NATIONAL NANOTECHNOLOGY INITIATIVE WORKSHOP
NANOMATERIALS AND THE ENVIRONMENT
OCTOBER 6-7, 2009

CHEMICAL TRANSFORMATION OF CARBONACEOUS NANOMATERIALS IN NATURAL AND ENGINEERED ENVIRONMENT

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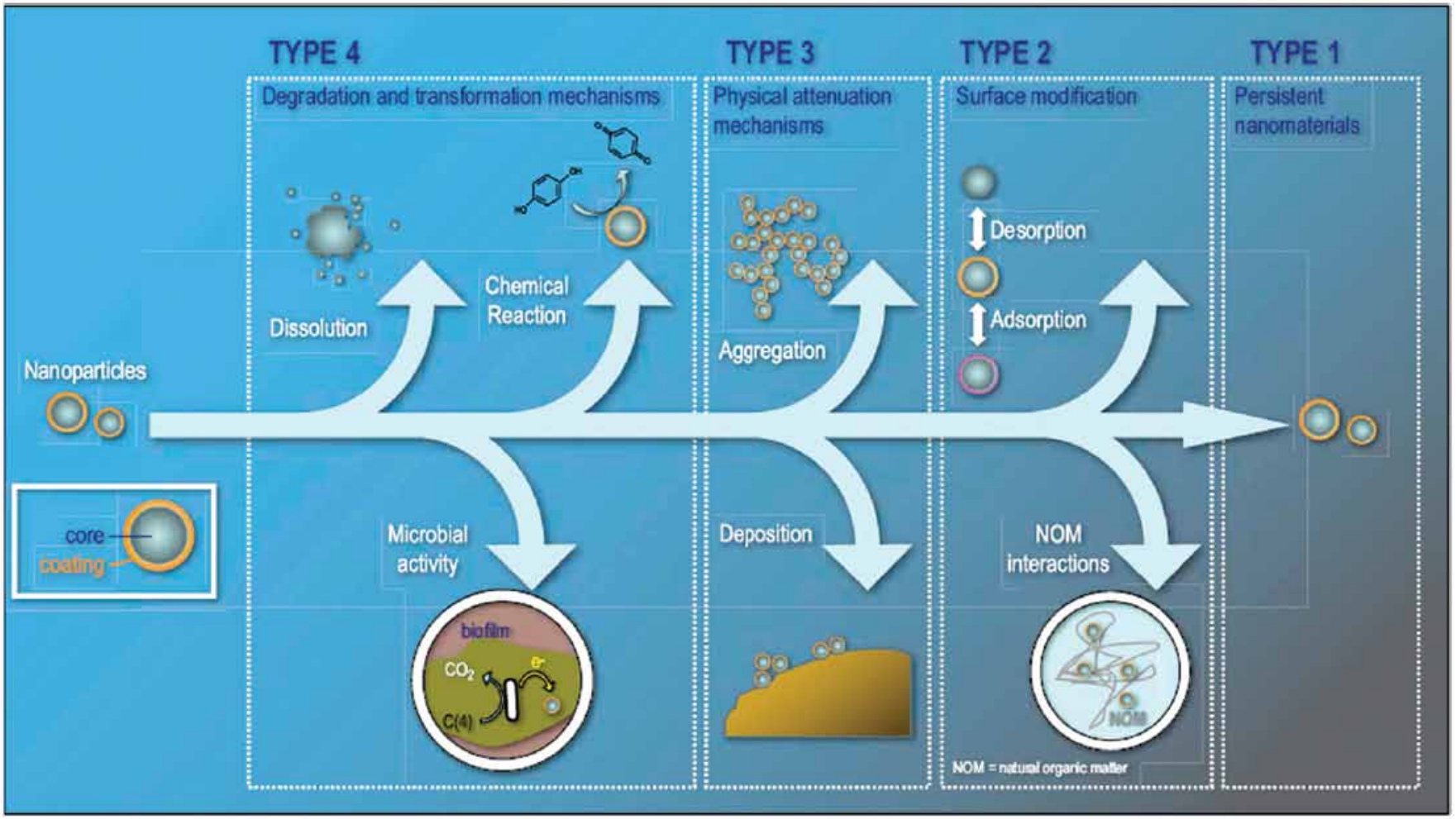
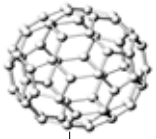
Georgia Institute of Technology

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

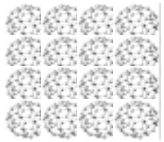
VARIOUS FORMS OF C_{60} IN THE AQUEOUS PHASE



STRONG PHOTOSENSITIZER
HIGH RADICAL REACTIVITY

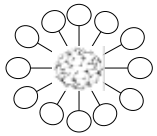
THREE KNOWN PATHWAYS TO STABILIZE IN WATER

1. AGGREGATE FORMATION



WATER STABLE COLLOIDS OF UNDERIVATIZED C_{60}
LOST MOST OF INTRINSIC C_{60} MOLECULAR PROPERTIES

2. SURFACE ENCAPSULATION (SURFACTANT)

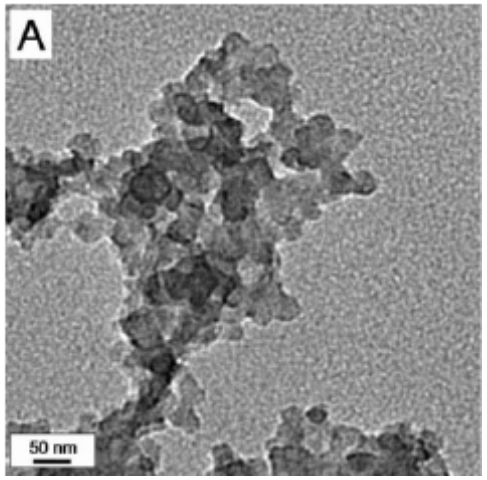


CLOSE TO MOLECULAR C_{60} IN PHOTOCHEMICAL AND CHEMICAL REACTIVITY

3. HYDROPHILIC FUNCTIONALIZATION

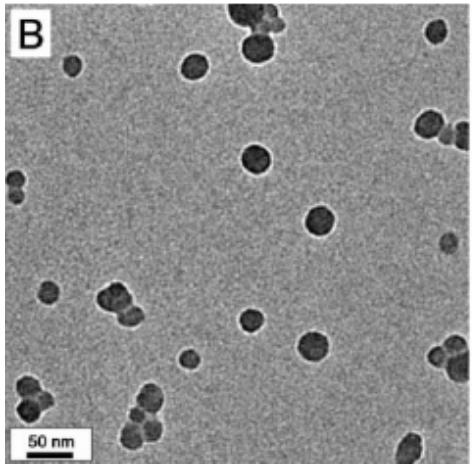
MOLECULARLY DISPERSED OR SMALL AGGREGATES
VARYING CHEMICAL AND PHOTOCHEMICAL PROPERTIES

VARIOUS FORMS OF nC_{60}



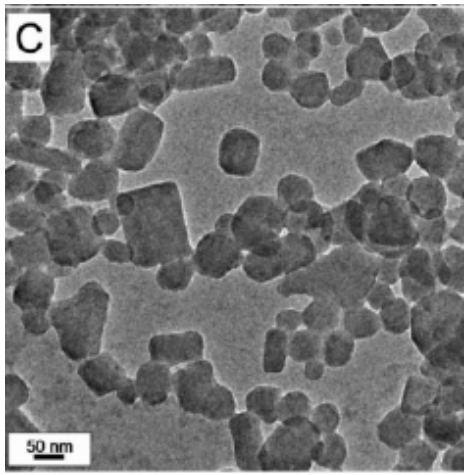
AQUA/nC_{60}

MIXING DRY C_{60} WITH WATER
FOR EXTENDED PERIOD



SON/nC_{60}

SONICATING BINARY
MIXTURE OF C_{60}/TOLUENE
AND WATER



THF/nC_{60}

EXCHANGING
ORGANIC SOLVENT (THF)
WITH WATER

LYON, D.Y., ALVAREZ, P.J. (2006). *ENVIRON. SCI. TECHNOL*
ANTIBACTERIAL ACTIVITY OF FULLERENE WATER SUSPENSIONS: EFFECTS OF PREPARATION METHOD AND PARTICLE SIZE

C_{60} AGGREGATES IN WATER: BRIEF REVIEW

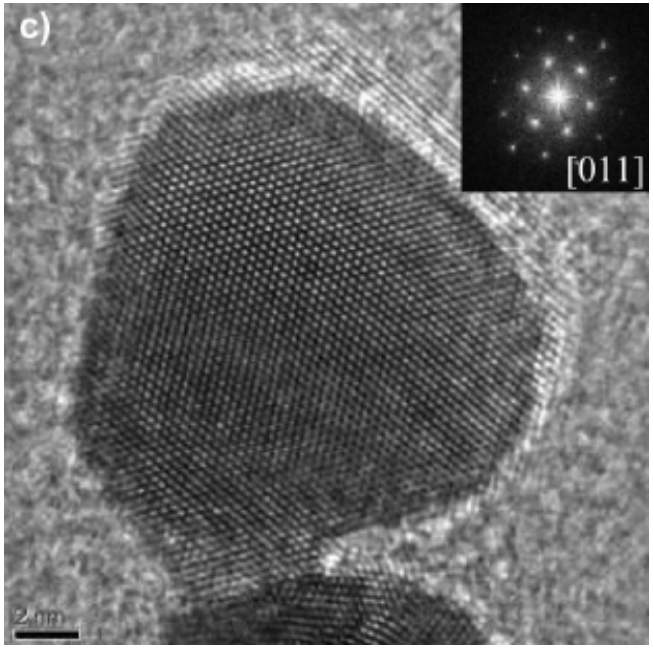
nC_{60} CAN BE PREPARED VIA **VARIOUS METHODS**

nC_{60} IS COMPRISED OF PRIMARILY OF **UNDERIVATIZED** C_{60}

DIFFRACTION ANALYSES INDICATE **CRYSTALLINE NATURE**

NEGATIVELY CHARGED SURFACE (ξ POTENTIAL = - 36 mV)

nC_{60} IS **STABLE** AT LOW IONIC STRENGTH



DUNCAN *ET AL*. *ES&T* 2008

ENVIRONMENTALLY RELEVANT REACTIONS AND CHEMICAL TRANSFORMATIONS

PHOTOSENSITIZATION (ROS PRODUCTION)

HYDROXYL RADICAL

ELECTRON REDUCTION/ABSORPTION (REDOX)

OZONATION (CHLORINATION)

PHOTOLYSIS (UV AND VISIBLE)

BIODEGRADATION

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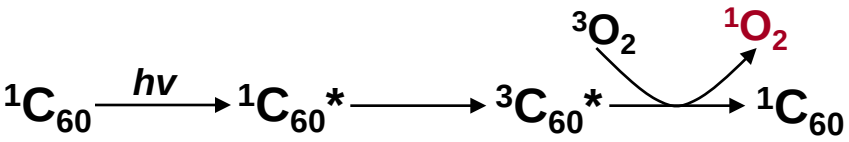
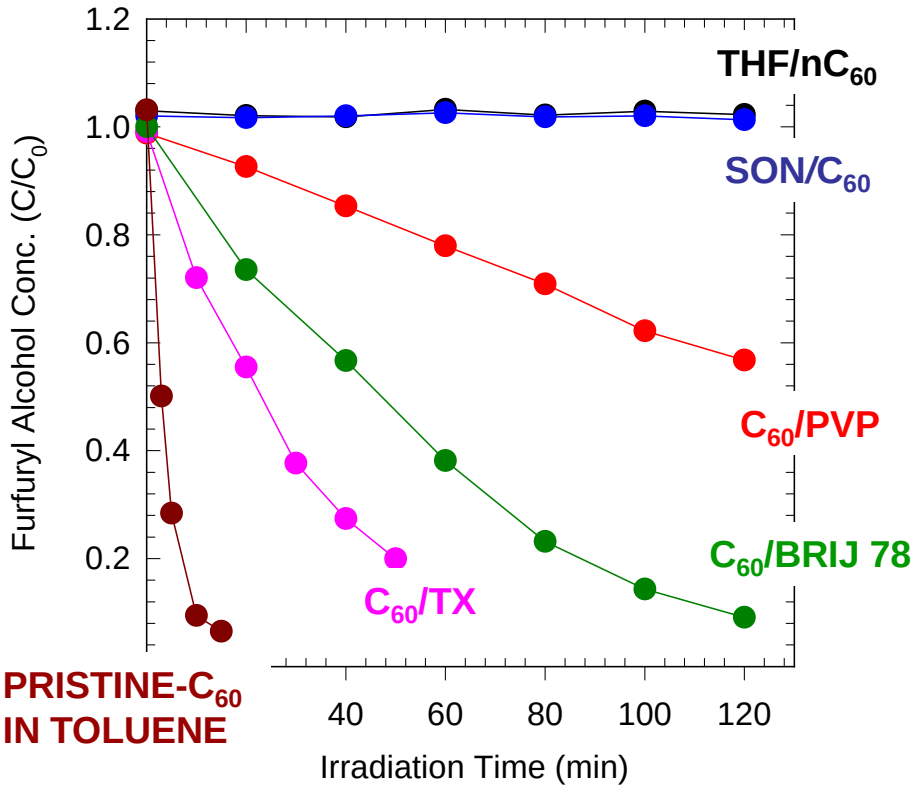
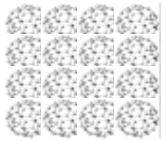
COMPARING PHOTOACTIVITY OF VARIOUS C_{60} SAMPLES

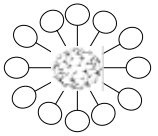




DISPERSED AS AGGREGATES



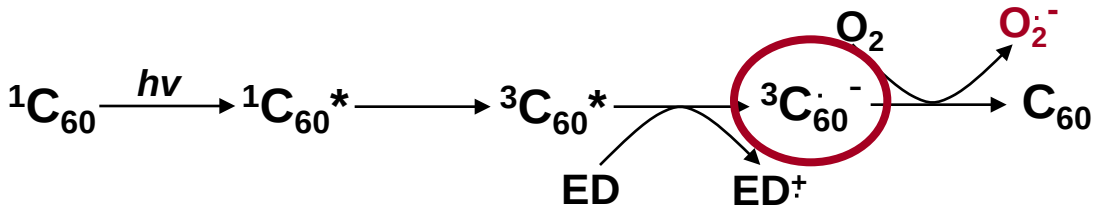
MOLECULARLY DISPERSED

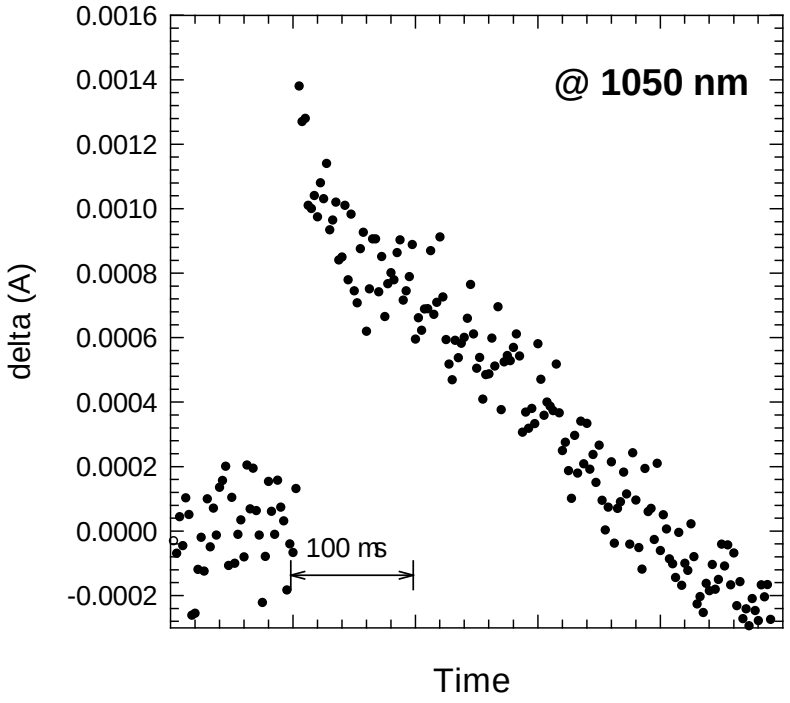


LEE, J., FORTNER, J.D., HUGHES, J.B., KIM, J.H. (2007) *ENVIRON. SCI. TECHNOL*
PHOTOCHEMICAL PRODUCTION OF REACTIVE OXYGEN SPECIES BY C_{60} IN THE AQUOUES PHASE DURING UV IRRADIATION

C_{60} AS AN ELECTRON ACCEPTOR

NANOSECOND TRANSIENT SPECTROSCOPY





C_{60} RADICAL ANION WAS DETECTED **ONLY WHEN DISPERSED VIA SURFACTANT MICELLES** (TX100 APPLIED ABOVE C.M.C.)

C_{60} RADICAL ANION WITH ANY DETECTABLE LIFE-TIME WAS NOT DETECTED FOR OTHER C_{60} SAMPLES

LEE, J., YAMAKOSHI, Y., HUGHES, J.B., KIM, J.H. (2008) *ENVIRON. SCI. TECHNOL*
MECHANISM OF C_{60} PHOTOREACTIVITY IN WATER: FATE OF TRIPLET STATE AND RADICAL ANION AND PRODUCTION OF REACTIVE OXYGEN SPECIES

RADICAL REACTIVITY OF C_{60} AGGREGATE

PULSE AND GAMMA RADIOLYSIS

UNDER N_2-SATURATED CONDITION

$$e_{aq}^- + A \longrightarrow A\bullet^-$$

$$(CH_3)_2CHOH + \bullet OH \longrightarrow (CH_3)_2C\cdot OH + H_2O$$

$$(CH_3)_2CHOH + H\bullet \longrightarrow (CH_3)_2C\cdot OH + H_2$$

UNDER N_2O-SATURATED CONDITION

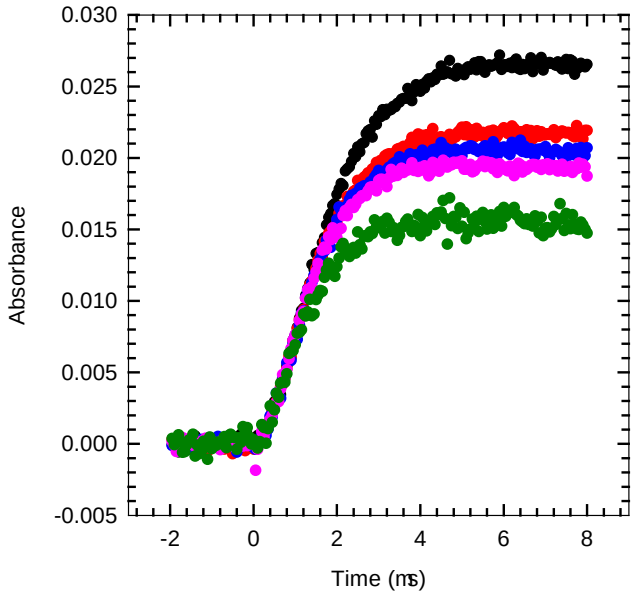
$$e_{aq}^- + N_2O + H_2O \longrightarrow N_2 + OH^- + \bullet OH$$

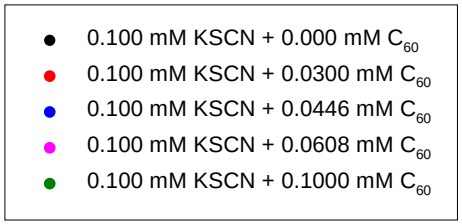
$$H\bullet + N_2O \longrightarrow N_2 + \bullet OH$$

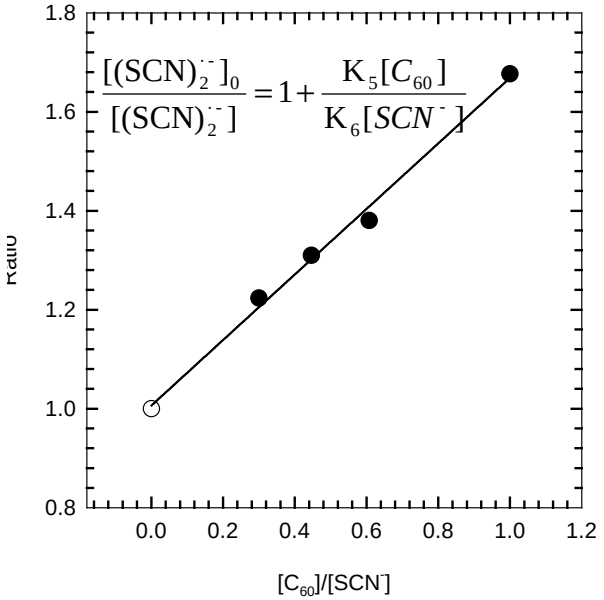
REACTIVITY OF nC_{60} WITH OH RADICAL

$$C_{60} + OH\bullet \xrightarrow{k_5} intermediate$$

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







$$\frac{[(SCN)_2^{\bullet-}]_0}{[(SCN)_2^{\bullet-}]} = 1 + \frac{K_5[C_{60}]}{K_6[SCN^-]}$$

SECOND-ORDER RATE CONSTANT = 7.34 ± 0.31 x 10^9 $M^{-1}s^{-1}$.

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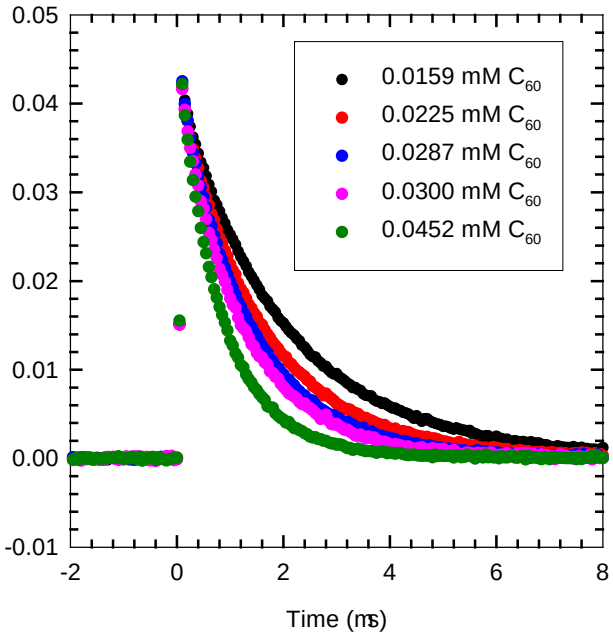
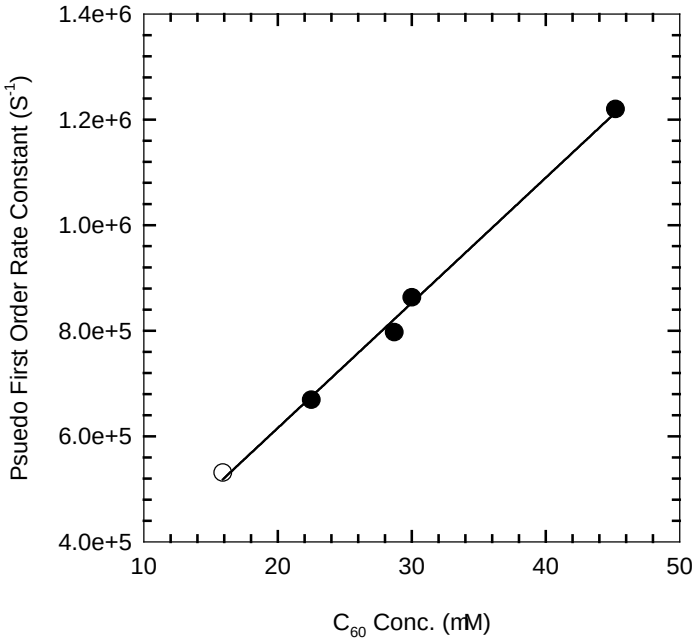
REACTIVITY OF nC_{60} WITH HYDRATED ELECTRONS

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 ± 0.02 x 10^{10} $M^{-1}s^{-1}$

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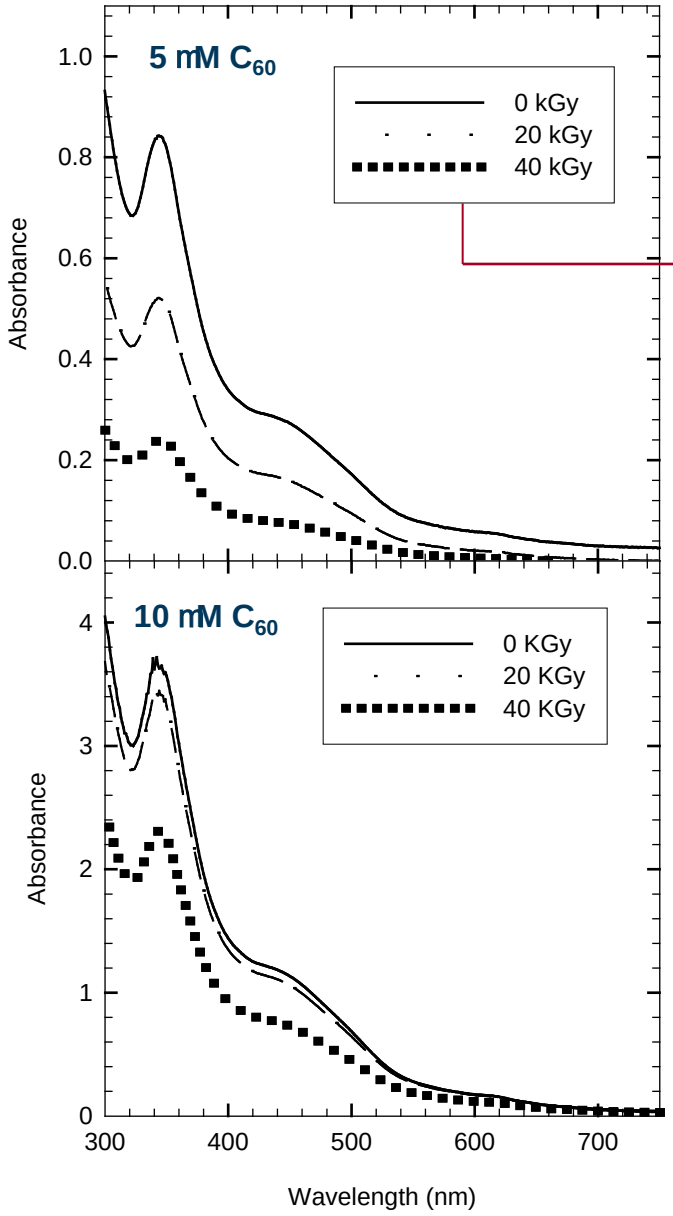
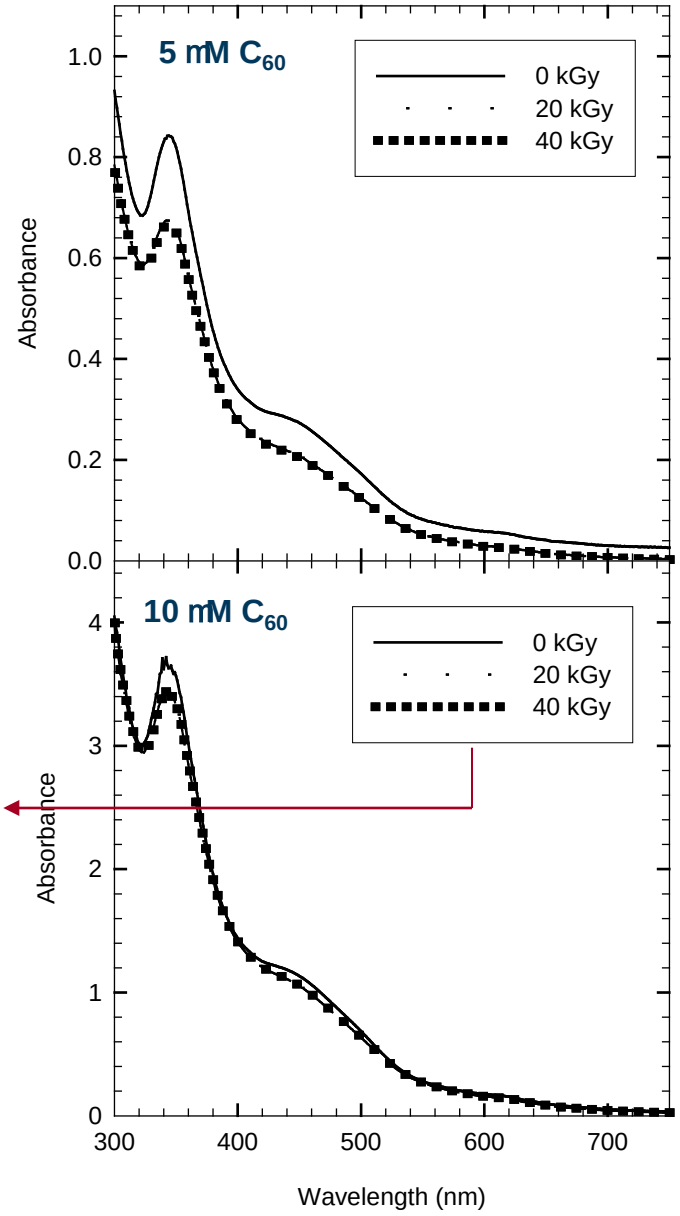
g-RADIOLYSIS STUDY



N_2O SATURATED CORRESPOND TO 11 AND 22 mM OF $^{\bullet}OH$

N_2 SATURATED CORRESPOND TO 5.4 and 11.8 mM OF e_{aq}^-



XPS ANALYSIS RESULT

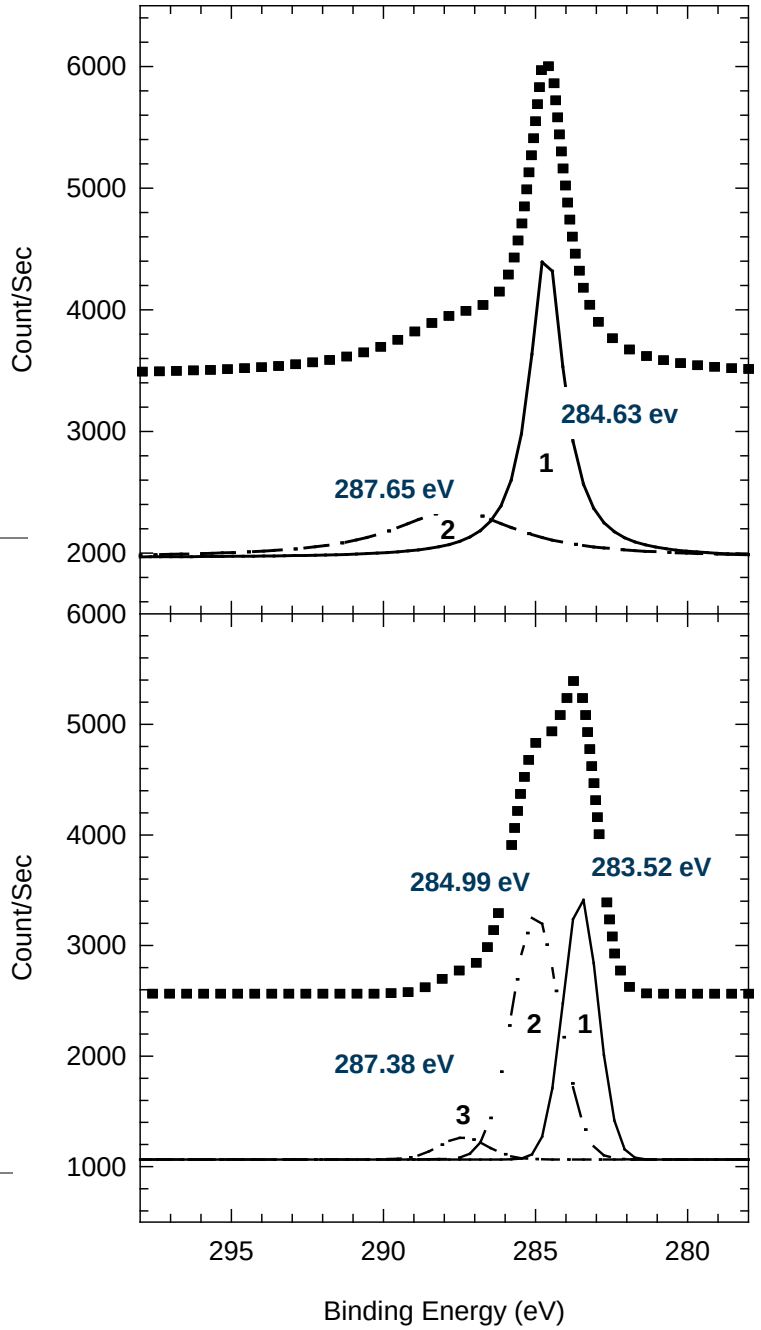
ON g-RADIOLYSIS PRODUCT

N_2O 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%



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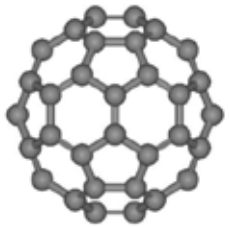
QUANTUM MECHANICAL INVESTIGATION

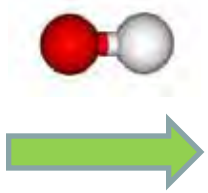
SINGLE C_{60} MOLECULE

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	HOMO = -6.683 eV	HOMO = -8.565 eV
LUMO = -7.770 eV	LUMO = -0.599 eV	LUMO = -8.252 eV
-2263.053334 Ha	**-75.140423 Ha**	**-2338.26528 Ha**

$$\Delta E_{binding} = E_{\bullet C60\text{-}OH} - (E_{C60} + E_{\bullet OH})$$

$$= -44.88 \text{ kcal/mol}$$

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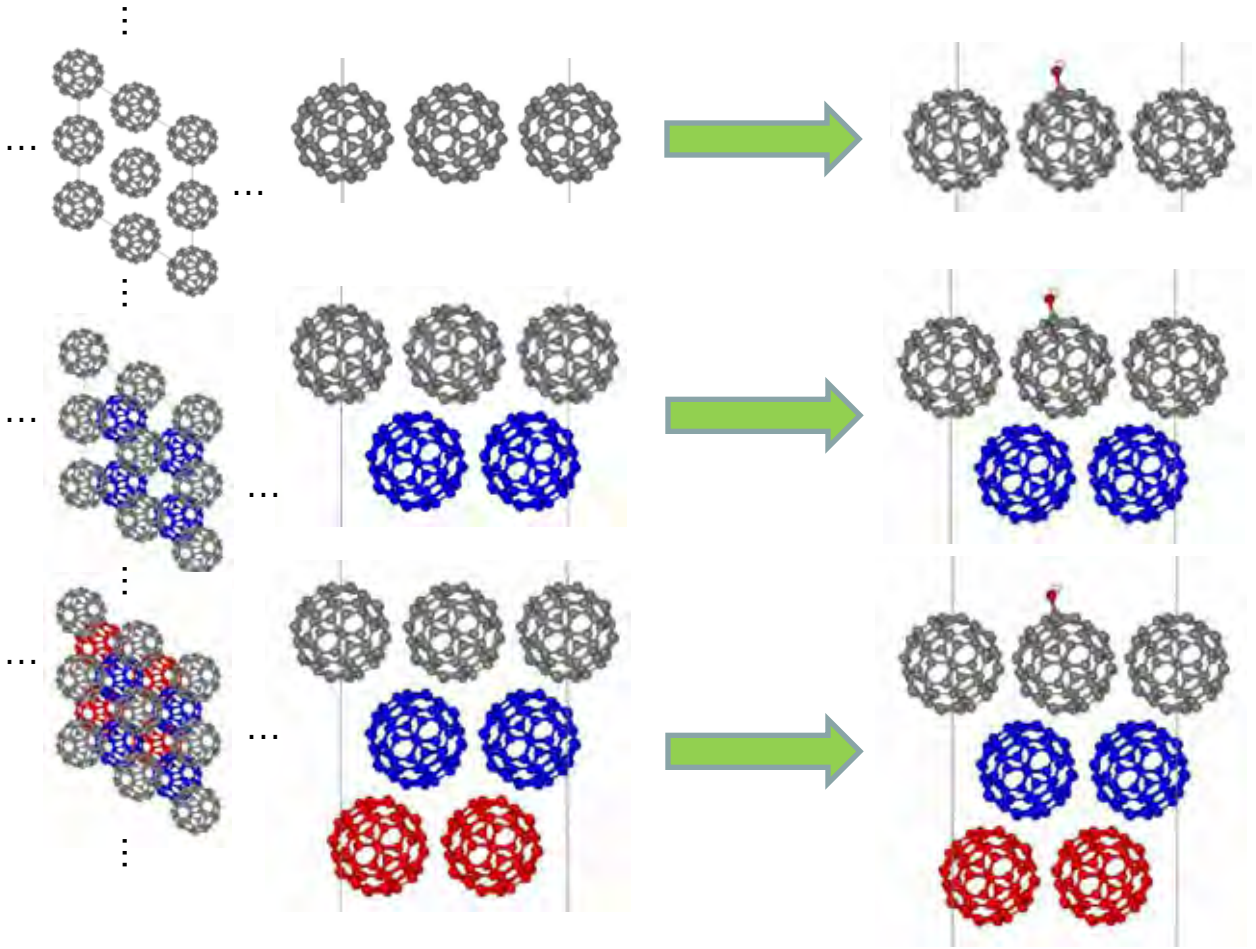
MODELING C_{60} CLUSTERS

TOP VIEW SIDE VIEW



1-INFINITE LAYER

$\Delta E_{binding}$= - 44.72 kcal/mol

2-INFINITE LAYER

$\Delta E_{binding}$= - 17.23 kcal/mol

3-INFINITE LAYER

$\Delta E_{binding}$= 51.37 kcal/mol

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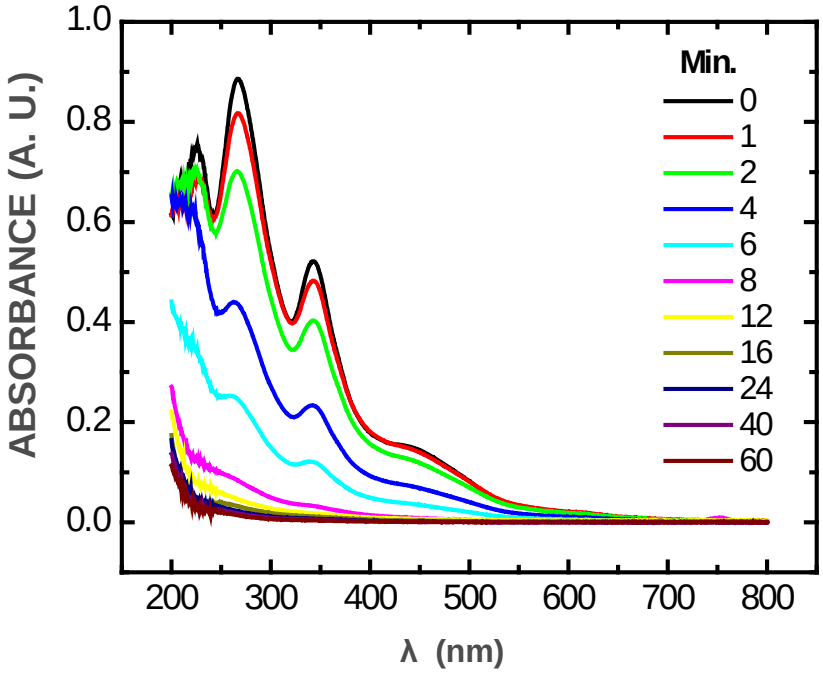
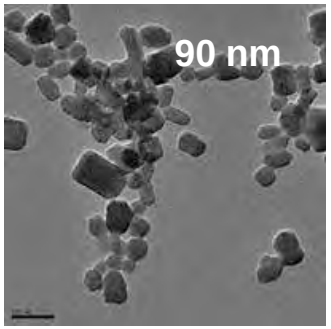
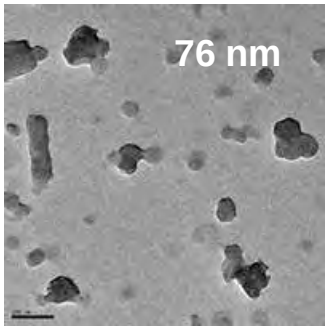
REACTION WITH O_3 IN THE AQUEOUS PHASE

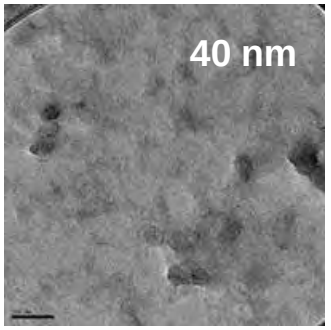




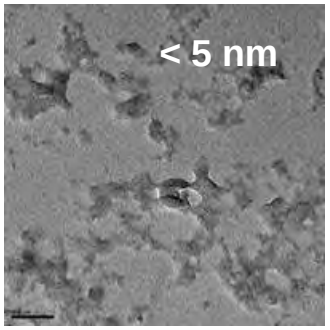
t = 0 min
CT = 0 mg-min/L



t = 5 min
CT = 6.6 mg-min/L



t = 15 min
CT = 28.5 mg-min/L

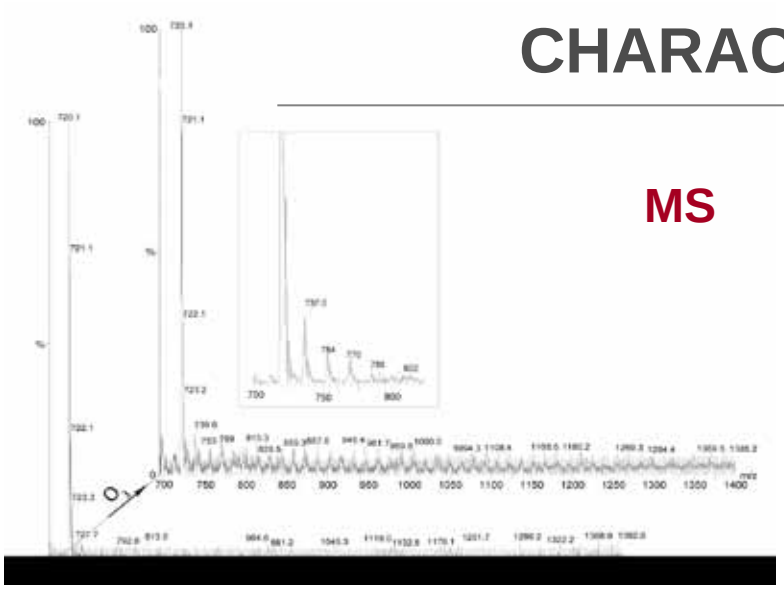


t = 30-60 min
CT = 74 - 150 mg-min/L

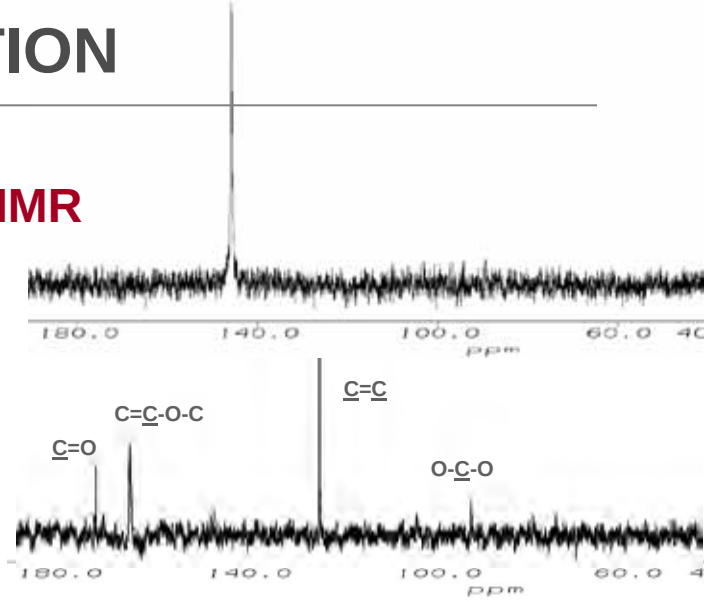
FORTNER ET AL. (2007). *ENVIRON. SCI. TECHNOL*
REACTION OF WATER-STABLE C_{60} AGGREGATES WITH OZONE

PRODUCT CHARACTERIZATION

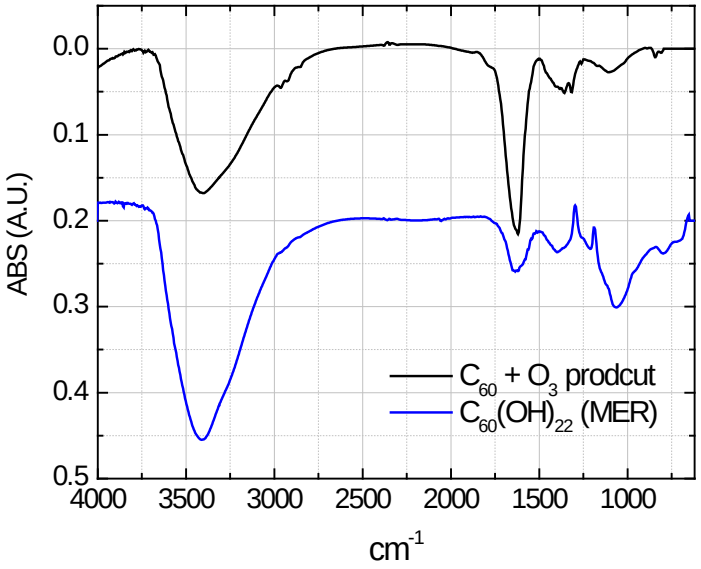
MS



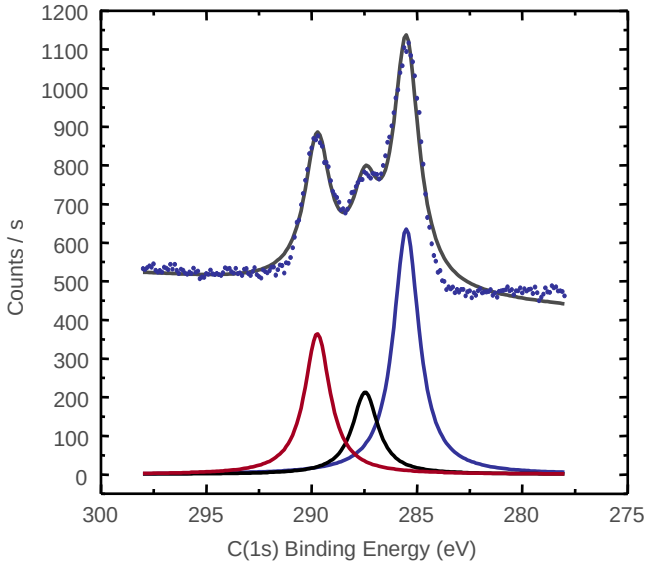
^{13}C NMR



FTIR

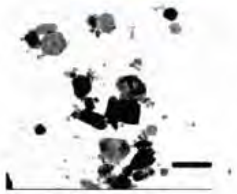
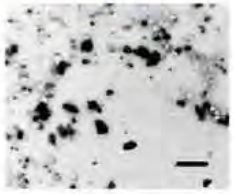
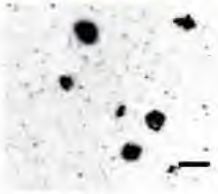
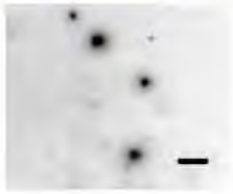


XPS



PHOTOCHEMICAL TRANSFORMATION IN SUNLIGHT

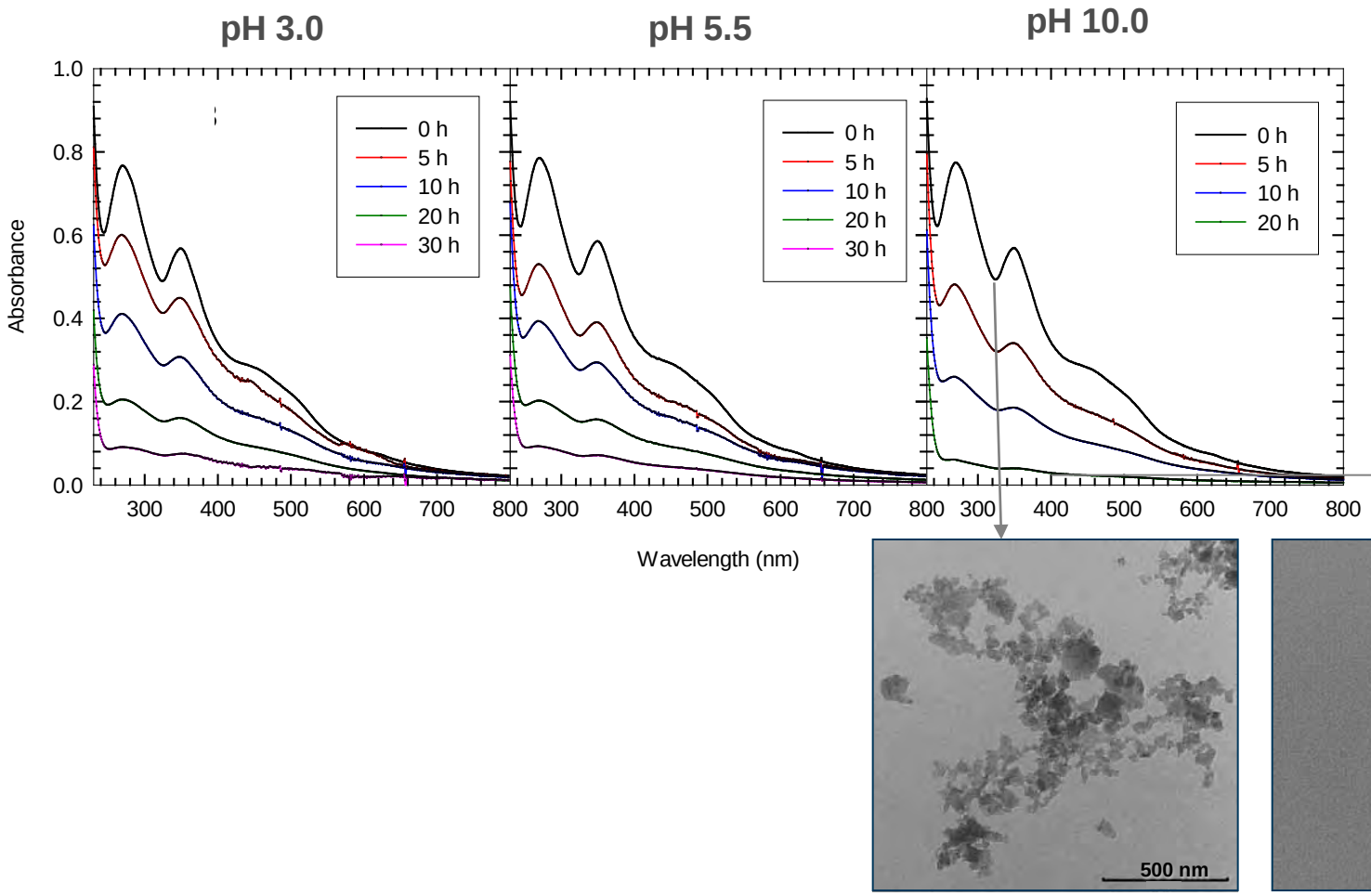
65 mg/L THF/nC_{60} IN LAMP LIGHT (l = 350 ± 50 nm)

Time (days)	0	10	30	65
[nC_{60}] (mg/L)	65	19.5	2.6	0.47
Color				
TEM image*				
Mean diameter** (nm)	500	320	250	160
After centrifugation***				

HOU, W.C., JAFVERT, C.T. (2009). *ENVIRON. SCI. TECHNOL.*
PHOTOCHEMICAL TRANSFORMATION OF AQUEOUS C60 CLUSTERS IN SUNLIGHT

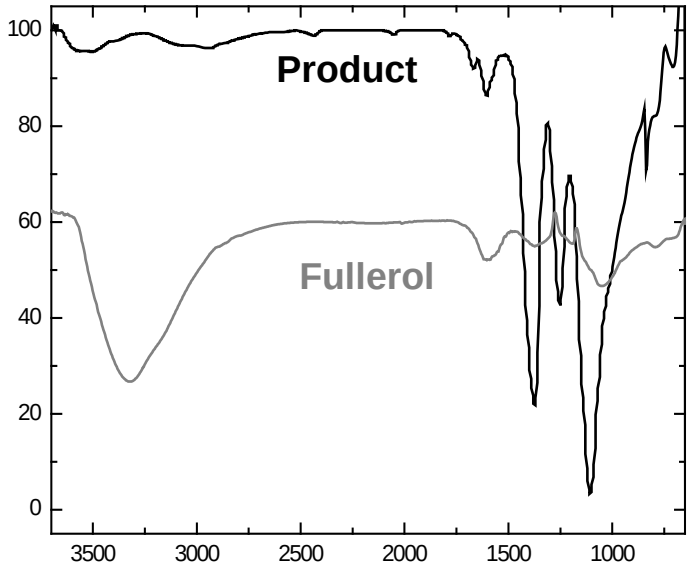
PHOTODEGRADATION OF nC_{60}

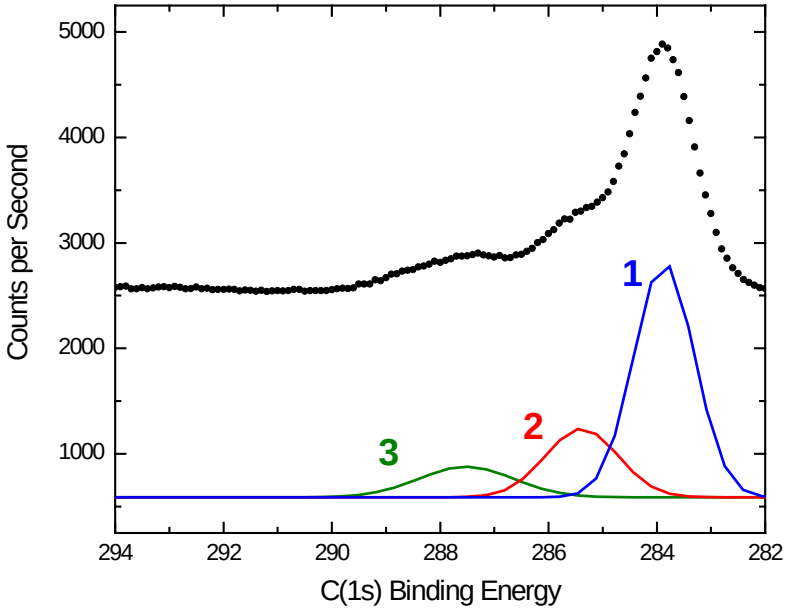
BY UV_{254} IRRADIATION



LEE ET AL. (2009). *ENVIRON. SCI. TECHNOL.*
TRANFORMATION OF AGGREGATED C_{60} IN THE AQUEOUS PHASE BY UV IRRADIATION

PRODUCT CHARACTERIZATION: FTIR AND XPS





Peak	Position	Area	% C(1s)	Carbon-ID
1	283.87	3112.2	64%	Underivatized C
2	285.39	1091.5	23%	Mono-oxidized C
3	287.52	638.39	13%	Di-oxidized C

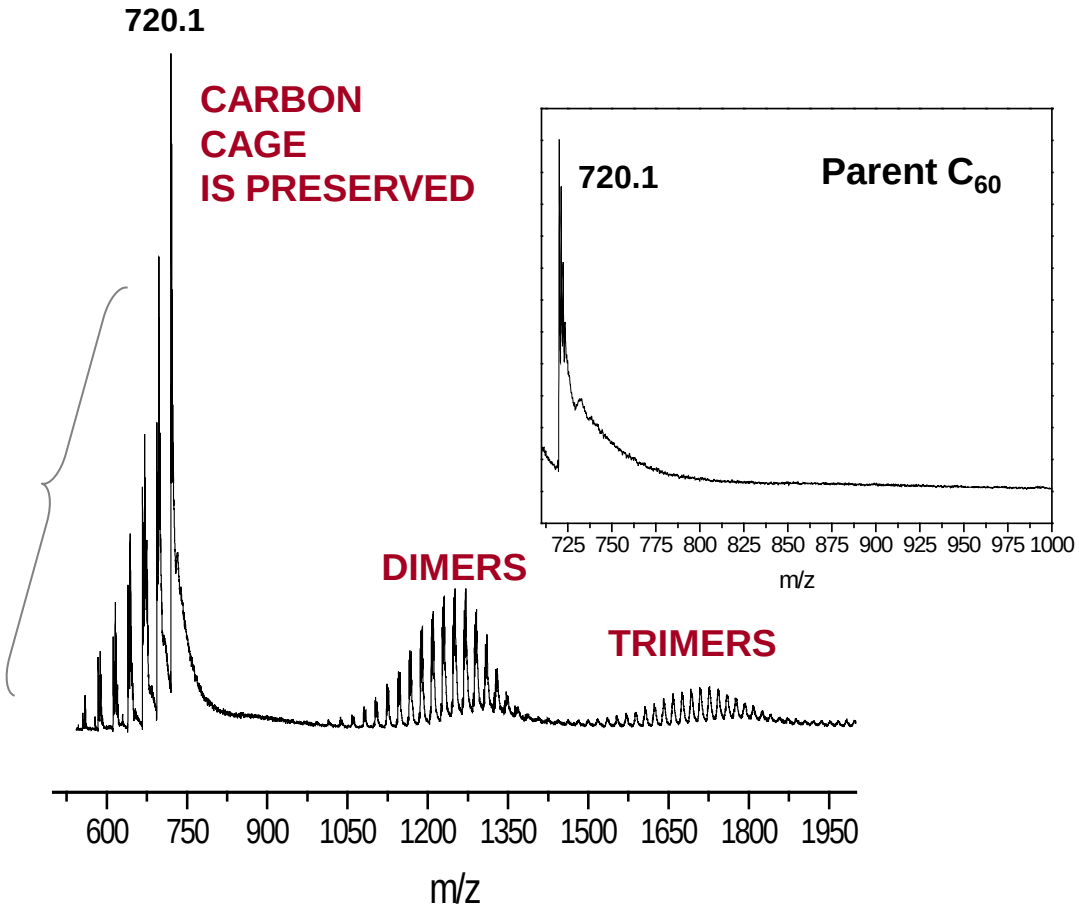
LEE ET AL. (2009). *ENVIRON. SCI. TECHNOL.*
TRANFORMATION OF AGGREGATED C_{60} IN THE AQUEOUS PHASE BY UV IRRADIATION

PRODUCT CHARACTERIZATION: LDI-MS

MULTIPLE PEAKS WITH **24 M/Z INTERVALS** BELOW THE PARENT COMPOUND PEAK

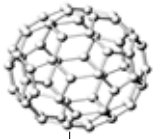
C_{60} WITH **STEPWISE LOSS OF C2 FRAGMENTS** DURING LDI

C_{60} OXIDE WITH **ETHER** OR **EPOXIDE** FUNCTIONAL GROUPS



LEE ET AL. (2009). *ENVIRON. SCI. TECHNOL.*
TRANFORMATION OF AGGREGATED C_{60} IN THE AQUEOUS PHASE BY UV IRRADIATION

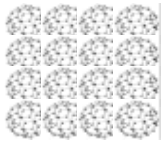
VARIOUS FORMS OF C_{60} IN THE AQUEOUS PHASE



STRONG PHOTOSENSITIZER
HIGH RADICAL REACTIVITY

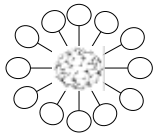
THREE KNOWN PATHWAYS TO STABILIZE IN WATER

1. AGGREGATE FORMATION



WATER STABLE COLLOIDS OF UNDERIVATIZED C_{60}
LOST MOST OF INTRINSIC C_{60} MOLECULAR PROPERTIES

2. SURFACE ENCAPSULATION (SURFACTANT)

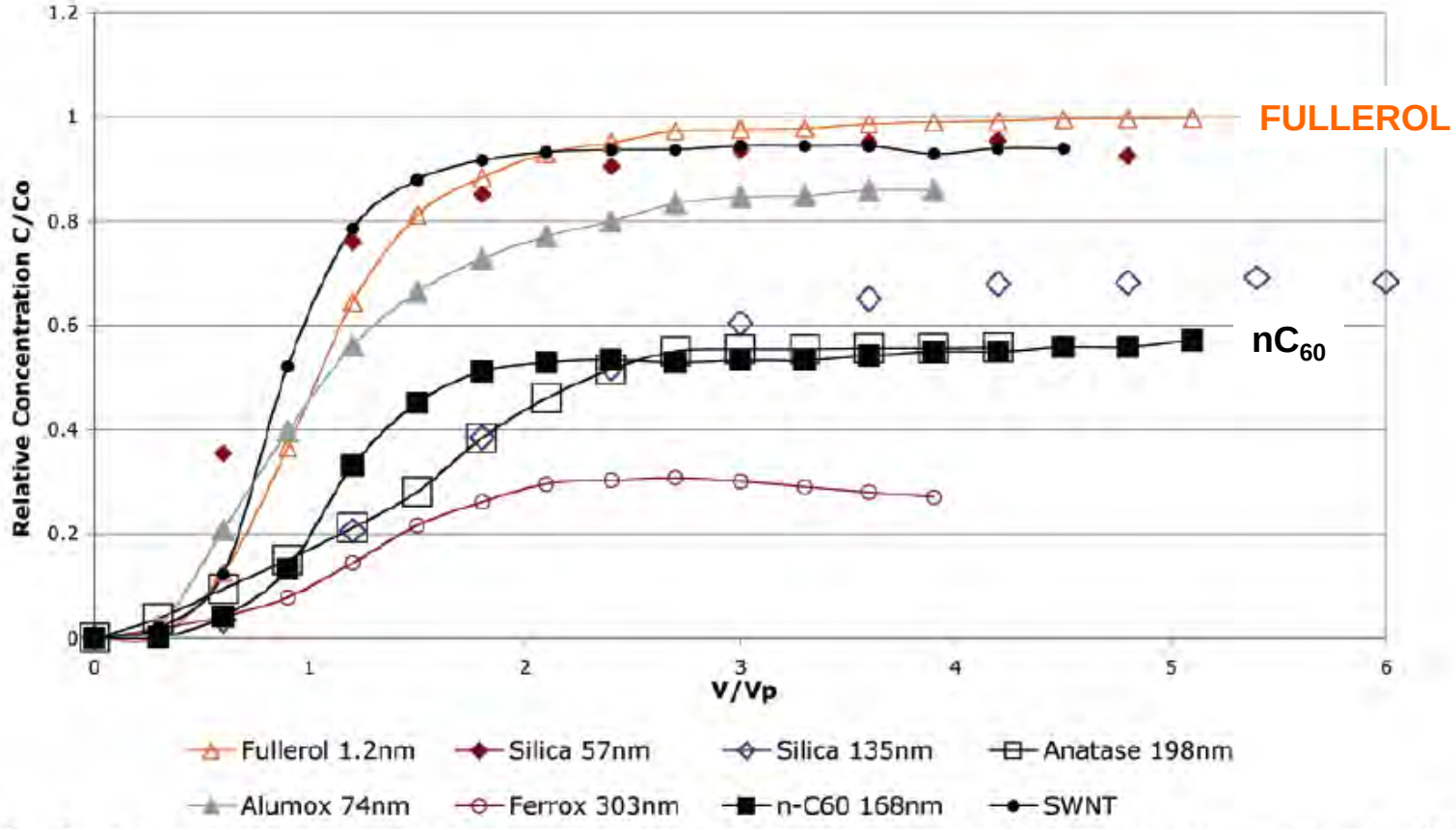


CLOSE TO MOLECULAR C60 IN PHOTOCHEMICAL AND CHEMICAL REACTIVITY

3. HYDROPHILIC FUNCTIONALIZATION

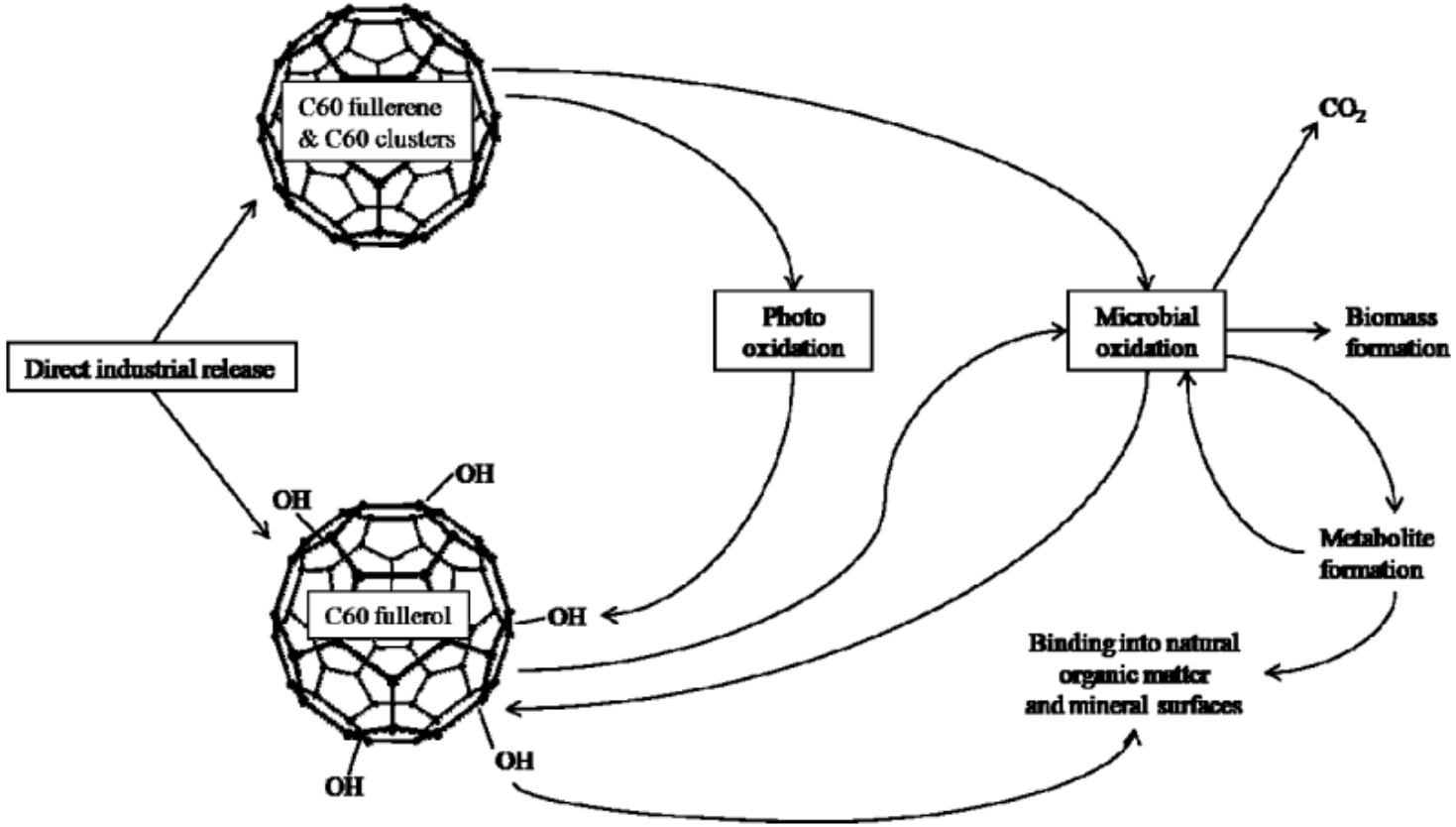
MOLECULARLY DISPERSED OR SMALL AGGREGATES
VARYING CHEMICAL AND PHOTOCHEMICAL PROPERTIES

C_{60} POROUS MEDIA TRANSPORT



LECOANET, H.F., BOTEERO, J., WIESNER, M.R. (2004) *ENVIRON. SCI. TECHNOL*
LABORATORY ASSESSMENT OF THE MOBILITY OF NANOMATERIALS IN POROUS MEDIA

BIOLOGICAL DECOMPOSITION OF C_{60}



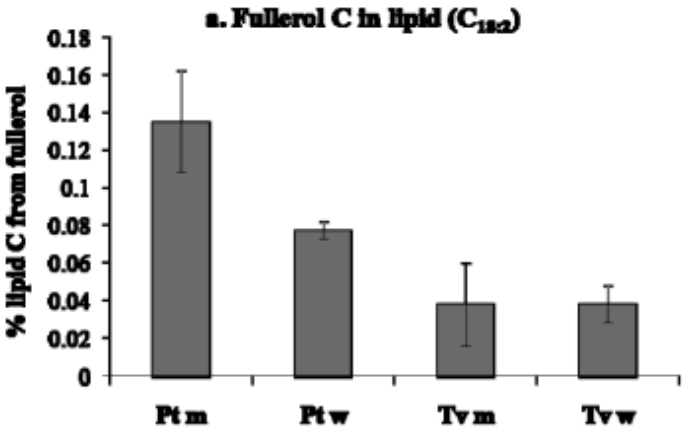
SHCREINER, K. M., FILLEY, T. R. ET AL. (2009) *ENVIRON. SCI. TECHNOL*
WHITE-ROT BASIDIOMYCETE-MEDIATED DECOMPOSITION OF C_{60} FULLEROL

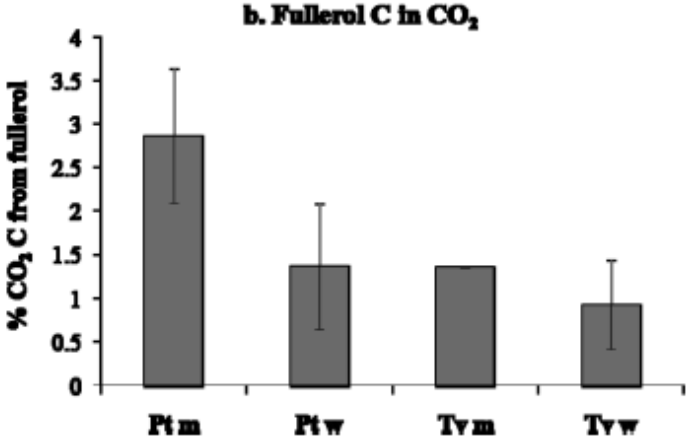
BIOLOGICAL DECOMPOSITION OF C_{60}

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

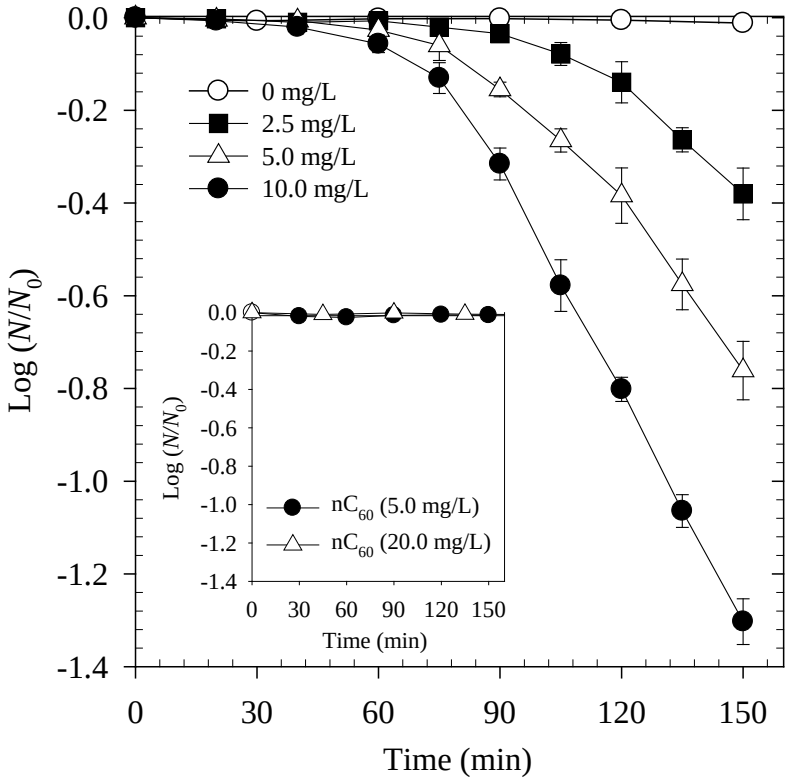
OXIDIZING SOME OF C_{60} CAGE CARBON TO CO_2



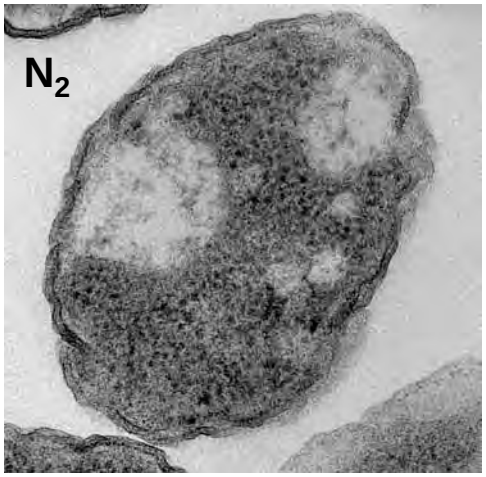


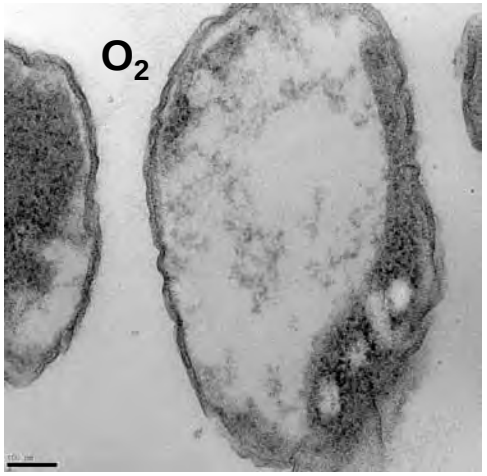
SHCREINER, K. M., FILLEY, T. R. ET AL. (2009) *ENVIRON. SCI. TECHNOL*
WHITE-ROT BASIDIOMYCETE-MEDIATED DECOMPOSITION OF C_{60} FULLEROL

OZONATED C_{60}: INTERACTION WITH *E.COLI*



OZONATED C_{60} INACTIVATES *E. COLI* ONLY IN THE PRESENCE OF O_2 AND LIGHT

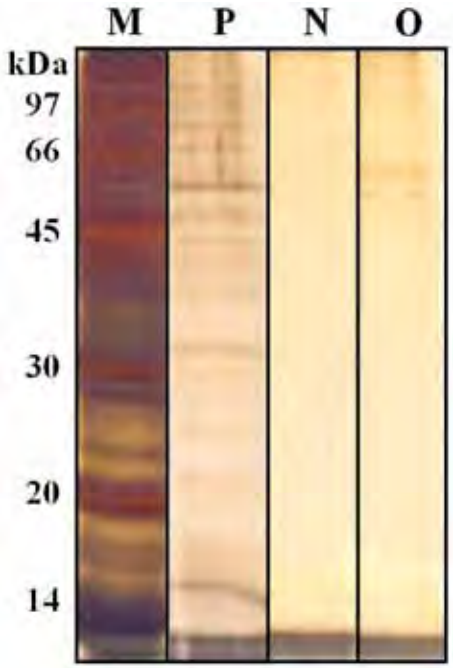




CHO, M. FORTNER, J.D., HIGHES, J.B., KIM, J.H. (2009) *ENVIRON. SCI. TECHNOL*
ESCHERICHIA COLI INACTIVATION BY WATER-SOLUBLE, OZONATED C_{60} DERIVATIVE: KINETICS AND MECHANISMS

MECHANISM OF *E.COLI* INACTIVATION

EXTRACTED PROTEIN ASSAY USING SDS-PAGE AFTER 1 LOG INACTIVATION



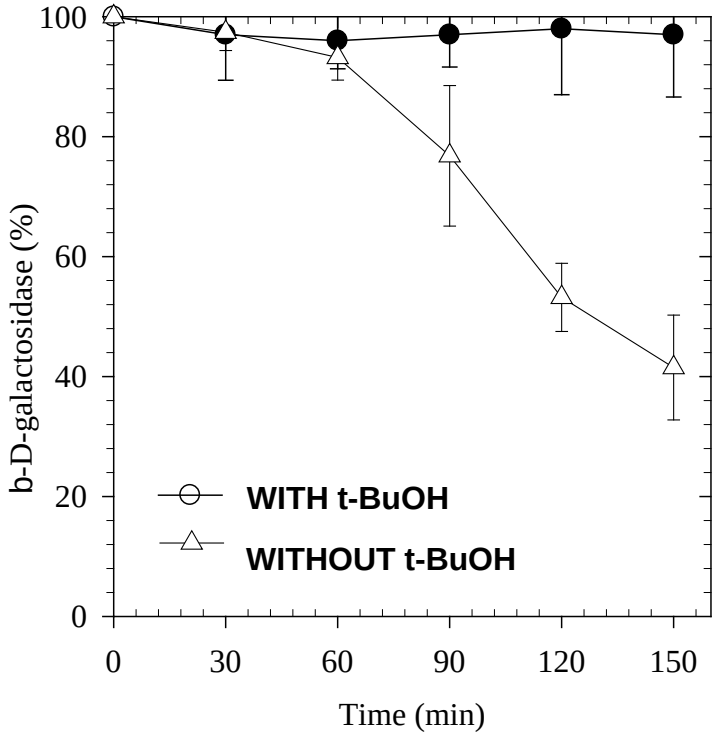
M: MARKER

P: POSITIVE CONTROL
O_3 + EXCESS H_2O_2

N: OZONATED nC_{60}
NITROGEN PURGING

O: OZONATED nC_{60}

DEGRADATION OF INTRACELLULAR ENZYME



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ESCHERICHIA COLI INACTIVATION BY WATER-SOLUBLE, OZONATED C_{60} DERIVATIVE: KINETICS AND MECHANISMS

TOXICITY OF UV PHOTOLYSIS PRODUCT

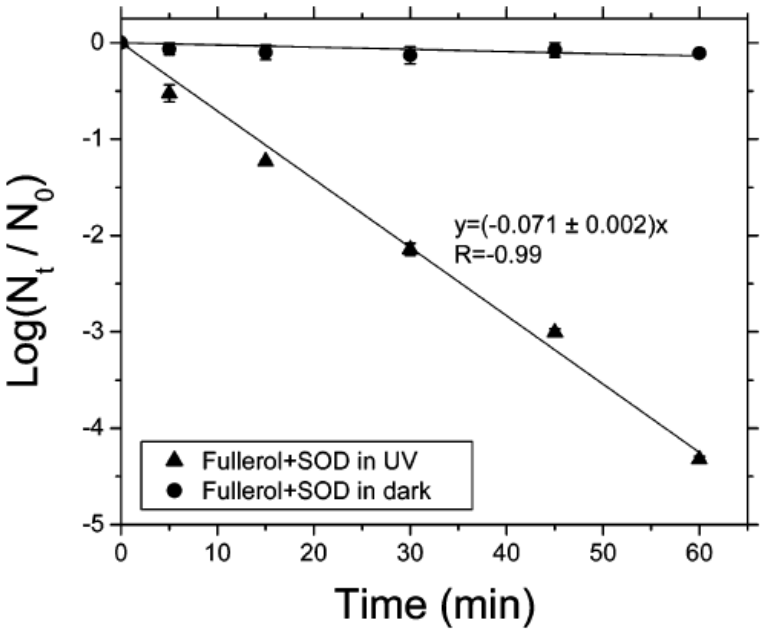
THE **MINIMAL INHIBITORY CONCENTRATIONS** OF PARENT nC_{60} AND THE UV PHOTOLYSIS PRODUCTS FOR *E.COLI*

CONCENTRATION OF C_{60} CLUSTER (OR UV-TREATED PRODUCTS) (mg/L)	UV ILLUMINATION TIME (hr)					
	0	25	50	70	90	110
0	+	+	+	+	+	+
1	+	+	+	+	+	+
2	-	-	+	+	+	+
4	-	-	-	+	+	+
6	-	-	-	+	+	+
8	-	-	-	-	+	+
10	-	-	-	-	-	+

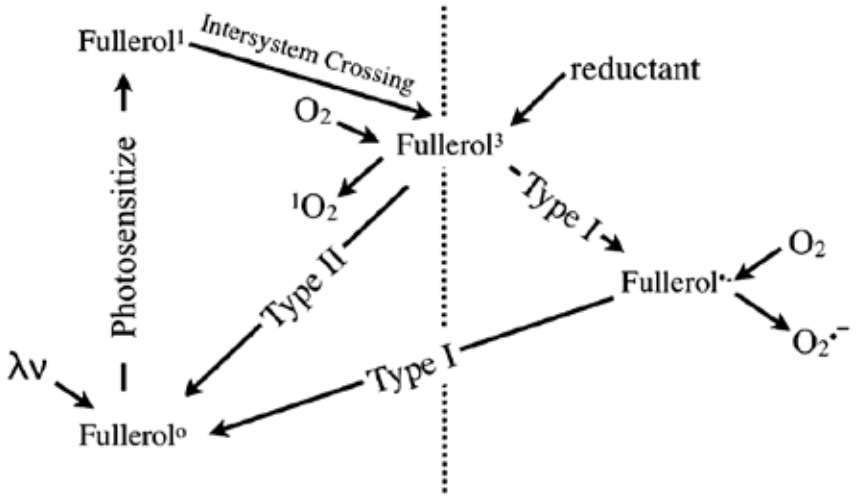
LEE, J. CHO, M. FORTNER, J.D., HIGHES, J.B., KIM, J.H. (2009) *ENVIRON. SCI. TECHNOL*
TRANSFORMATION OF AGGREGATED C_{60} IN THE AQUEOUS PHASE BY UV IRRADIATION

INTERACTION WITH VIRUS

MS2 INACTIVATION WITH PHOTOACTIVATED FULLEROL



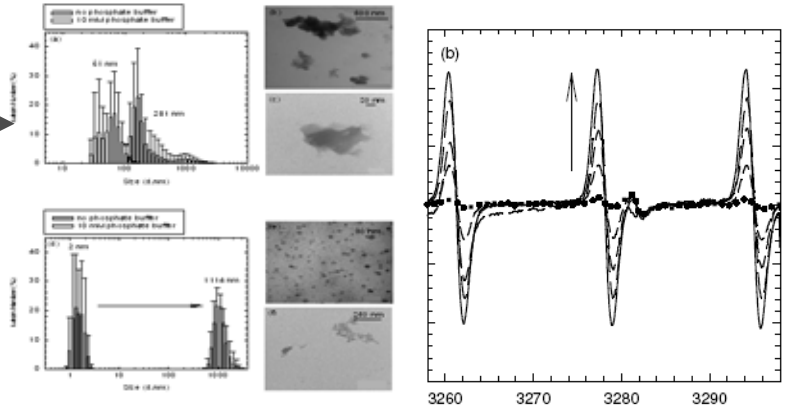
PHOTOSENSITIZATION PATHWAYS



BRADIREDDY, A.R. ALVAREZ, P.J., WIESNER, M.R. (2007) *ENVIRON. SCI. TECHNOL*
INACTIVATION OF BACTERIOPHAGES VIA PHOTOSENSITIZATION OF FULLEROL NANOPARTICLES

C_{60} DERIVATIVE APPLICATION

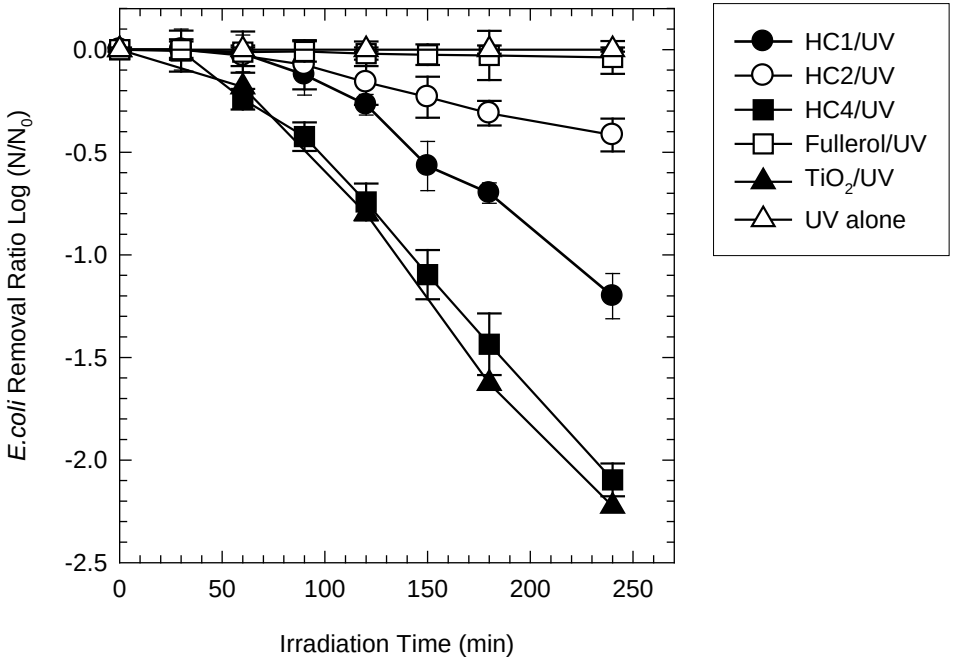
Chemical Structure	Abbreviation	R'	R''	Charge at pH 7
	HC1	$-CO_2H$	$-CO_2H$	anionic
	HC2	$-CO_2H$		anionic
	HC3	$-NHCH(CH_2OH)_2$	$-NHCH(CH_2OH)_2$	neutral
	HC4	$-CO_2(CH_2)_2NH_3^+ CF_3CO_2^-$	$-CO_2(CH_2)_2NH_3^+ CF_3CO_2^-$	cationic



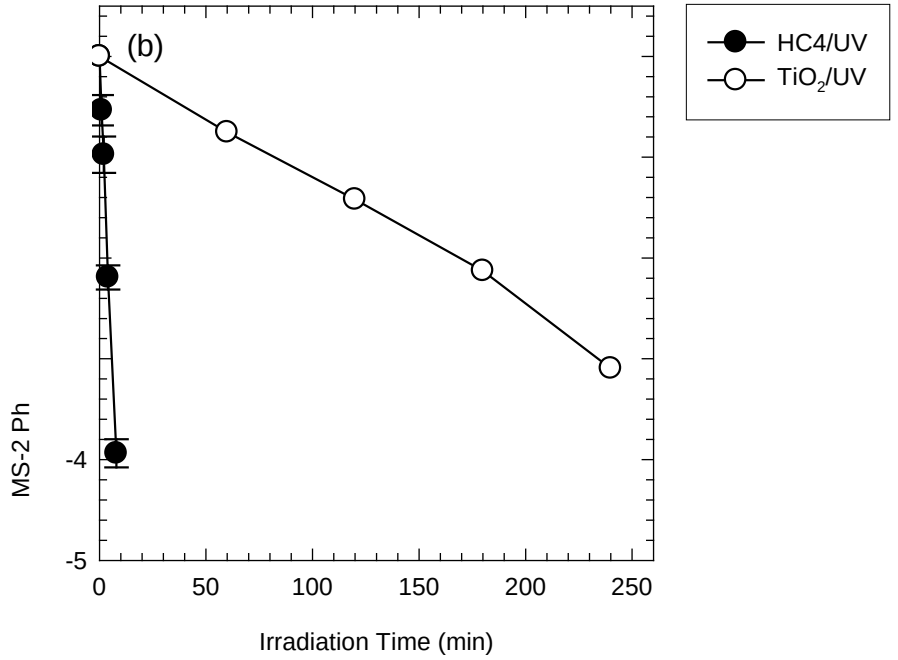
LEE ET AL. (2009) *ENVIRON. SCI. TECHNOL*
PHOTOCHEMICAL AND ANTIMICROBIAL PROPERTIES OF NOVEL C_{60} DERIVATIVES IN AQUEOUS SYSTEMS

C_{60} DERIVATIVE APPLICATION

E. COLI INACTIVATION



MS2 PHAGE INACTIVATION

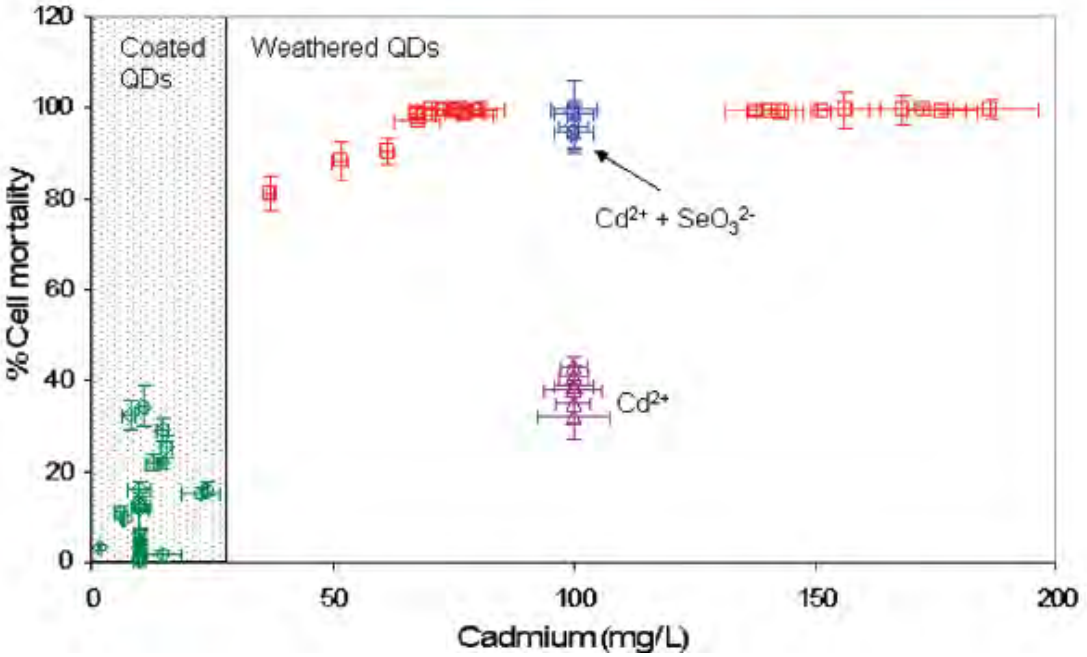


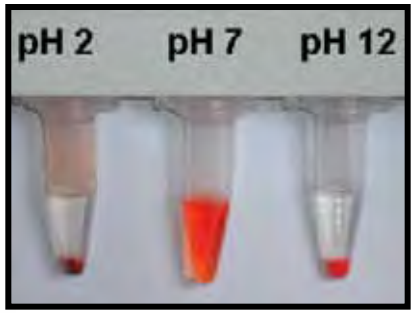
LEE ET AL. (2009) *ENVIRON. SCI. TECHNOL*
PHOTOCHEMICAL AND ANTIMICROBIAL PROPERTIES OF NOVEL C_{60} DERIVATIVES IN AQUEOUS SYSTEMS

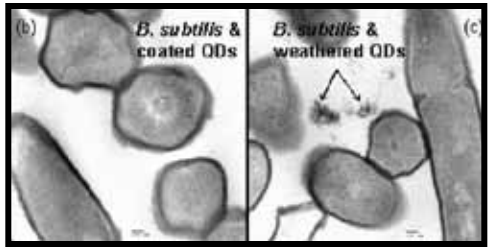
NANOPARTICLE WEATHERING: QUANTUM DOTS

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

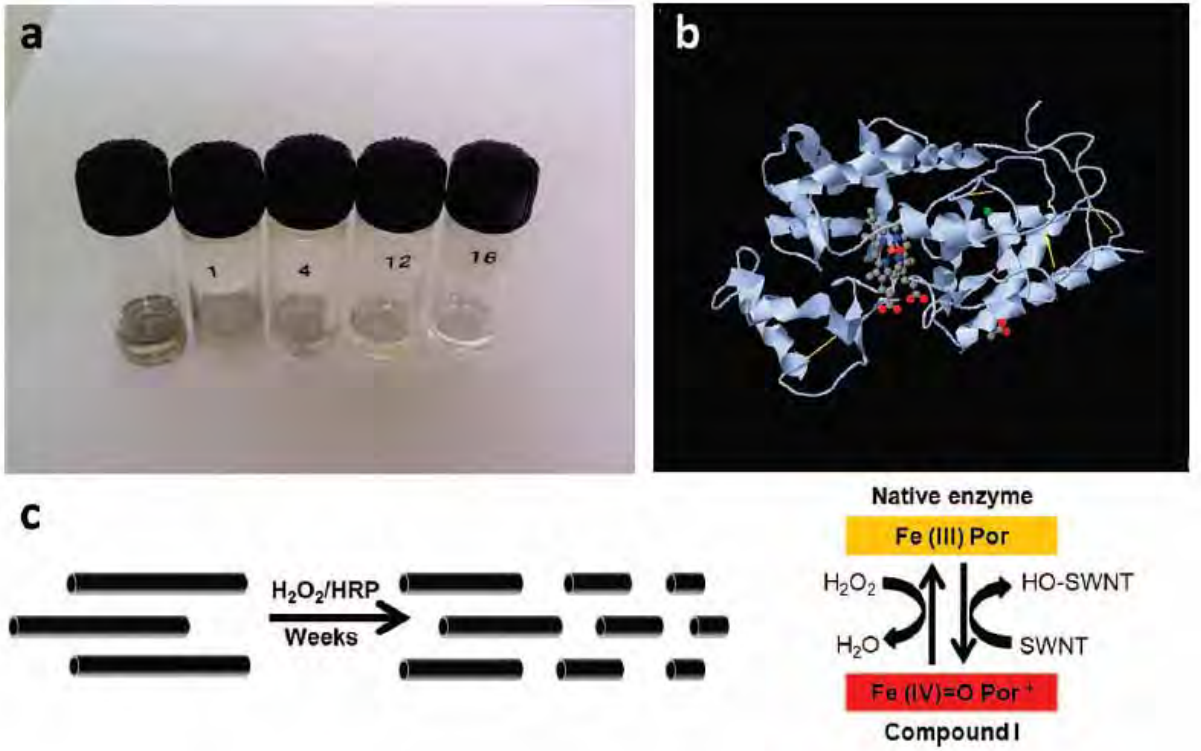






MAHENDRA, S., ZHU, H., COLVIN, V., ALVAREZ, P. (2008) *ENVIRON. SCI. TECHNOL*
QUANTUM DOT WEATHERING RESULTS IN MICROBIAL TOXICITY

BIODEGRADATION OF CARBON NANOTUBES



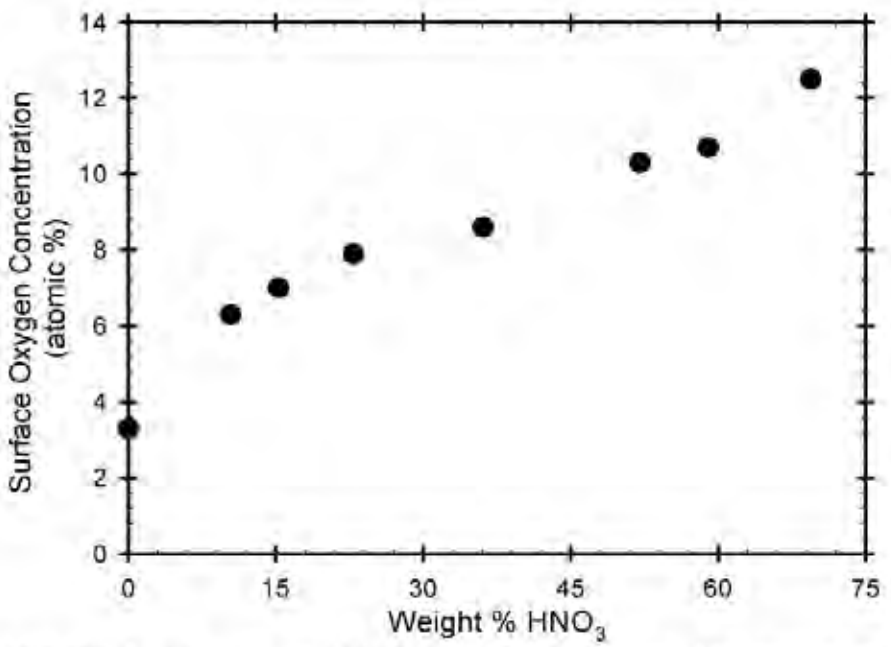
BIODEGRADATION OF CARBON NANOTUBES BY **HORSERADISH PEROXIDASE/H_2O_2** OVER THE PERIOD OF SEVERAL WEEKS

PROMISING POSSIBILITY FOR NANOTUBES BE **DEGRADED IN ENVIRONMENTALLY RELEVANT SETTINGS** (OTHER PEROXIDASES IN PLANT AND ANIMALS)

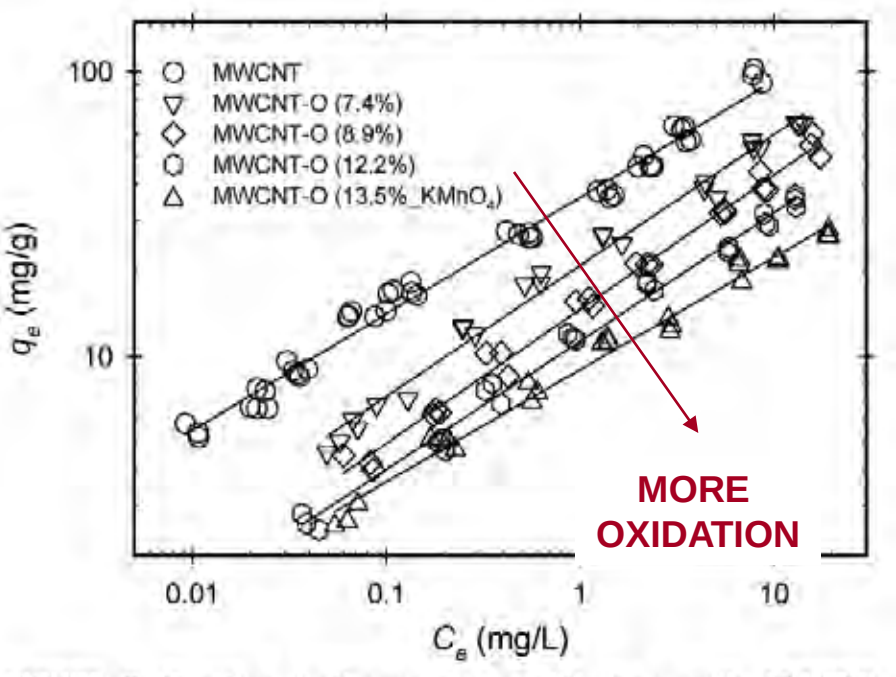
ALLEN, B. L, STAR, A. ET AL. (2008) NANO LETTERS
BIODEGRADATION OF SINGLE-WALLED CARBON NANOTUBES THROUGH ENZYMATIC CATALYSIS

ADSORPTIVE BEHAVIOR OF CARBON NANOTUBE

INFLUENCE OF HNO_3 CONCENTRATION ON THE EXTENT OF **MWCNT SURFACE OXIDATION**



SORPTION ISOTHERMS FOR **NAPHTHALENE** WITH MWCNT AND OXIDIZED MWCNT



CHO, H.H., SMITH, B.A., WNUK, J.D., FAIRBROTHER D.H., BALL, W.P. (2008) *ENVIRON. SCI. TECHNOL*
INFLUENCE OF SURFACE OXIDES ON THE ADSORPTION OF NAPHTHALENE ONTO MULTIWALLED CARBON NANOTUBES