N. M. Dimitrijevic, Z. V. Saponjic, B. M. Rabatic, O. G. Poluektov, T. Rajh, "The Effect of Size and Shape of Nanocrystalline $\mathrm{TiO}_{2}$ on Photogenerated Charges, an EPR Study"

## Supporting information:

I. Field-swept echo spectra of anatase nano-object under 355 nm illumination obtained with Bruker Elexsys E580 spectrometer equipped with a dialectric MD4 cavity and an Oxford CF935 helium flow cryostat with ITC-5025 temperature controller. The first ( $\pi / 2$ ) and second $(\pi)$ pulse durations were 16 and 32 ns , respectively. Changing the time between pulses ( $\tau$ ) from 100 to 400 ns did not affect spectra.

II. g-tensor values and spin-spin relaxation times of photogenerated charges in anatase nanoobjects.

Table 1: EPR Parameters of the g Matrix for Paramagnetic Species formed upon Band Gap Excitation of Anatase Nano-objects

| Nano-objects | Electrons, $\left(\mathrm{Ti}^{3+}\right)_{\text {latt }}$ |  |  |  | Holes, $\left(\mathrm{Ti4}^{+} \mathrm{O}\right)_{\text {surf }}$ |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{g}_{\perp}$ | $\mathrm{g}_{\\|}{ }^{1}$ | $\mathrm{~g}_{\\|}{ }^{2}$ | $\mathrm{~g}_{\mathrm{z}}$ | $\mathrm{g}_{\mathrm{y}}$ | $\mathrm{g}_{\mathrm{x}}$ |
| Spherical particles $(<10 \mathrm{~nm})$ | 1.990 | 1.961 | 1.958 | 2.007 | 2.014 | 2.024 |
| Faceted particles $(<10 \mathrm{~nm})$ | 1.993 | 1.964 | - | 2.007 | 2.015 | 2.024 |
| Rods (50x300 nm) | 1.990 | 1.961 |  | 2.007 | 2.014 | 2.024 |
| Brick-like particles (10x20) | 1.993 | 1.964 | - | 2.007 | 2.015 | 2.024 |

Table 2: Spin-spin ( $\mathrm{T}_{2}$ ) Relaxation Times for Paramagnetic Species at 7 K Formed upon Band Gap Excitation of Anatase Nano-objects

| Nano-objects | Electrons, $\left(\mathrm{Ti}^{3+}\right)_{\text {latt }}$ | Holes, $\left(\mathrm{Ti}^{4+} \mathrm{O}\right)_{\text {surf }}$ |
| :--- | :--- | :--- |
| Spherical particles $(4.5 \mathrm{~nm})$ | $(155 \pm 4) \mathrm{ns}$ | $(2.2 \pm 0.2) \mu \mathrm{s}$ |
| Spherical particles $(\sim 10 \mathrm{~nm})$ | $(155 \pm 4) \mathrm{ns}$ | $(2.2 \pm 0.2) \mu \mathrm{s}$ |
| Faceted particles $(<10 \mathrm{~nm})$ | $(1.5 \pm 0.2) \mu \mathrm{s}$ | $(1.5 \pm 0.3) \mu \mathrm{s}$ |
| Rods $(50 \times 300 \mathrm{~nm})$ | $(2.0 \pm 0.3) \mu \mathrm{s}$ | $(2.2 \pm 0.3) \mu \mathrm{s}$ |
| Brick-like particles $(10 \times 20 \mathrm{~nm})$ | $(2.0 \pm 0.3) \mu \mathrm{s}$ | $(1.5 \pm 0.1) \mu \mathrm{s}$ |

