEATHERING OF QDS UNDER ACIDIC OR ALKALINE CONDITIONS SIGNIFICANTLY INCREASED BACTERICIDAL ACTIVITY DUE TO RAPID RELEASE OF CADMIUM AND SELENITE IONS FOLLOWING QD DESTABILIZATION UPON LOSS OF ORGANIC COATING.
BIODEGRADATION OF CARBON NANOTUBES by Horseradish Peroxidase/H₂O₂ over the period of several weeks.

Promising possibility for nanotubes be degraded in environmentally relevant settings (other peroxidases in plant and animals)

Biodegradation of single-walled carbon nanotubes through enzymatic catalysis
INFLUENCE OF HNO₃ CONCENTRATION ON THE EXTENT OF MWCNT SURFACE OXIDATION

SORPTION ISOTHERMS FOR NAPHTHALENE WITH MWCNT AND OXIDIZED MWCNT

INFLUENCE OF SURFACE OXIDES ON THE ADSORPTION OF NAPHTHALENE ONTO MULTIWALLED CARBON NANOTUBES