

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

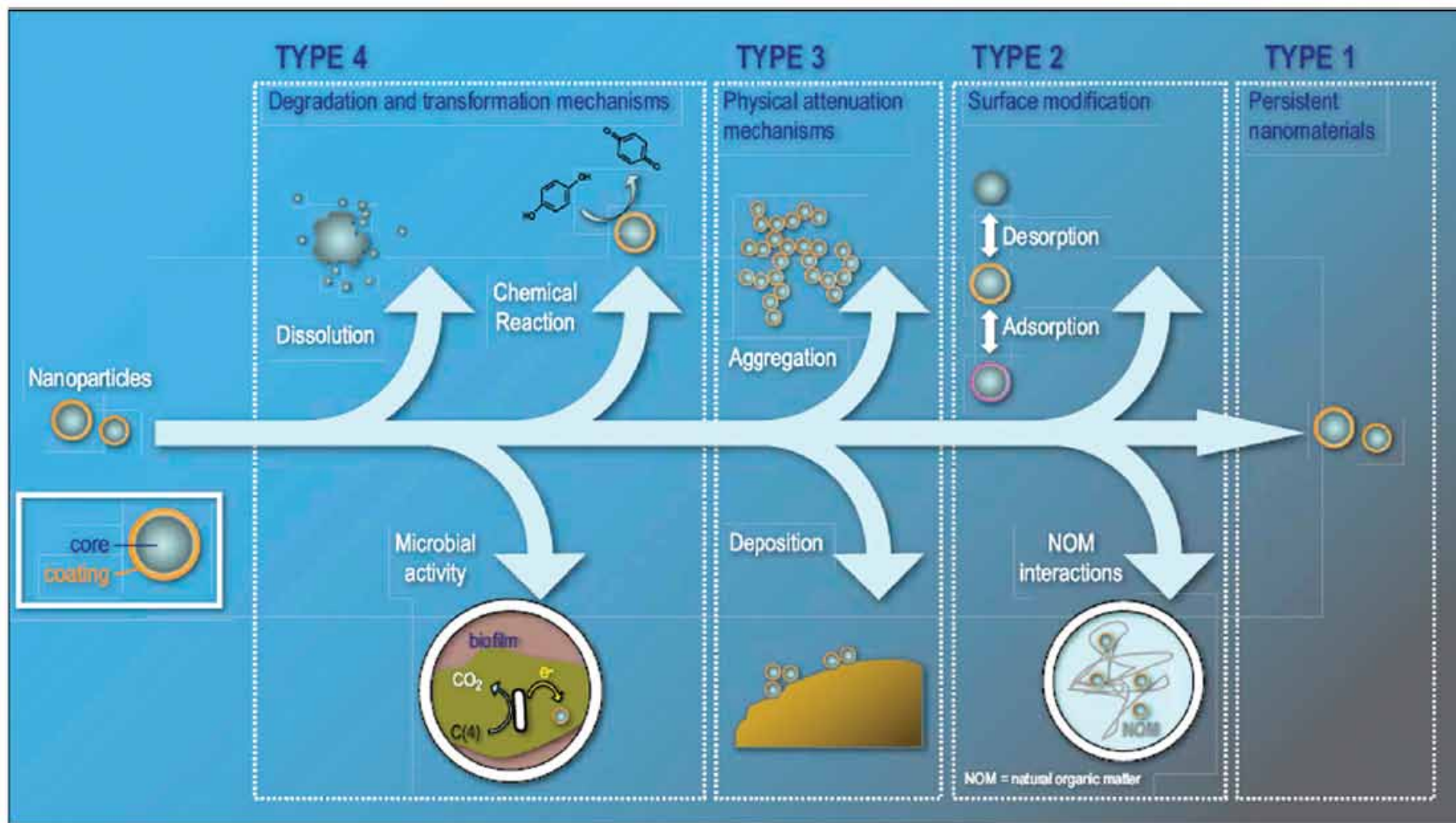
CHEMICAL TRANSFORMATION OF CARBONACEOUS NANOMATERIALS IN NATURAL AND ENGINEERED ENVIRONMENT



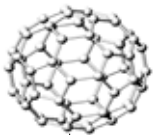
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ASSOCIATE PROFESSOR

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
GEORGIA INSTITUTE OF TECHNOLOGY

POSSIBLE NANOPARTICLE MODIFICATIONS IN THE ENVIRONMENT



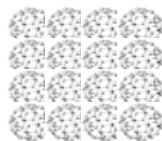
VARIOUS FORMS OF C₆₀ IN THE AQUEOUS PHASE



STRONG PHOTOSENSITIZER
HIGH RADICAL REACTIVITY

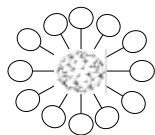
THREE KNOWN PATHWAYS TO STABILIZE IN WATER

1. AGGREGATE FORMATION



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

2. SURFACE ENCAPSULATION (SURFACTANT)

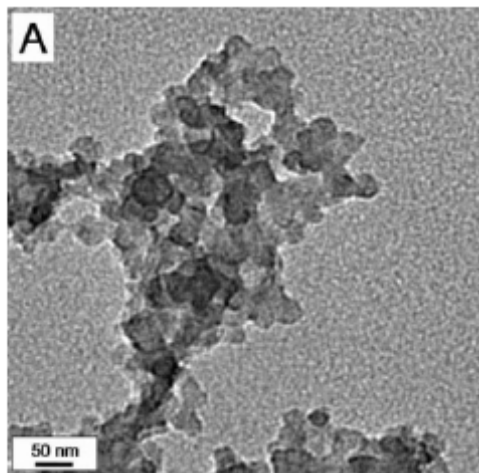
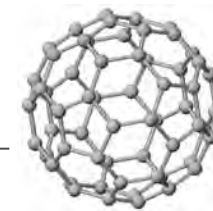


CLOSE TO MOLECULAR C₆₀ IN PHOTOCHEMICAL AND
CHEMICAL REACTIVITY

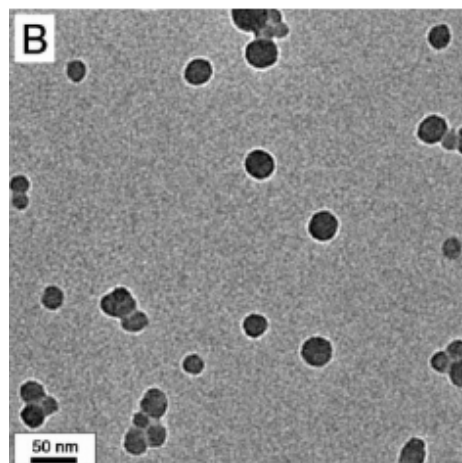
3. HYDROPHILIC FUNCTIONALIZATION

MOLECULARLY DISPERSED OR SMALL AGGREGATES
VARYING CHEMICAL AND PHOTOCHEMICAL PROPERTIES

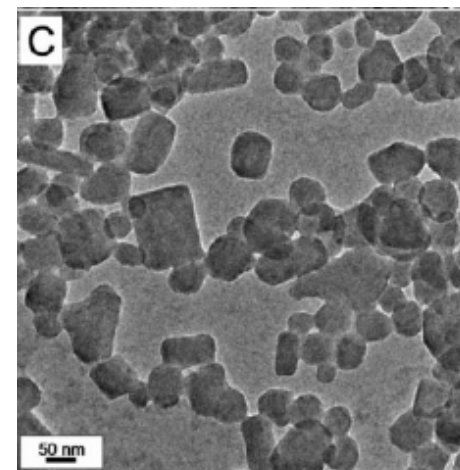
VARIOUS FORMS OF nC_{60}



AQUA/ nC_{60}
MIXING DRY C_{60} WITH WATER
FOR EXTENDED PERIOD

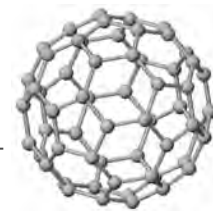


SON/ nC_{60}
SONICATING BINARY
MIXTURE OF C_{60} /TOLUENE
AND WATER



THF/ nC_{60}
EXCHANGING
ORGANIC SOLVENT (THF)
WITH WATER

C₆₀ AGGREGATES IN WATER: BRIEF REVIEW



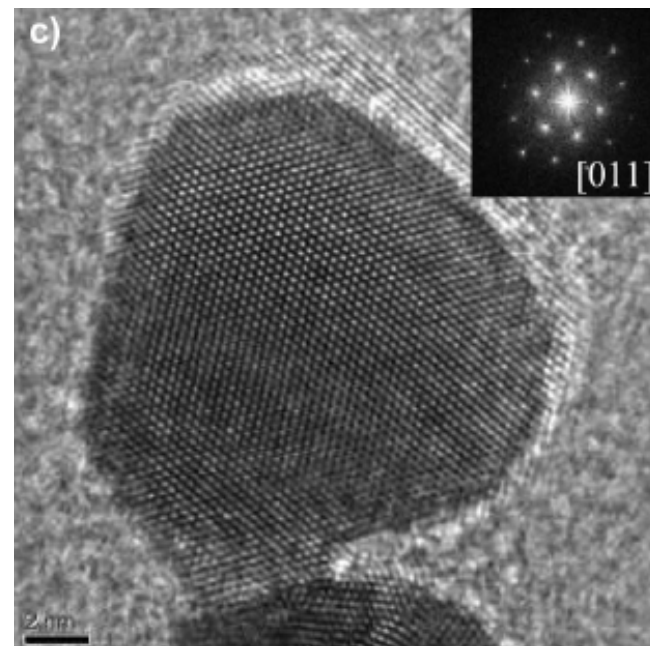
nC₆₀ CAN BE PREPARED VIA **VARIOUS METHODS**

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)

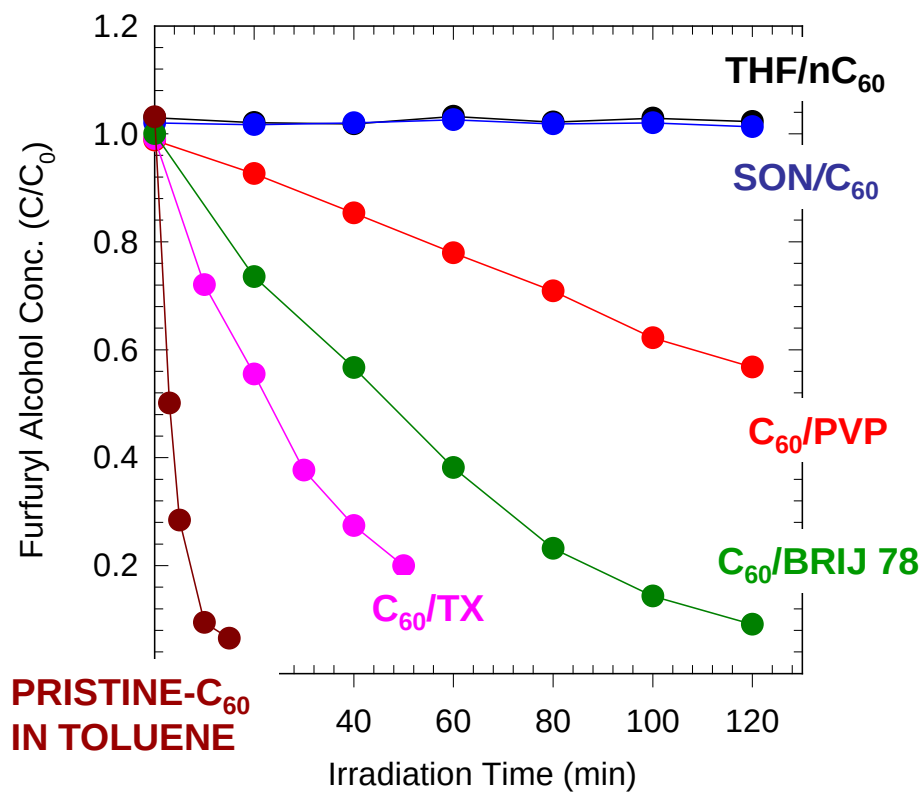
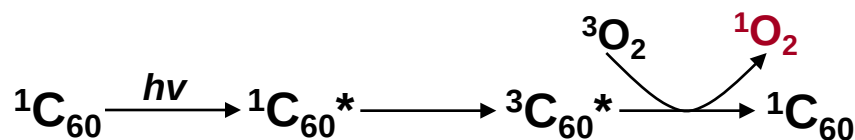
OZONATION (CHLORINATION)

PHOTOLYSIS (UV AND VISIBLE)

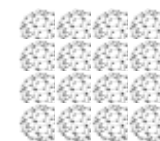
BIODEGRADATION



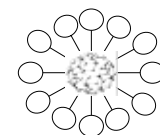
COMPARING PHOTOACTIVITY OF VARIOUS C₆₀ SAMPLES



DISPERSED AS
AGGREGATES



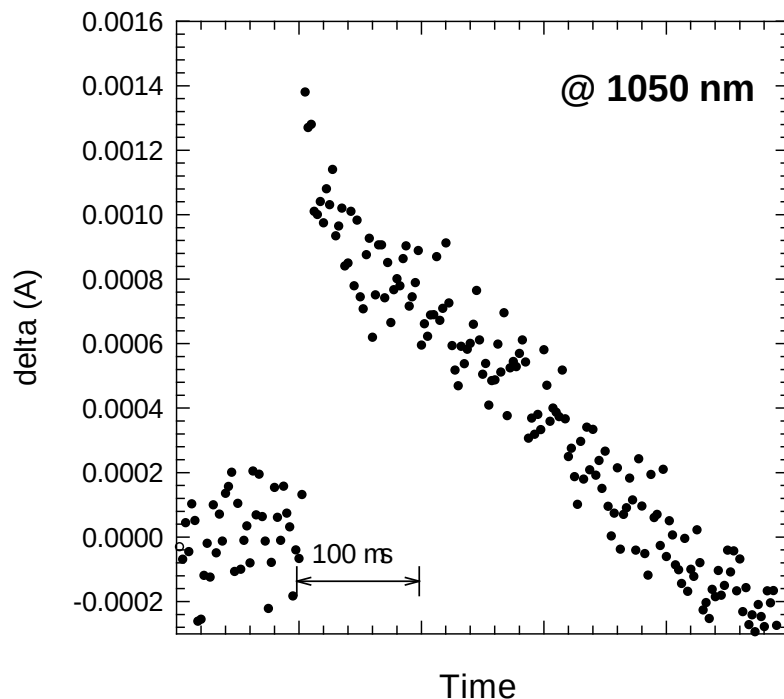
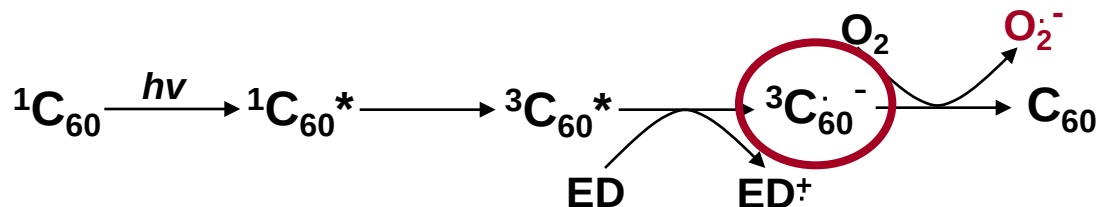
MOLECULARLY
DISPERSED



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.)

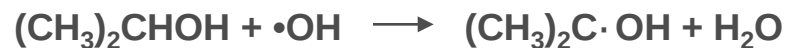
C₆₀ RADICAL ANION WITH ANY
DETECTABLE LIFE-TIME WAS NOT
DETECTED FOR OTHER C₆₀ SAMPLES

RADICAL REACTIVITY OF C₆₀ AGGREGATE

PULSE AND GAMMA RADIOLYSIS



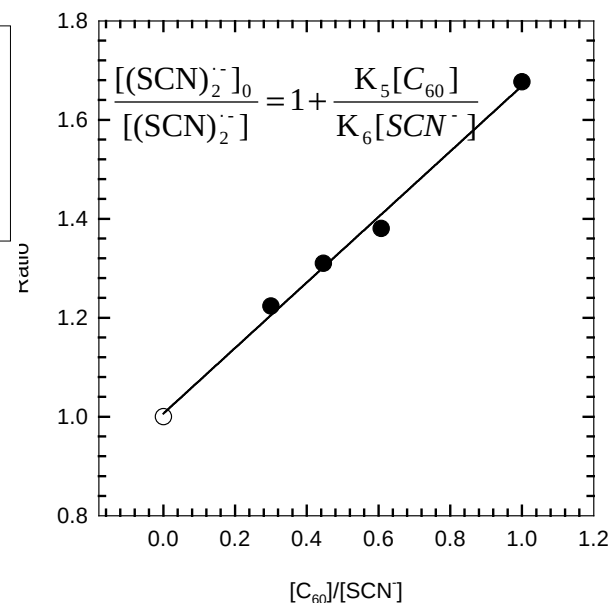
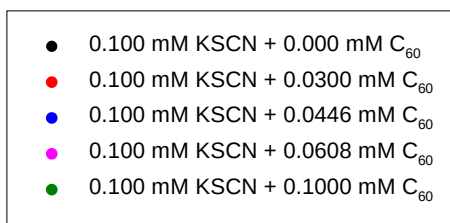
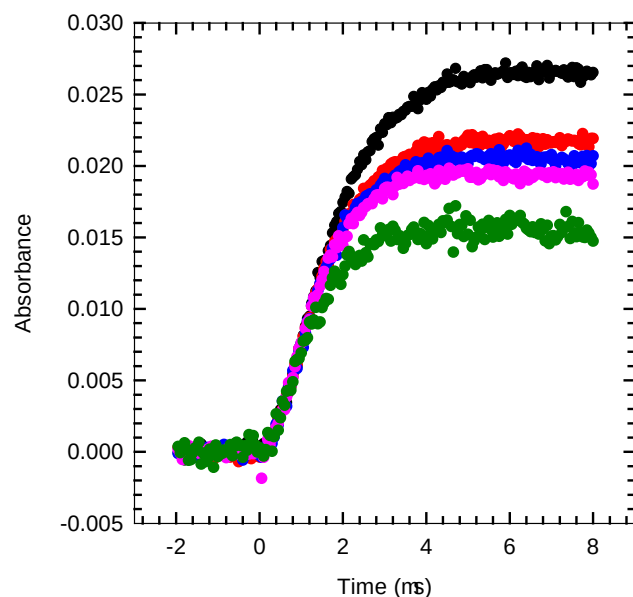
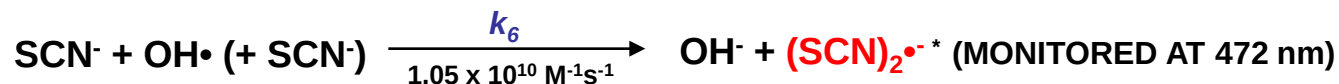
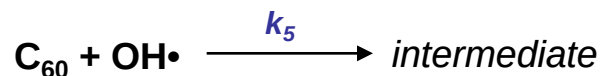
UNDER **N₂-SATURATED** CONDITION



UNDER **N₂O-SATURATED** CONDITION



REACTIVITY OF nC_{60} WITH OH RADICAL

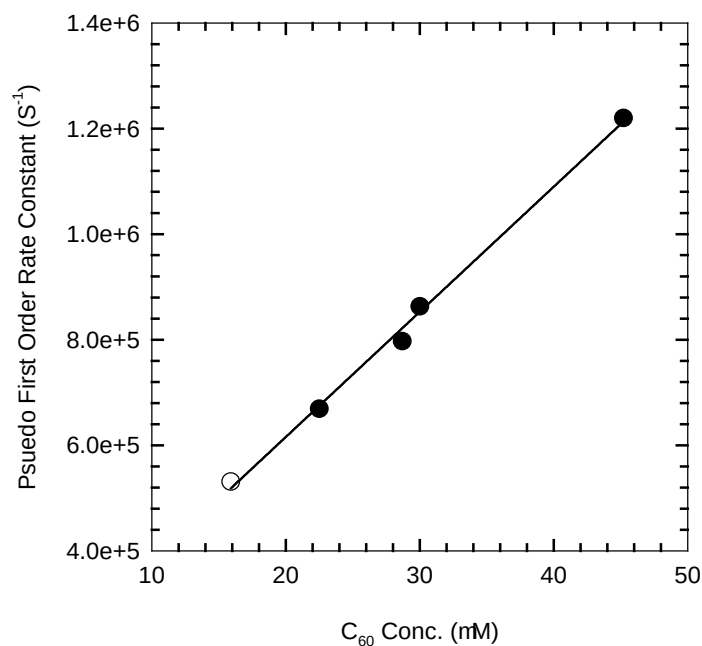
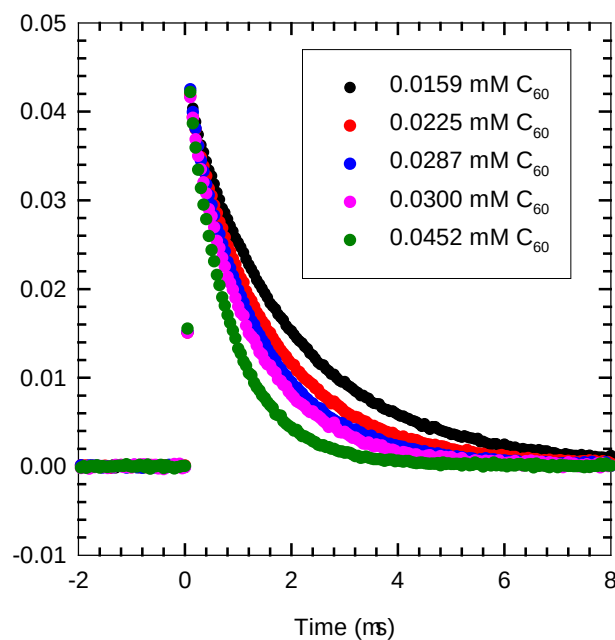


SECOND-ORDER RATE CONSTANT = $7.34 \pm 0.31 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.

REACTIVITY OF nC_{60} WITH HYDRATED ELECTRONS

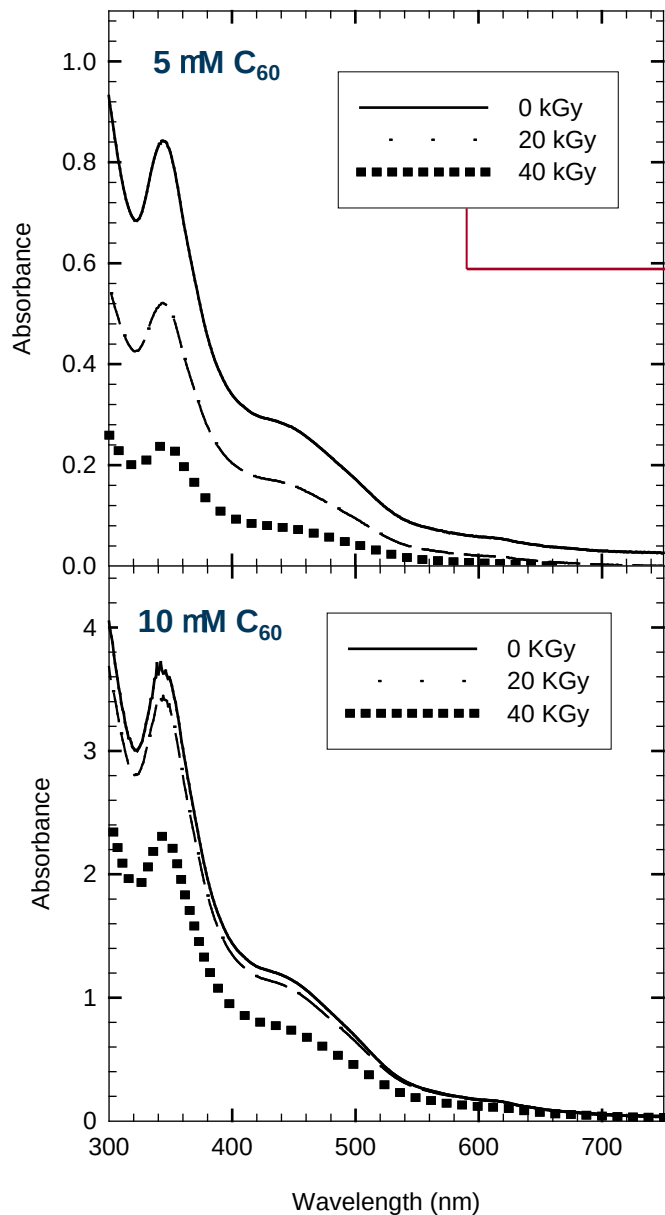


DIRECTLY MONITORING OF THE DECAY KINETICS OF HYDRATED ELECTRON
AT 700 nm IN THE PRESENCE OF nC_{60} AT DIFFERENT CONCENTRATIONS.



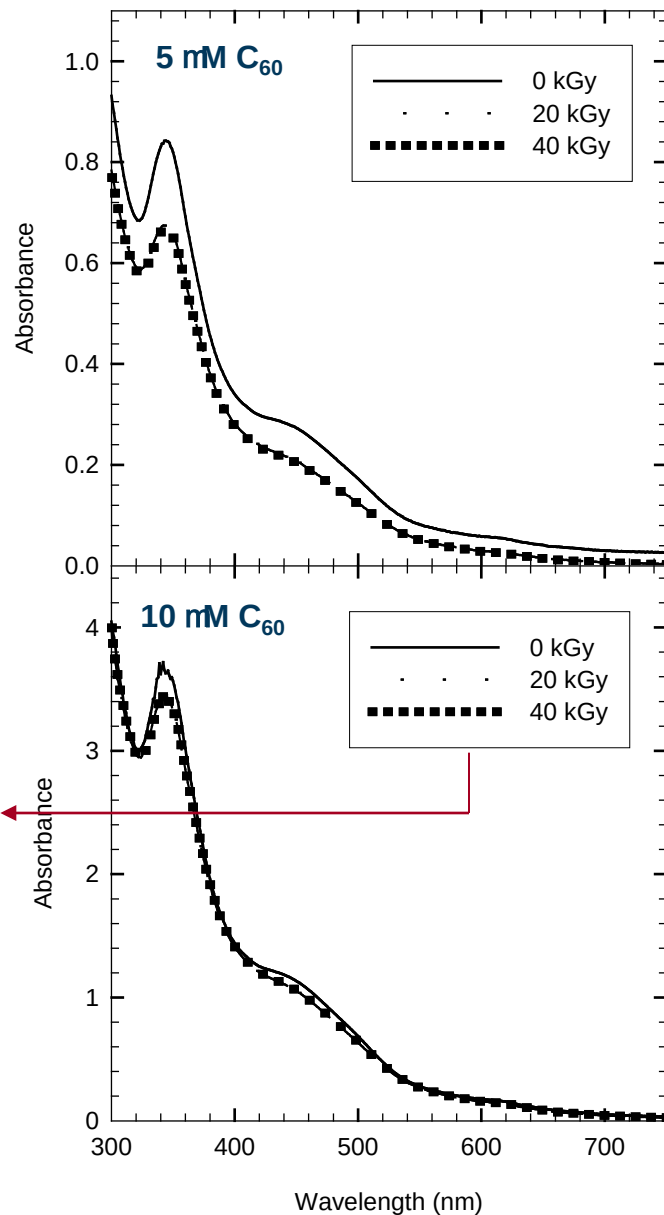
SECOND-ORDER RATE CONSTANT = $2.34 \pm 0.02 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$

γ -RADIOLYSIS STUDY



N_2O SATURATED
CORRESPOND TO
11 AND 22 mM OF $\cdot OH$

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



XPS ANALYSIS RESULT

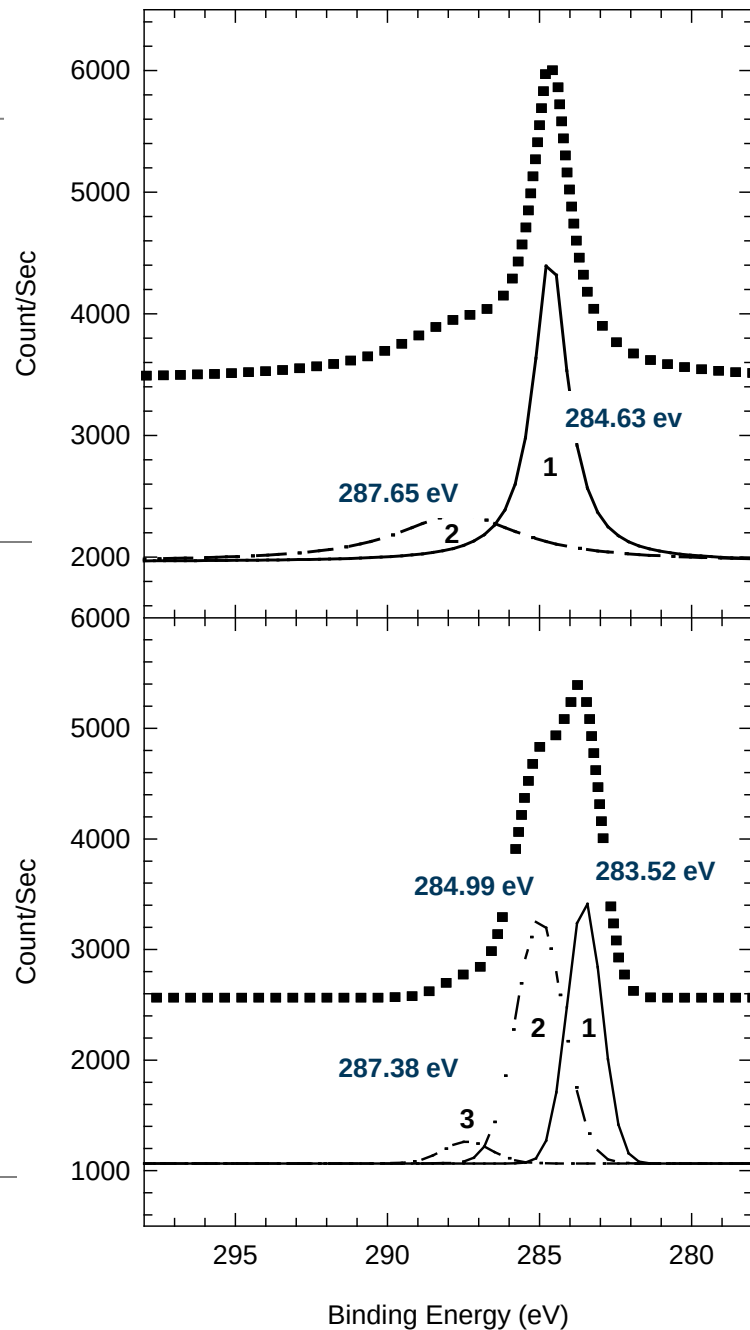
ON g-RADIOLYSIS PRODUCT

N₂O SATURATED CONDITION

- 1. UNDERIVATIZED CARBON: 64.2%
- 2. MONOOXIDIZED CARBON: 35.8%

N₂ SATURATED CONDITION

- 1. REDUCED CARBON: 41.6%
- 2. UNDERIVATIZED CARBON: 53.6%
- 3. MONO-OXIDIZED CARBON: 4.75%



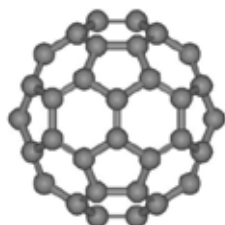
QUANTUM MECHANICAL INVESTIGATION



SINGLE C₆₀ MOLECULE

DENSITY FUNCTIONAL THEORY

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



C₆₀ (SINGLET)

HOMO = -9.345 eV

LUMO = -7.770 eV

-2263.053334 Ha

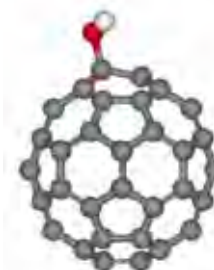


•OH
(DOUBLET)

HOMO = -6.683 eV

LUMO = -0.599 eV

-75.140423 Ha



•C₆₀-OH (DOUBLET)

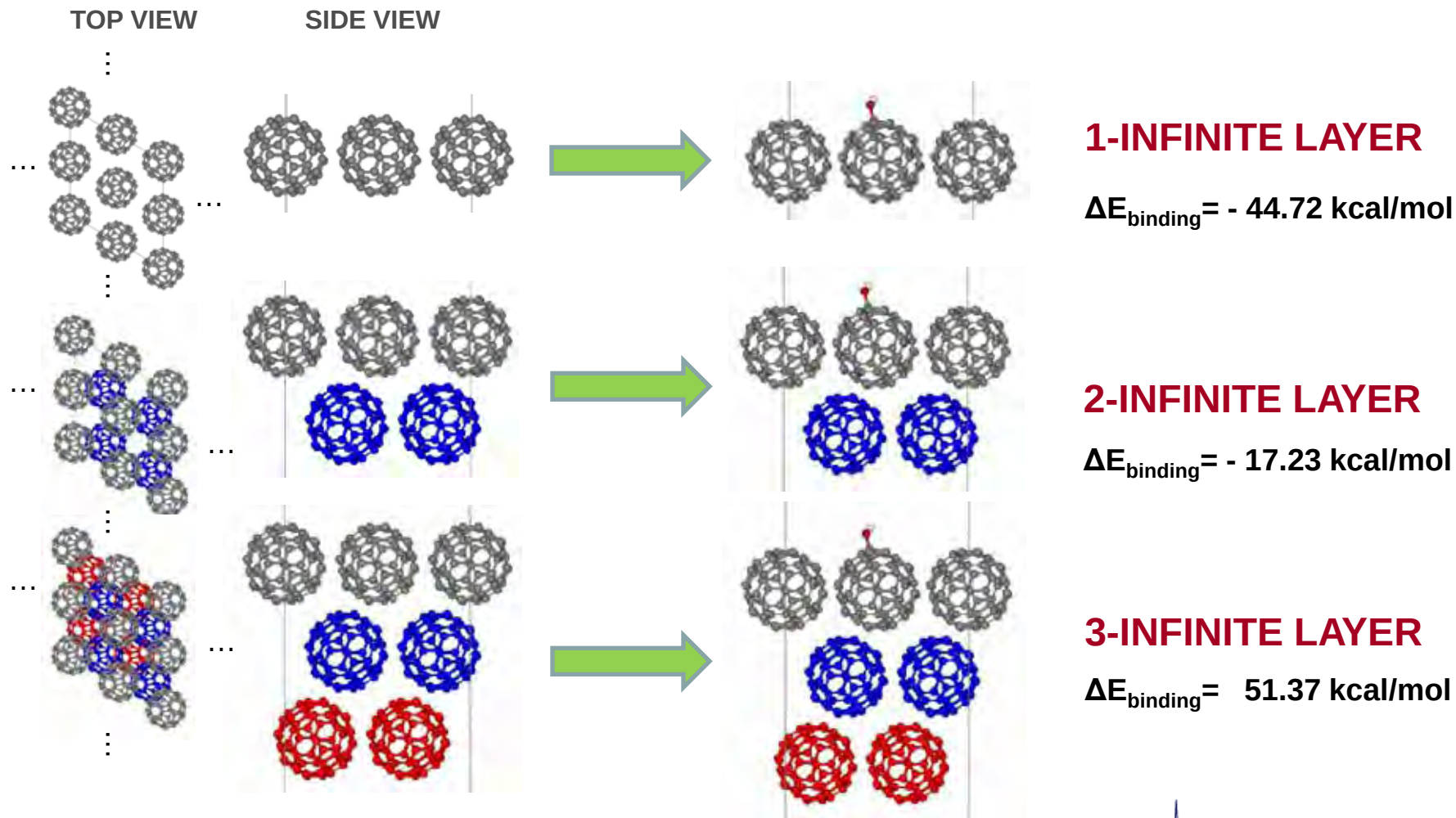
HOMO = -8.565 eV

LUMO = -8.252 eV

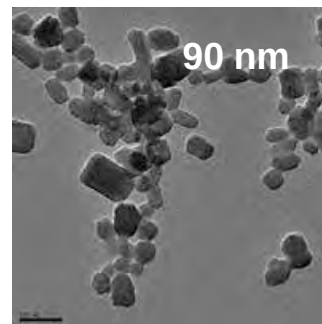
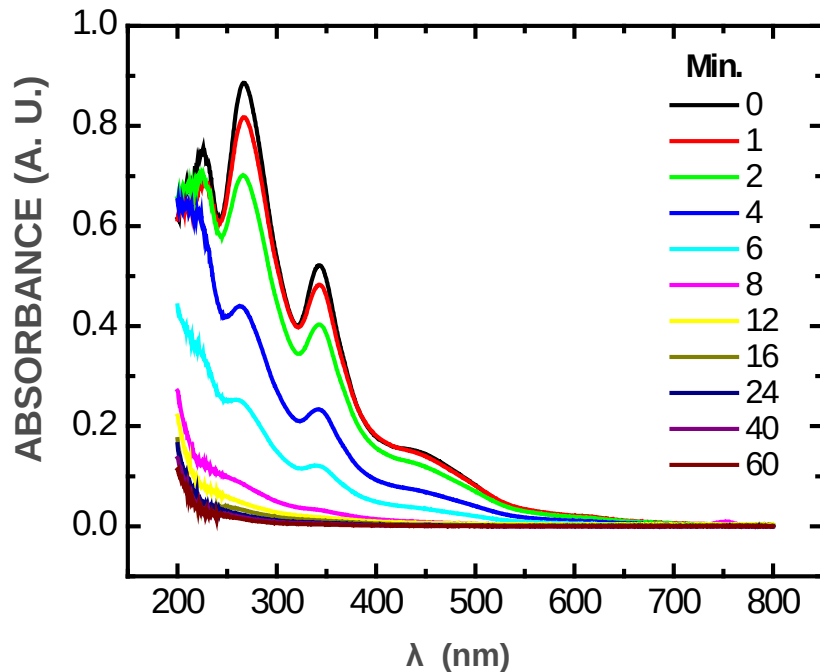
-2338.26528 Ha

$$\begin{aligned}\Delta E_{\text{binding}} &= E_{\text{•C}_{60}\text{-OH}} - (E_{\text{C}_{60}} + E_{\text{•OH}}) \\ &= -44.88 \text{ kcal/mol}\end{aligned}$$

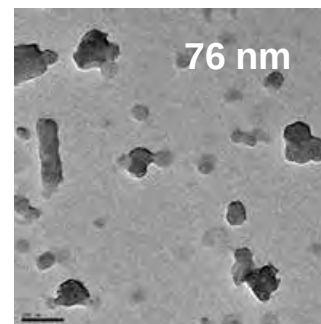
MODELING C₆₀ CLUSTERS



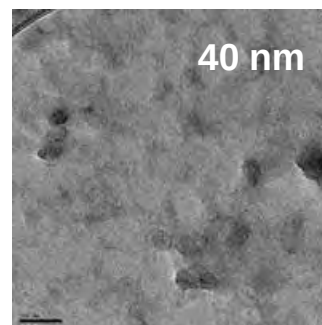
REACTION WITH O₃ IN THE AQUEOUS PHASE



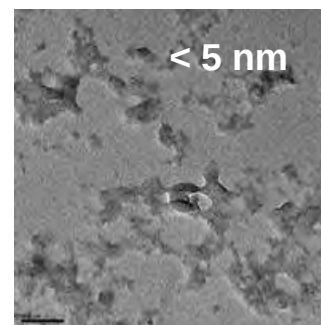
t = 0 min
CT = 0 mg-min/L



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

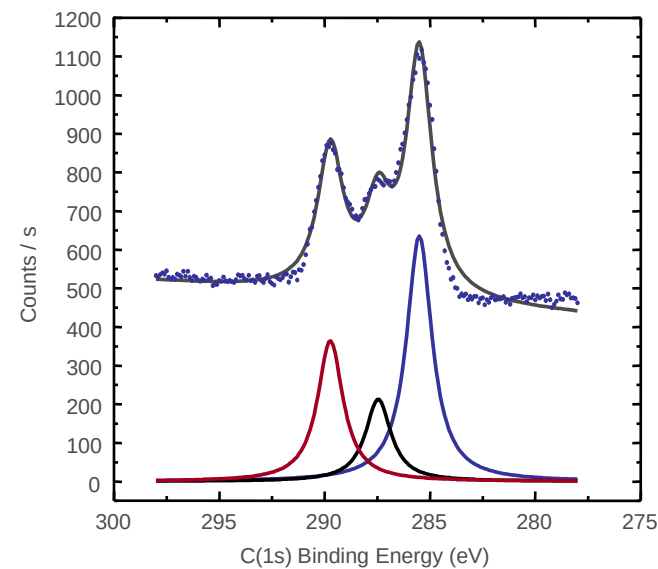
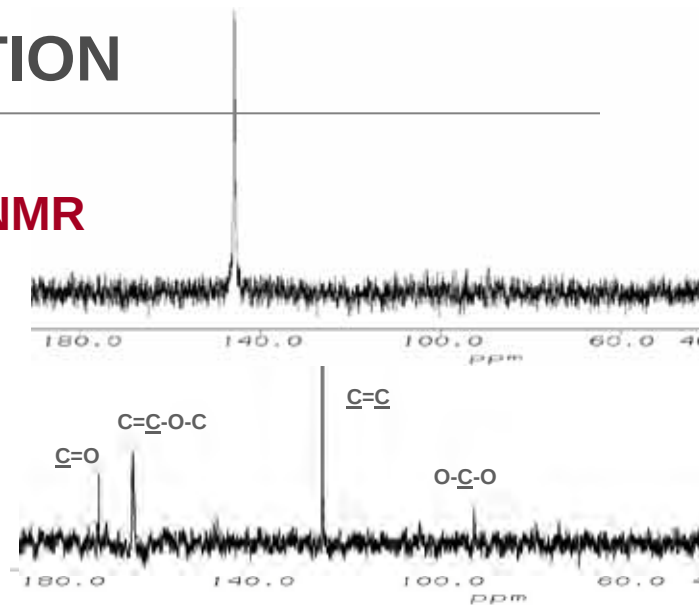


t = 15 min
CT = 28.5 mg-min/L



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

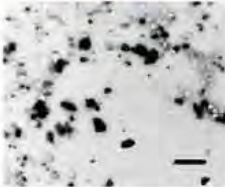
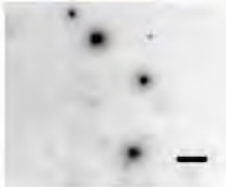
¹³C NMR



PHOTOCHEMICAL TRANSFORMATION IN SUNLIGHT

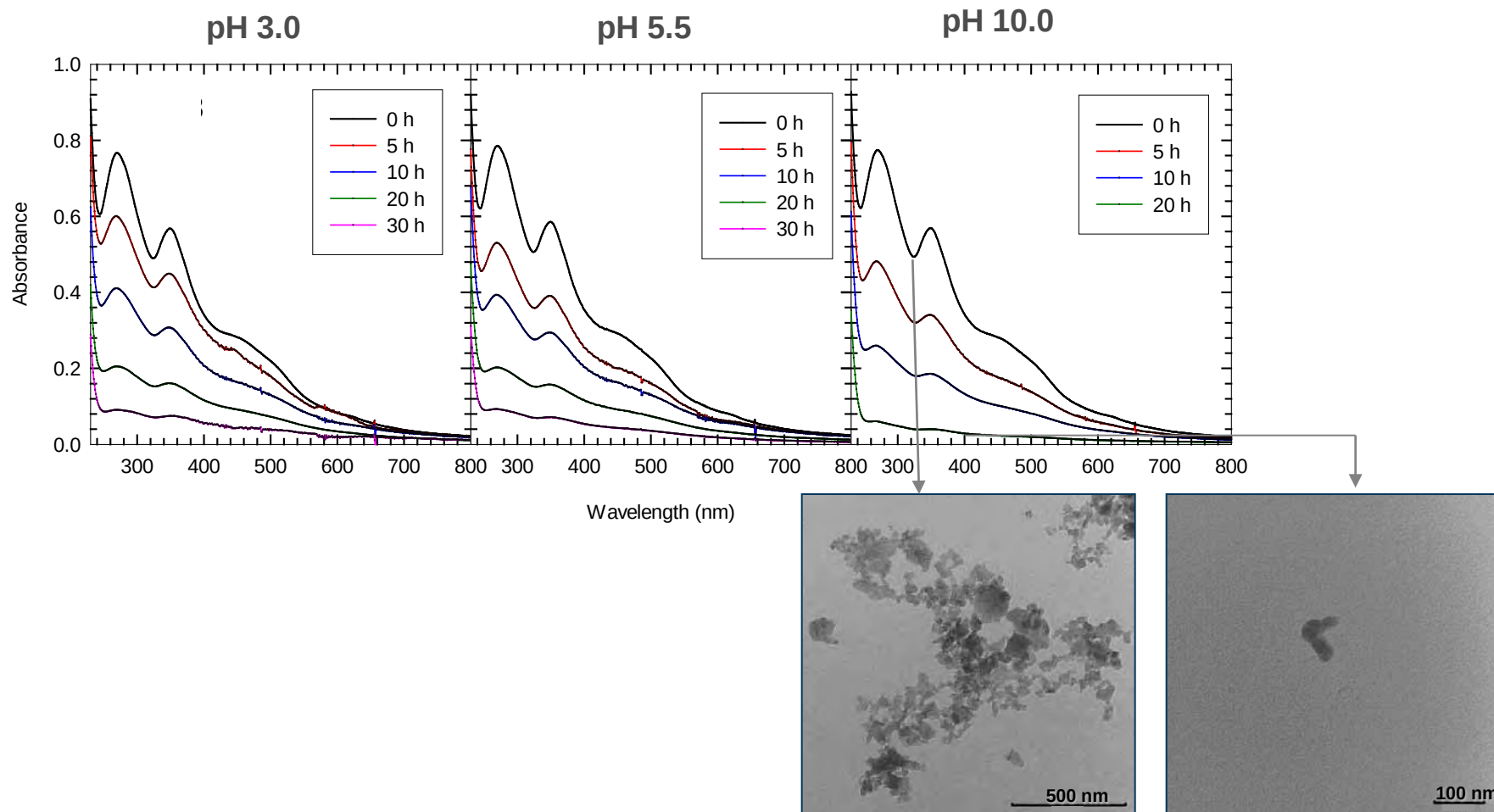


65 mg/L THF/ nC_{60} IN LAMP LIGHT ($I = 350 \pm 50 \text{ nm}$)

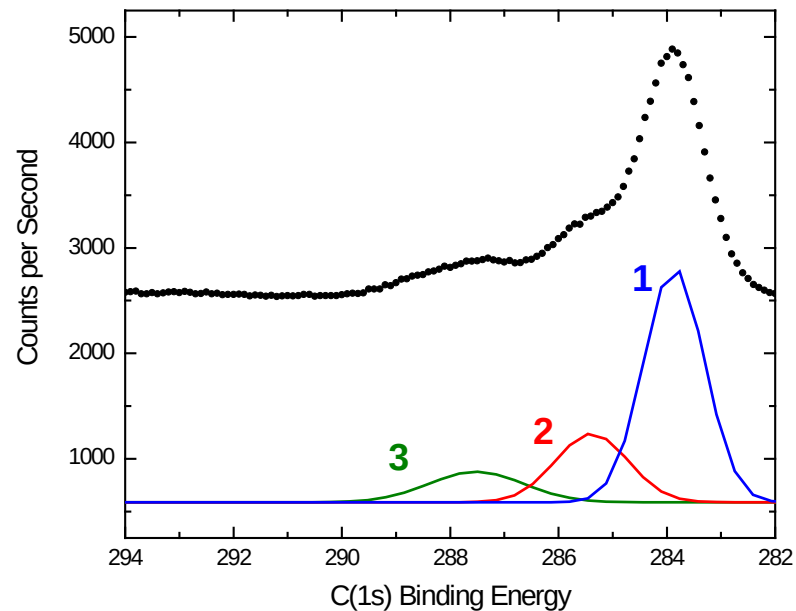
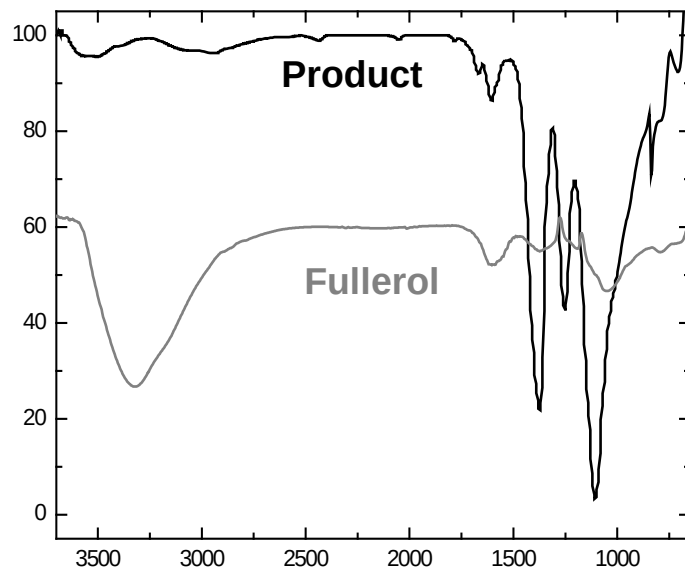
Time (days)	0	10	30	65
[nC_{60}] (mg/L)	65	19.5	2.6	0.47
Color				
TEM image*				
Mean diameter** (nm)	500	320	250	160
After centrifugation***				

PHOTODEGRADATION OF nC_{60}

BY UV_{254} 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

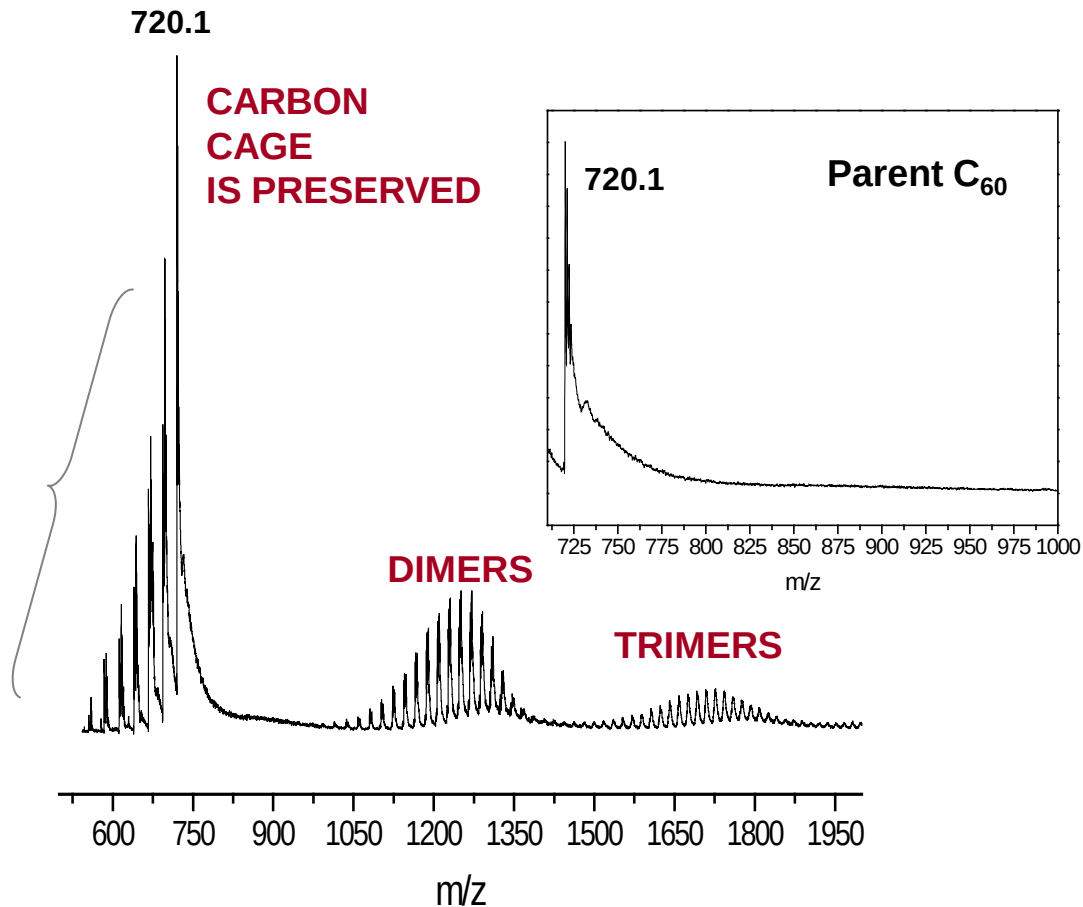
PRODUCT CHARACTERIZATION: LDI-MS



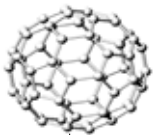
MULTIPLE PEAKS WITH
24 M/Z INTERVALS BELOW THE
PARENT COMPOUND PEAK

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

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



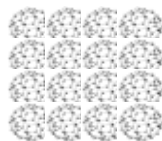
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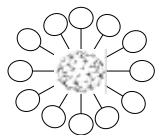
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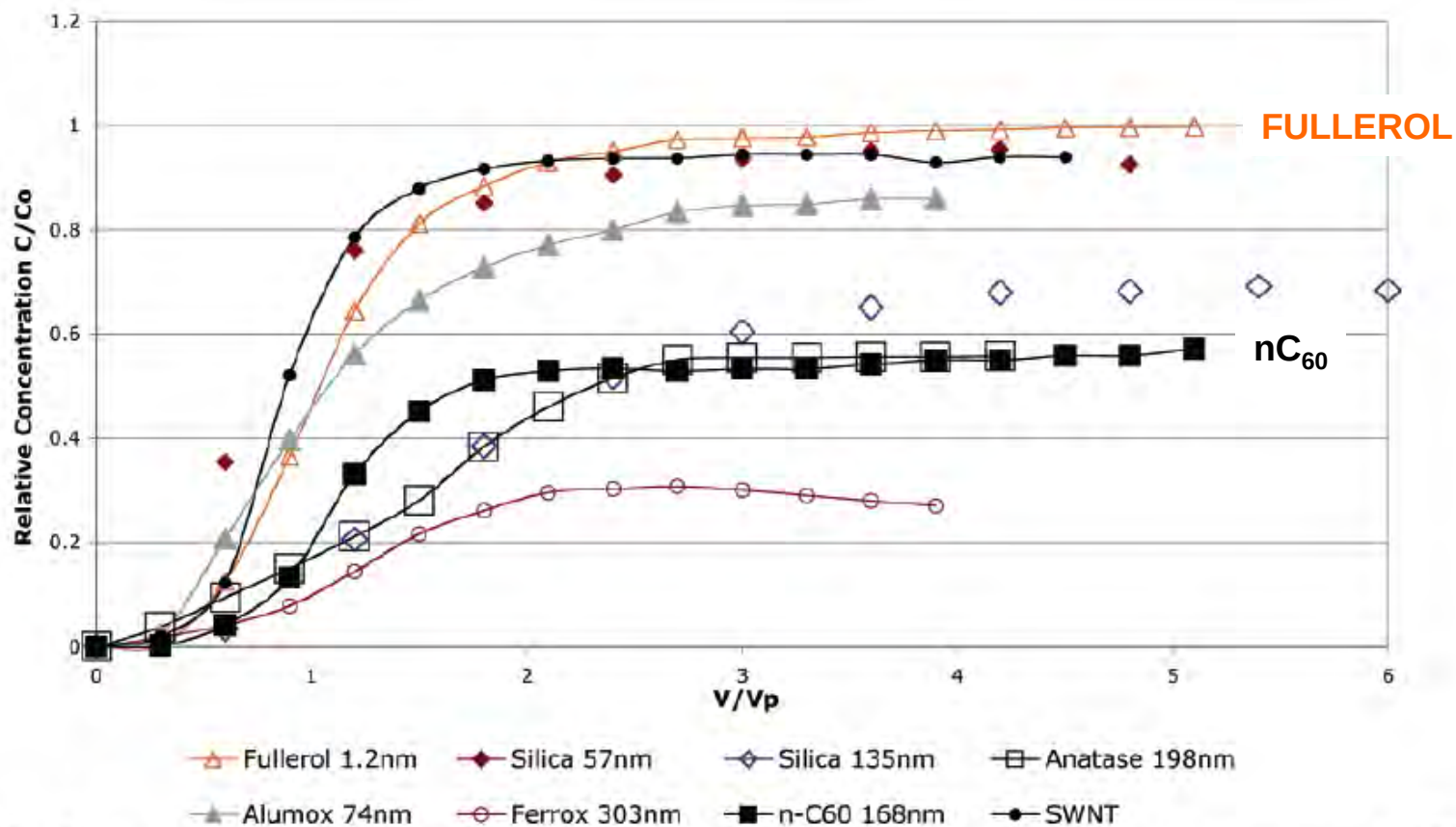
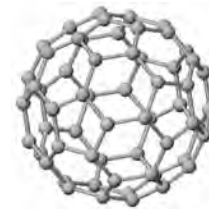


CLOSE TO MOLECULAR C₆₀ IN PHOTOCHEMICAL AND
CHEMICAL REACTIVITY

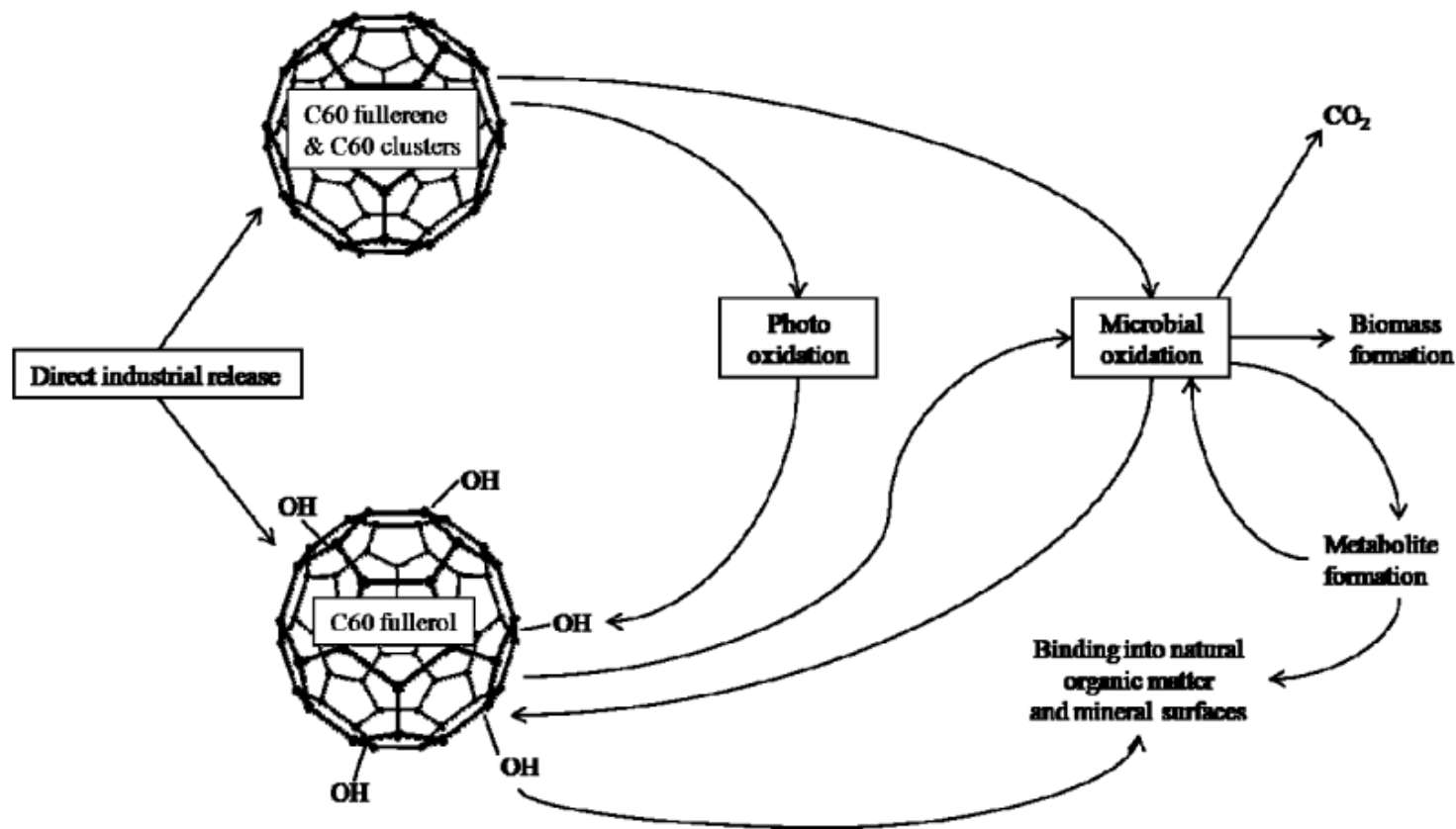
3. HYDROPHILIC FUNCTIONALIZATION

MOLECULARLY DISPERSED OR SMALL AGGREGATES
VARYING CHEMICAL AND PHOTOCHEMICAL PROPERTIES

C₆₀ POROUS MEDIA TRANSPORT



BIOLOGICAL DECOMPOSITION OF C₆₀



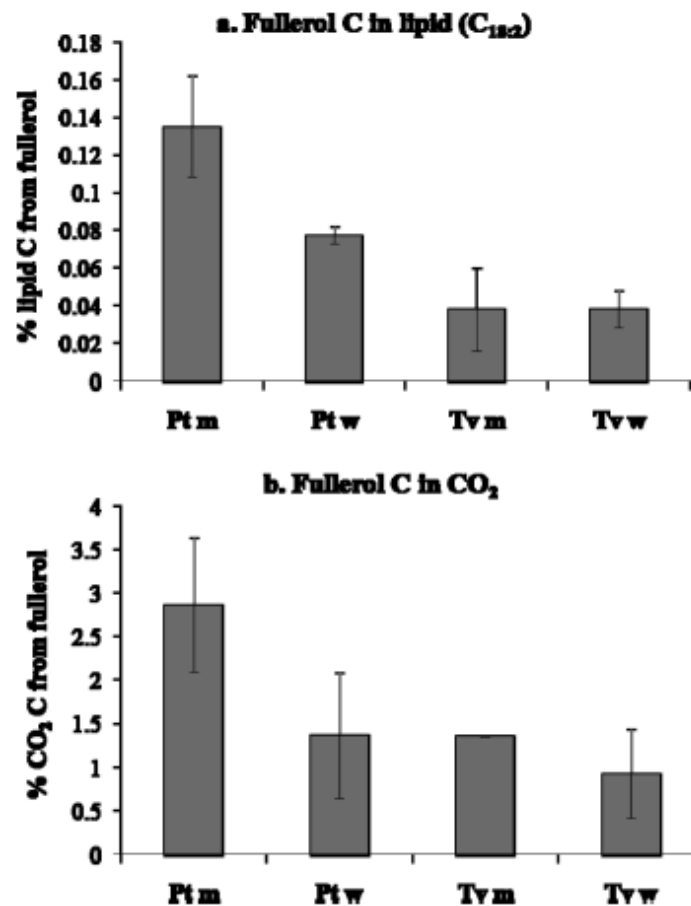
BIOLOGICAL DECOMPOSITION OF C₆₀



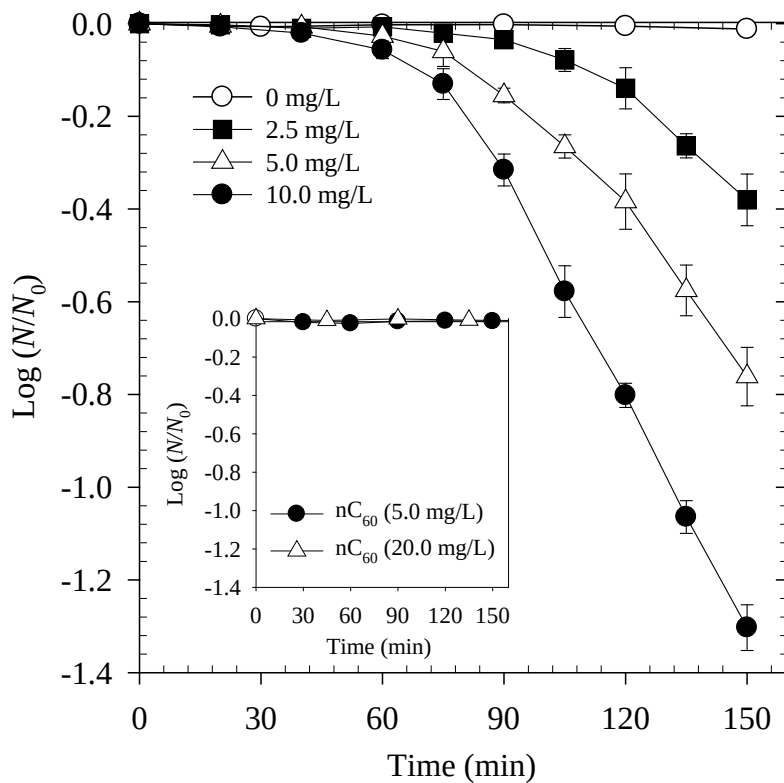
THESE WHITE ROT BASIDIOMYCETE FUNGI (*TRAMETES VERSICOLOR*, *PHLEBIA TREMELLOSA*) ARE CAPABLE OF

INCORPORATING THE FULLEROL CARBON INTO FUNGAL BIOMASS, ALTHOUGH ONLY TO A SMALL DEGREE

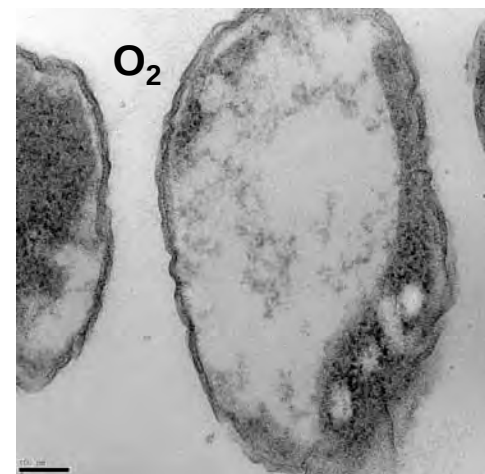
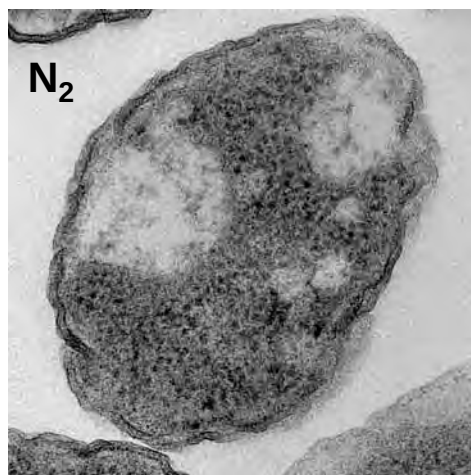
OXIDIZING SOME OF C₆₀ CAGE CARBON TO CO₂



OZONATED C₆₀: INTERACTION WITH *E. COLI*



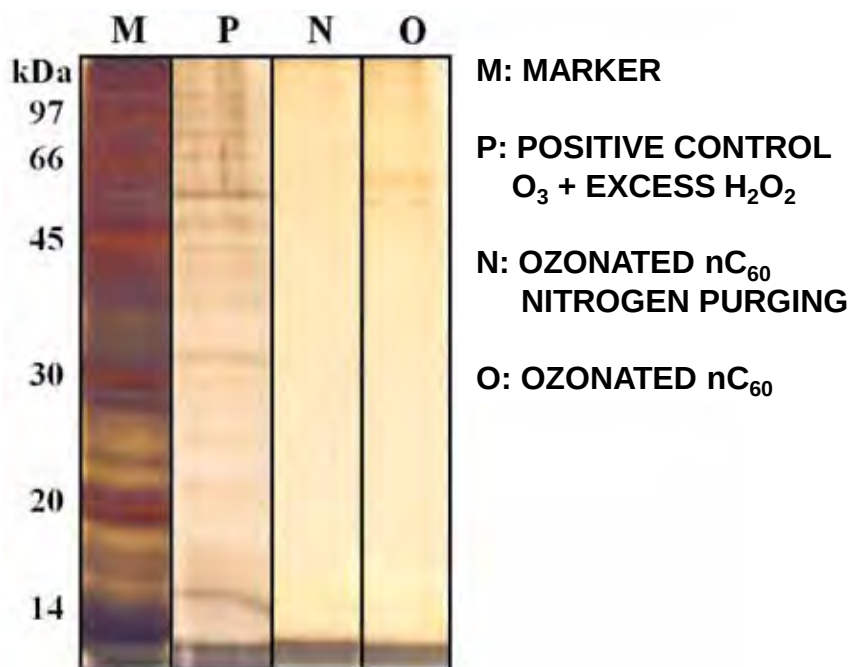
**OZONATED C₆₀ INACTIVATES *E. COLI*
ONLY IN THE PRESENCE OF O₂ AND LIGHT**



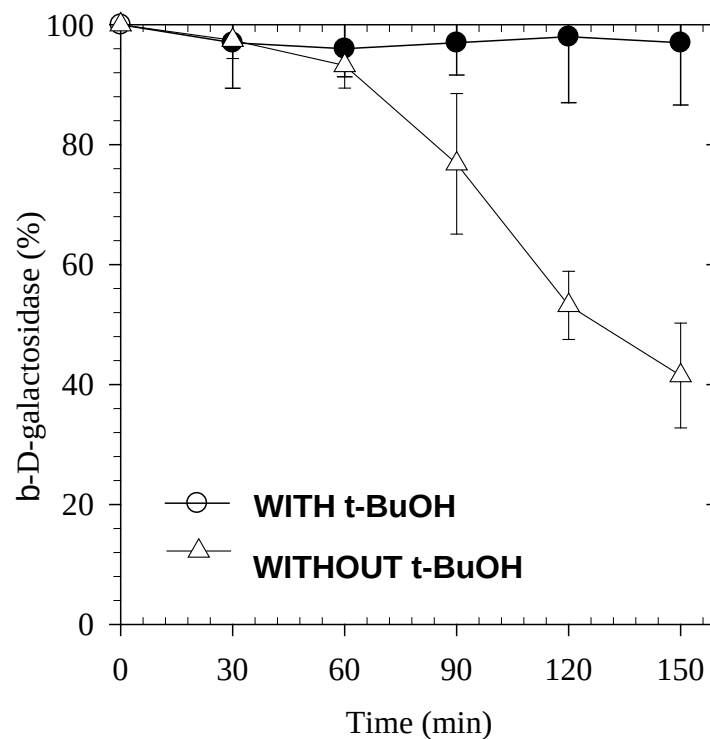
MECHANISM OF *E. COLI* INACTIVATION



EXTRACTED PROTEIN ASSAY USING SDS-PAGE AFTER 1 LOG INACTIVATION



DEGRADATION OF INTRACELLULAR ENZYME



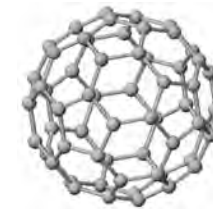
TOXICITY OF UV PHOTOLYSIS PRODUCT



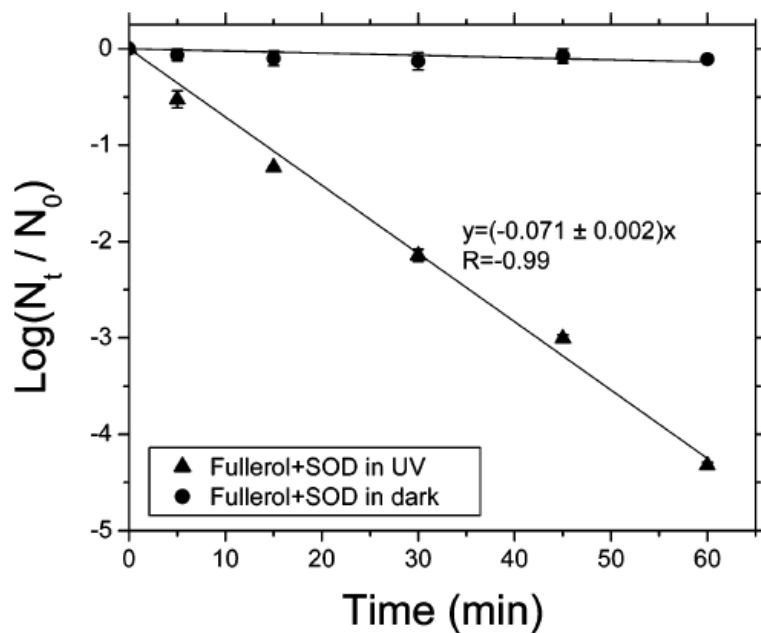
THE **MINIMAL INHIBITORY CONCENTRATIONS** OF
PARENT nC_{60} AND THE UV PHOTOLYSIS PRODUCTS FOR *E.COLI*

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	-	-	-	-	-	+

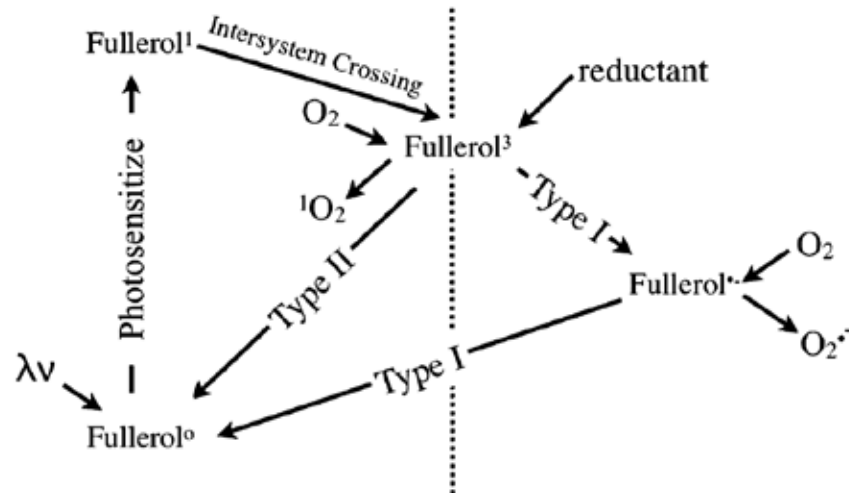
INTERACTION WITH VIRUS



MS2 INACTIVATION WITH PHOTOACTIVATED FULLEROL



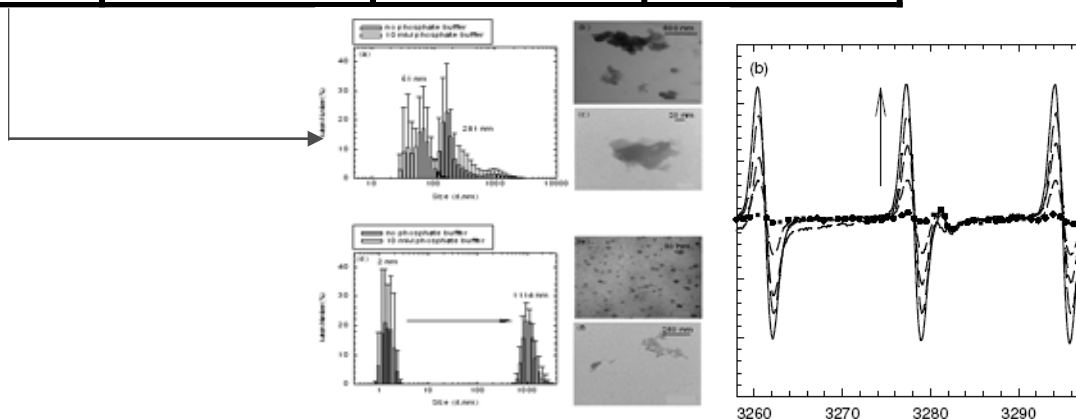
PHOTOSENSITIZATION PATHWAYS



C₆₀ DERIVATIVE APPLICATION



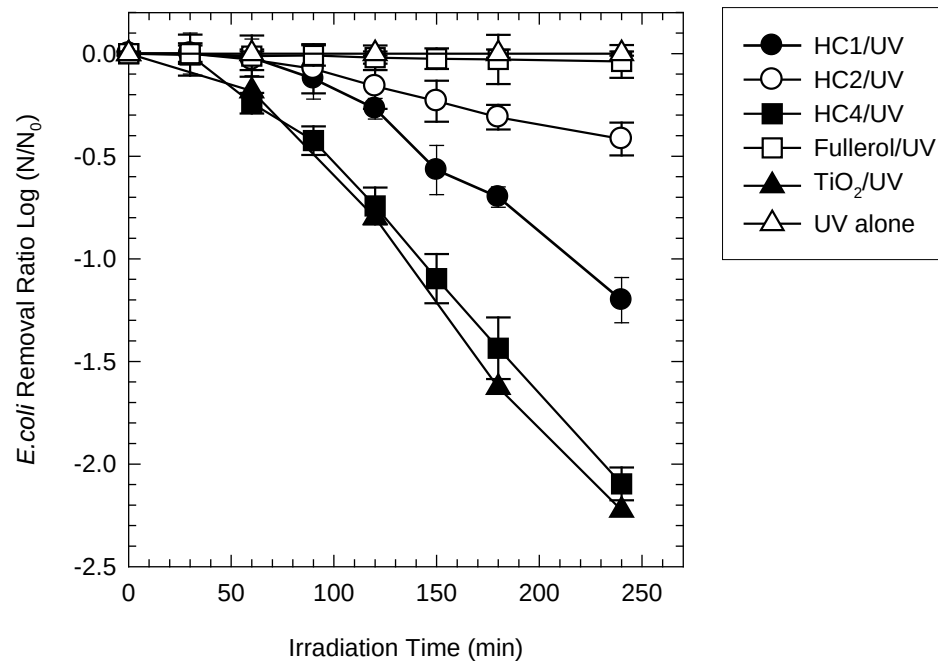
Chemical Structure	Abbreviat ion	R'	R''	Charge at pH 7
	HC1	-CO ₂ H	-CO ₂ H	anionic
	HC2	-CO ₂ H		anionic
	HC3	NHCH(CH ₂ OH) ₂	NHCH(CH ₂ OH) ₂	neutral
	HC4	-CO ₂ (CH ₂) ₂ NH ₃ ⁺ CF ₃ CO ₂ ⁻	-CO ₂ (CH ₂) ₂ NH ₃ ⁺ CF ₃ CO ₂ ⁻	cationic



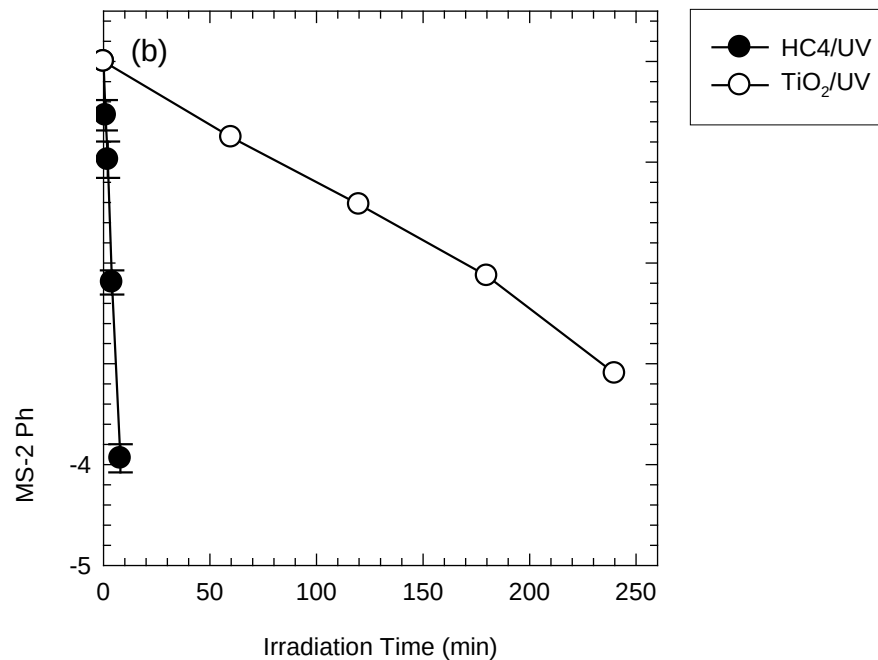
C₆₀ DERIVATIVE APPLICATION



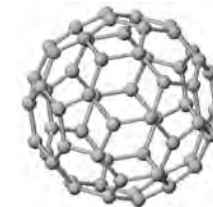
E. COLI INACTIVATION



MS2 PHAGE INACTIVATION

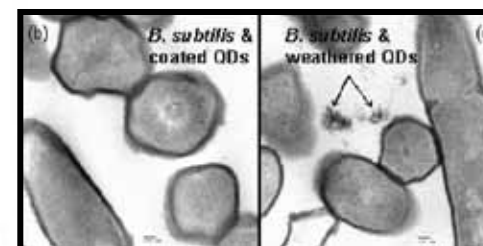
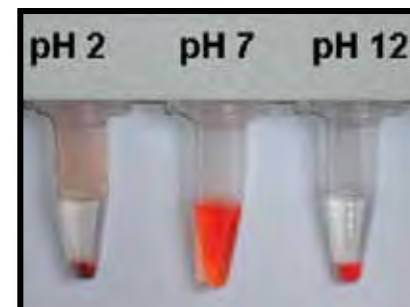
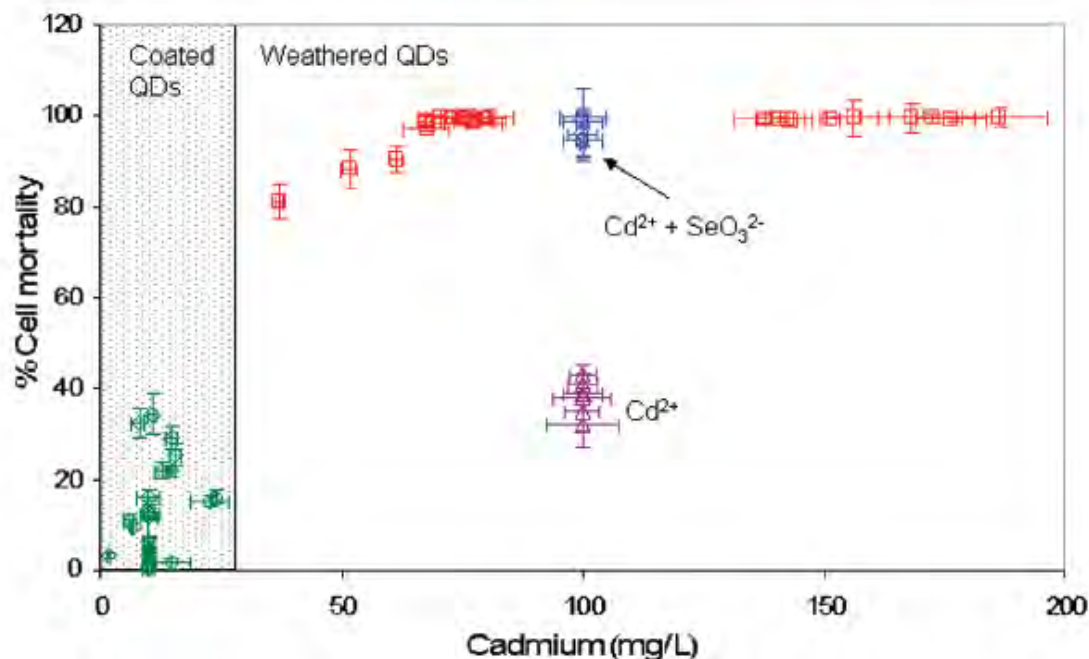


NANOPARTICLE WEATHERING: QUANTUM DOTS

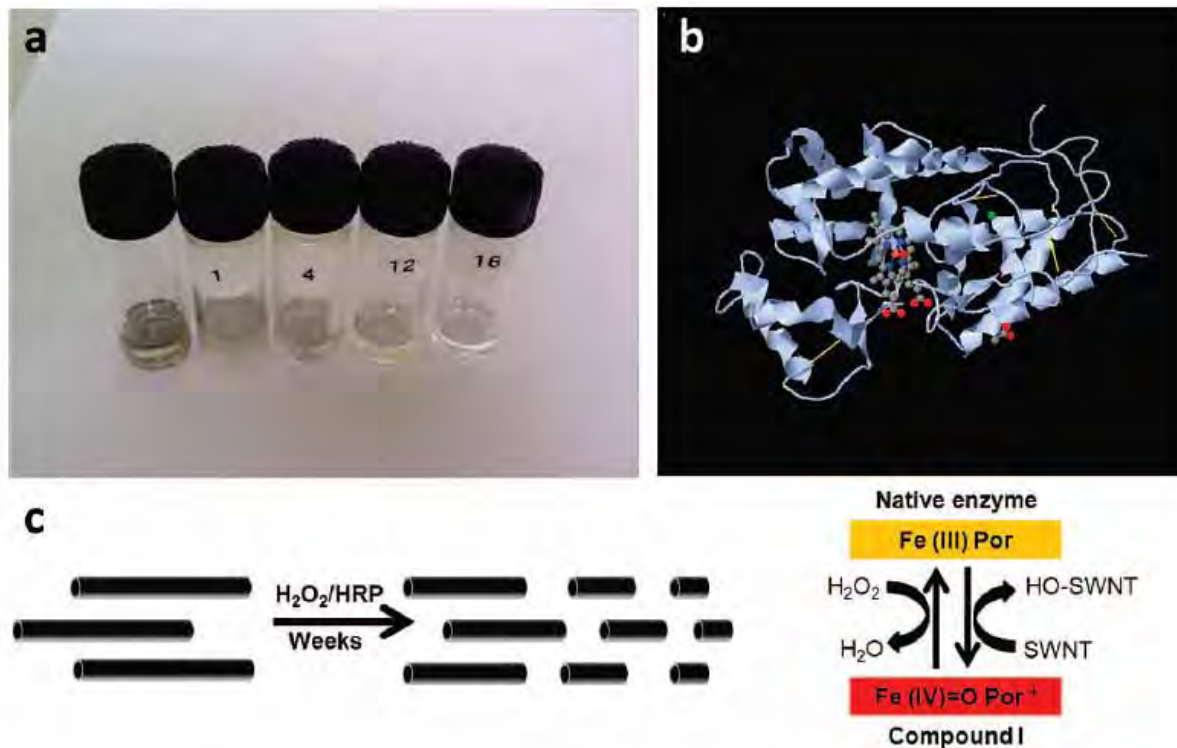


QUANTUM DOTS WITH INTACT SURFACE COATINGS DECREASED GROWTH RATES OF *B. SUBTILIS* AND *E. COLI* BUT WERE **NOT BACTERICIDAL**.

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



BIODEGRADATION OF CARBON NANOTUBES



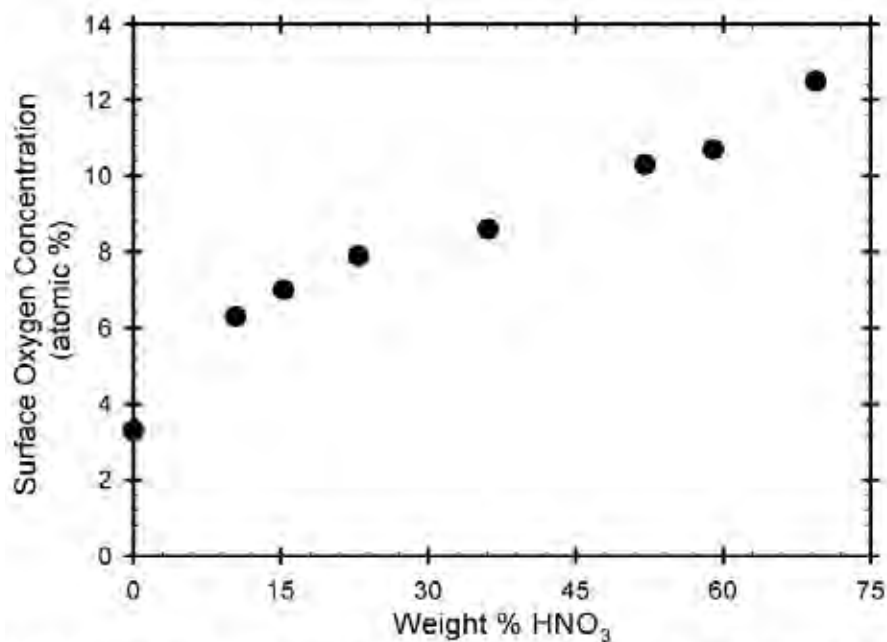
BIODEGRADATION OF CARBON NANOTUBES BY **HORSERADISH PEROXIDASE/H₂O₂** OVER THE PERIOD OF SEVERAL WEEKS

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

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

