Supplementary material for the article

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# Supplementary Material

# Enhancement of nano titanium dioxide coatings by fullerene and polyhydroxy fullerene in the photocatalytic degradation of the herbicide mesotrione

Aleksandar Djordjevic[a], Daniela Šojić Merkulov[a], Marina Lazarević[a], Ivana Borišev[a], Igor Medić[a], Vladimir Pavlović[b], Bojan Miljević[c], Biljana Abramović[a],*

[a]*University of Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia*

[b]*Serbian Academy of Sciences and Arts, Institute of Technical Sciences, Knez Mihajlova 35, 11080 Belgrade, Serbia*

[c]*University of Novi Sad, Faculty of Tehnology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia*

*Chemicals, solutions and catalysts*

All chemicals were of reagent grade and were used without further purification. Mesotrione (CAS No 104206-82-8, $C_{14}H_{13}NO_7S$, $M_r = 339.32$, PESTANAL®, analytical standard, 99.9% purity), was purchased from Fluka; 85% $H_3PO_4$ and 35% HCl were obtained from Lachema (Neratovice, Czech Republic); 99.8% $CH_3CN$, 30% $H_2O_2$, *tert*-butanol and ethylenediaminetetraacetic acid (EDTA) from Sigma-Aldrich; $KBrO_3$ from Merck and NaF form Kemika (Zagreb, Croatia). All solutions were made using doubly distilled water (DDW). $TiO_2$ Hombikat alone (Sigma-Aldrich), and in combination with $THF-nC_{60}$ or FNP were used as photocatalysts. For synthesis of $THF-nC_{60}$ and FNP, chemicals THF, $Br_2$, $FeBr_3$, NaOH, EtOH and fullerene $C_{60}$ (99.8%) purchased from Sigma-Aldrich were used.

*Nanoparticles characterization*

Dynamic light scattering (DLS) was used for the determination of hydrodynamic size, and electrophoretic light scattering (ELS) for measurements of the surface charge (zeta potential, $\zeta$) of analyzed samples. The measurements were conducted on a Zetasizer Nano ZS instrument (Malvern Instruments Inc, UK). All DLS analysis was done in triplicate, and the zeta potential measurements were performed in duplicate. The results were presented as mean values of obtained results for all repetitions.

Transmission electron microscopy (TEM) analyses were conducted on the JEM 1400 microscope with an accelerating voltage of 120 kV on copper grid 300 mesh.

The samples for scanning electron microscopy (SEM) measurements were prepared on grid size 300 mesh × 83 μm pitch, copper, and analyses were performed on instrument JEOL JSM 6460 LV.

The absorbance ($\alpha$) of the $TiO_2$, $TiO_2$/THF-$nC_{60}$ and $TiO_2$/FNP suspensions was measured by UV-VIS spectrophotometer Evolution 600, Thermo Scientific in the range between 240 nm and 840 nm with the step of 1 nm and speed of 10 nm $min^{-1}$. Demineralized water was used as reference. Brunauer–Emmett–Teller (BET) surface area analysis of the measured samples was performed using a gas adsorption porosimeter Surfer, Thermo Scientific following a standard procedure and by using liquid nitrogen.

*Synthesis of THF-$nC_{60}$, FNP, $TiO_2$/THF-$nC_{60}$ and $TiO_2$/FNP nanoparticles*

A solution of THF-$nC_{60}$ was obtained by intensive stirring of 250 mL of THF and 6.25 mg of fullerene $C_{60}$ in a nitrogen atmosphere, in the dark, at a temperature of 22 °C for two days. A saturated solution of fullerene $C_{60}$ in THF was filtered through a 100 nm filter. Then, 250 mL

of DDW pH-adjusted at 5 was added into the filtered $C_{60}$ solution and stirred. The excess of THF was evaporated by bubbling with $N_2$ at a temperature of 40 °C in the dark. A stable solution of fullerene $C_{60}$ nanoparticles in water was obtained, with residual amounts of the nanoparticles in the THF. The nanoparticles THF-$nC_{60}$ is pale yellow in color.

A solution of FNP was synthesized from a polybromine derivative $C_{60}Br_{24}$, obtained in a catalytic reaction of fullerene $C_{60}$ in $Br_2$ with $FeBr_3$ as the catalyst, by complete substitution of bromine with hydroxyl groups (Djordjevic et al., 1998; Mirkov et al., 2004). The obtained brown powder of FNP was stored in the dark.

*Characterization of THF-$nC_{60}$, FNP, $TiO_2$, $TiO_2$/THF-$nC_{60}$, and $TiO_2$/FNP nanoparticles*
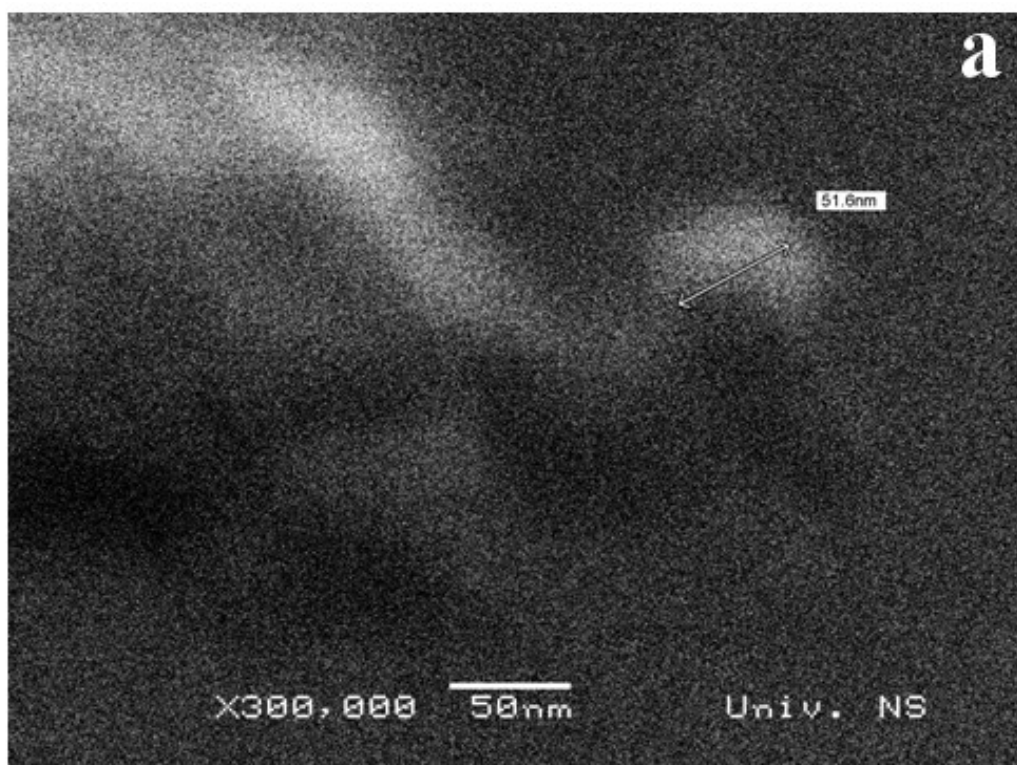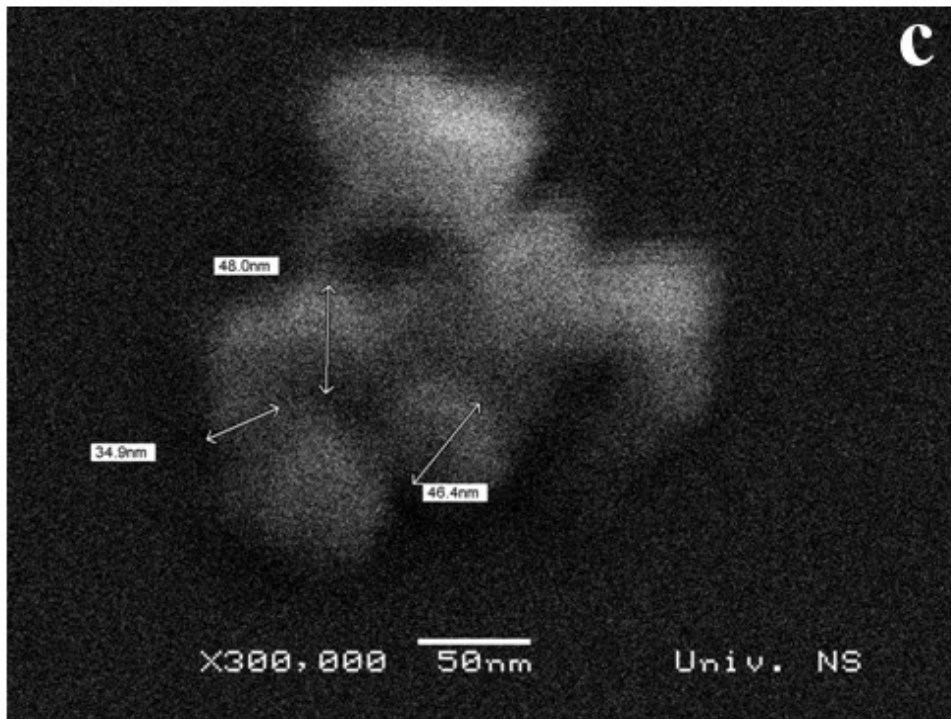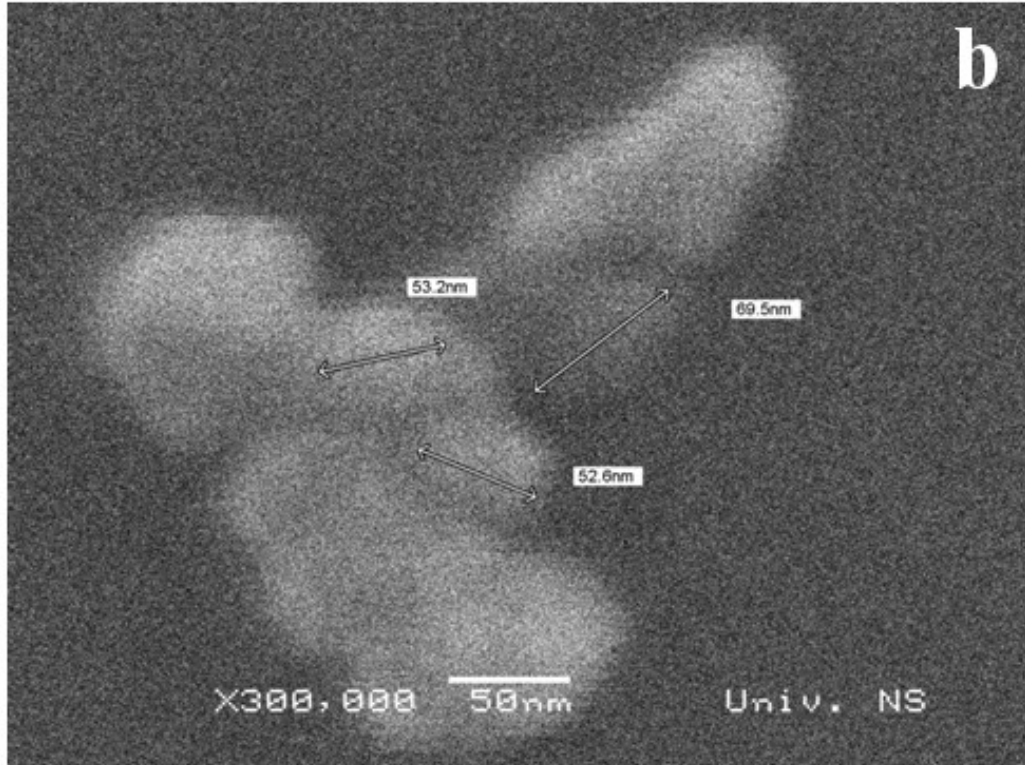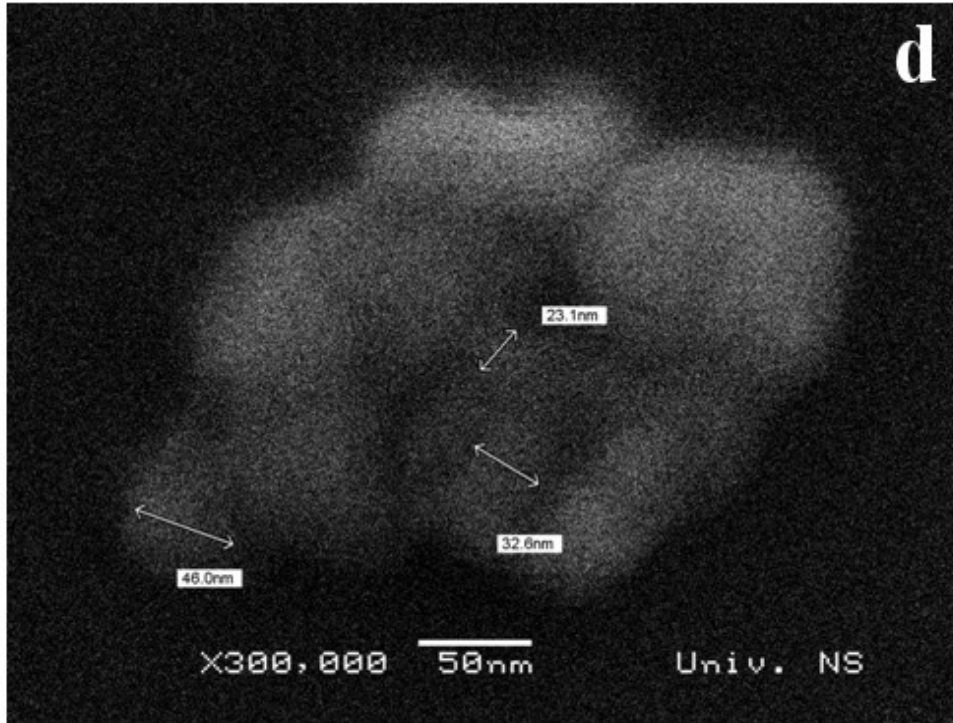
Fig. S1. SEM micrographs of (a) THF-nC$_{60}$, (b) TiO$_2$, (c) TiO$_2$/THF-nC$_{60}$ and (d) TiO$_2$/FNP.

Band gap energies ($E_g$) of the samples was determined using the Tauc's plot (Tauc, 1968). The method is based on the fact that the absorption of the light is dependent on the band gap energy of the absorbing material (Kubelka-Munk theory) (Kubelka, 1948; Kubelka and Munk, 1931). A relation between $\alpha$ and $E_g$ is given by López and Gómez (2012):

$$\alpha \times h\nu = C(h\nu - E_g)^{\frac{1}{n}} \qquad (1)$$

with the $h$ being a Planck's constant, $\nu$ the frequency (linked to the measured wavelength by $\nu = c/\lambda$, $c$ is the speed of light in vacuum) and $C$ an energy-independent constant. The factor $n$ depends on the transition type and it was assumed to be a direct allowed ($n = 2$). The band gap

energy can be determined from a plot of the modified absorbance $(\alpha \times h\nu)^n$ vs. the energy $h\nu$ by

extrapolating the linear fit of the straight section to the $\alpha = 0$ intercept of the energy coordinate.

Table S1. Band gap energies and their corresponding wavelengths.

| Sample | $E_g$ (eV) | $\lambda$ (nm) |
|---|---|---|
| $TiO_2$ | 2.55 | 486 |
| $TiO_2$/THF-n$C_{60}$ | 2.64 | 470 |
| $TiO_2$/FNP | 2.14 | 579 |
| FNP* | 1.99 | 623 |

*Results graphically not shown here.

Table S2. Specific surface area of the measured samples.

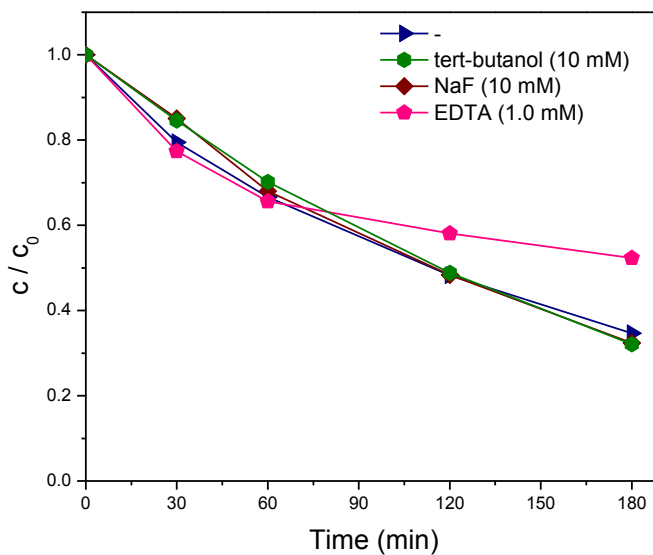| Sample | BET surface area ($m^2\ g^{-1}$) |
|---|---|
| $TiO_2$ | 49.62 |
| $TiO_2$/THF-n$C_{60}$ | 46.61 |
| $TiO_2$/FNP | 45.73 |

*Effect of hydroxyl and holes scavengers*



Fig. S2. Effect of hole and radical scavengers on the efficiency of mesotrione ($c_0 = 5.0 \times 10^{-2}$ mM) photocatalytic degradation in the presence of TiO$_2$/FNP (0.5 mg mL$^{-1}$/40 µl) suspension under simulated sunlight.

*Evaluation of mineralization*

Table S3. The degree of mineralization for the most efficient systems.

| No. | System | Mineralization (%) |
|---|---|---|
| 1. | 5.0 mM H$_2$O$_2$ | 2.7 |
| 2. | 3.0 mM H$_2$O$_2$ and 20 µl FNP | 12.7 |
| 3. | 7.0 mM KBrO$_3$ | 29.2 |
| 4. | 7.0 mM KBrO$_3$ and 40 µl FNP | 35.8 |

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