Supplementary Material

## Unusual Reduction of Graphene oxide by Titanium dioxide electrons Produced by Ionizing radiation. Reaction Products and Mechanism

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Raman spectra of GO-rGO solutions at different stages of GO reduction by  $e_{TiO2}$  are presented in Fig. S1. The peaks intensities were normalized to the intensity of 1330 cm<sup>-1</sup>. The maxima at ~1330 and ~1600 cm<sup>-1</sup> are assigned to the well-known D and G peaks, respectively, both dominated by the sp<sup>2</sup> phase, as excitation resonates with  $\pi$  states.<sup>1</sup> In a nutshell, the G peak is associated with the bond stretching of sp<sup>2</sup> atoms in both rings and chains, while the D peak is associated with the breathing modes of sp<sup>2</sup> atoms in rings, but requires sp<sup>3</sup> defects to be activated.<sup>2</sup> The 2D peak associated with overtone of TO phonons in GO and rGO (~2700 cm<sup>-1</sup>) remains very week suggesting introduction of sp<sup>3</sup> defect like structures rather than reestablishing of graphitic structures upon reduction of GO.<sup>3</sup>



Figure S1. Development of normalized Raman spectra upon reduction of GO to rGO The reduced GO expressed in terms of percent (100x[rGO]/[GO]<sub>0</sub>).

The much larger cross section of interaction of  $sp^2$  phase compared to  $sp^3$  (50-250 times) makes it difficult to quantitatively analyze the concentration of the  $sp^3$ -type defects. The ratio of intensities I(D)/I(G) is typically used to observe qualitative changes in  $sp^2$  induced by introduction of  $sp^3$  defects.<sup>4</sup> The I(D)/I(G) ratio in nanoscale structures initially sharply decreases upon introduction of a topological disorder into the graphene-like structures. The bonding remains mainly  $sp^2$ , but the weaker bonds affect the vibrational modes. At low [rGO]/[GO]<sub>0</sub> fractions (red curve, Fig. S2) there is an initial sharp decrease of I(D)/I(G). This is followed by conversion of  $sp^2$  to  $sp^3$  sites and the consequent change of  $sp^2$  configuration from rings to chains, which is associated with increasing I(D)/I(G) (Fig. S2, blue curve). This process is usually accompanied with a shift of the G peak, due to the confinement of  $\pi$  electrons in shorter chains. In Fig. S3 a decrease in the intensity of the low energy part of the G peak and overall shift of intensity toward 1600cm<sup>-1</sup> is observed above 50% conversion of GO to rGO.



Figure S2. Variation of I(D)/I(G) as the reduction of GO proceeds. This is in agreement with



earlier studies of transformation of graphitic like structures upon introduction of sp<sup>3</sup> defects.<sup>2, 4</sup> Figure S3. Development of G peak shape of the Raman spectra upon reduction of GO to rGO (expressed in terms of percent  $(100x[rGO]/[GO]_0))$ 

 Wu, J. B.; Lin, M. L.; Cong, X.; Liu, H. N.; Tan, P. H., Raman Spectroscopy of Graphene-Based Materials and Its Applications in Related Devices. *Chemical Society Reviews* 2018, 47, 1822-1873.

2. Ferrari, A. C.; Robertson, J., Raman Spectroscopy of Amorphous, Nanostructured, Diamond-Like Carbon, and Nanodiamond. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* **2004**, *362*, 2477-2512.

3. Moon, I. K.; Lee, J.; Ruoff, R. S.; Lee, H., Reduced Graphene Oxide by Chemical Graphitization. *Nature Communications* **2010**, *1*.

4. Ferrari, A. C., Raman Spectroscopy of Graphene and Graphite: Disorder, Electron-

Phonon Coupling, Doping and Nonadiabatic Effects. Solid State Communications 2007, 143, 47-

57.