

Electronic Supplementary Information of Enhanced Photoactivity and Conductivity in Transparent TiO₂ Nanocrystals/Graphene Hybrid Anode

C. Ingrosso^{a,†,*} G. V. Bianco^{b,‡} V. Pifferi,^c P. Guffanti,^c F. Petronella,^a R. Comparelli,^a A.

Agostiano^{a,d}, M. Striccoli,^a I. Palchetti,^e L. Falciola,^c M. L. Curri^a and G. Bruno^b

^aCNR-IPCF Sez. Bari, c/o Dip. di Chimica, Università degli Studi di Bari, via Orabona 4, 70126,

Bari, Italy. *Email: c.ingrosso@ba.ipcf.cnr.it

^bCNR-NANOTEC, c/o Dip. di Chimica, Università degli Studi di Bari, via Orabona 4, 70126,

Bari, Italy.

^cDip. di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy.

^dDip. di Chimica, Università degli Studi di Bari, via Orabona 4, 70126, Bari, Italy.

^eDip. di Chimica Ugo Schiff, Università degli Studi di Firenze, via della Lastruccia 3-13, 50019,

Sesto Fiorentino (FI), Italy.

The inset of Panel A of Fig. S1 reports TEM images of as-synthesized OLEA-coated and PBA treated TiO₂ NCs. The as-synthesized nano-objects are spherical in shape and have an average diameter of 6 nm, appearing rather well spaced and separated on the grid, because of the presence of the long alkyl chain OLEA molecules,¹ and after the capping exchange with PBA the

nanoparticles preserve their morphology. The same panel A of Figure 1 displays UV-Vis spectra of TiO₂ NCs, surface coordinated by OLEA and surface modified with PBA, respectively. Both spectra show the typical featureless line-shape of a high band gap TiO₂ semiconductor,¹ and upon treatment with PBA, the NCs almost display the same spectroscopic behavior.

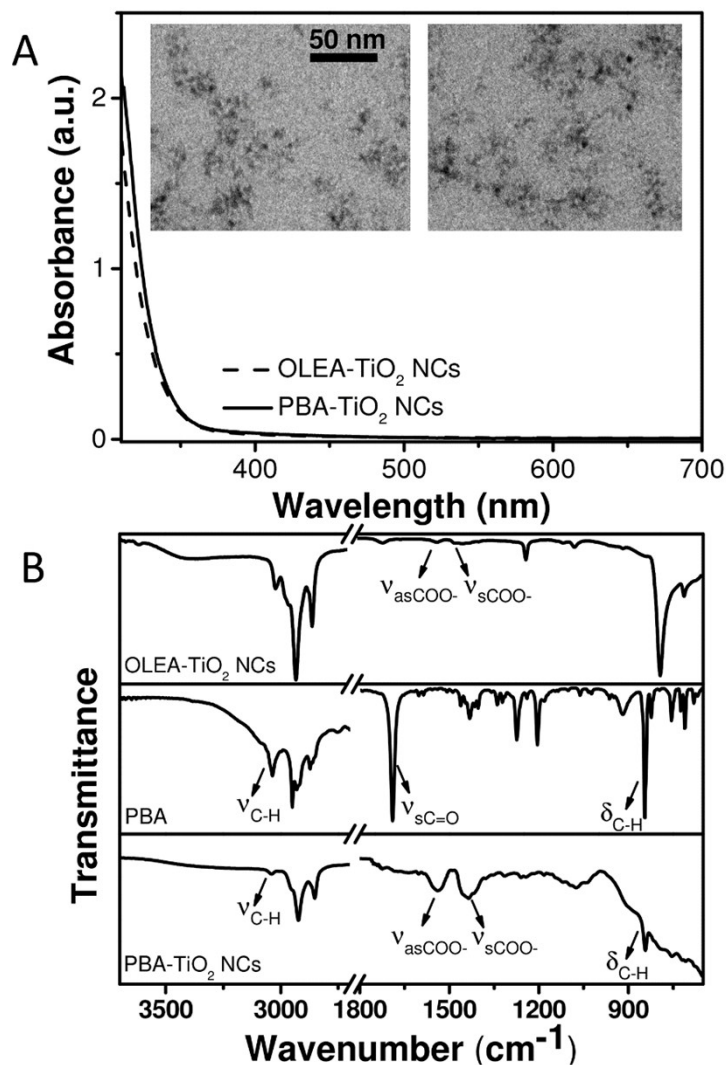


Fig. S1. (A) UV-vis absorption spectra and (in the inset) TEM micrographs of oleic acid (OLEA, left)- and pyrene butyric acid (PBA, right)-coated TiO₂ NCs. (B) ATR-FTIR spectra of OLEA-TiO₂ NCs, PBA and PBA-TiO₂ NCs.

Panel B of Fig.S1 compares the infrared spectra of the PBA-coated TiO₂ NCs with those recorded from the pristine OLEA-capped TiO₂ NCs and from bare PBA molecules. The high wavenumber region of the spectrum of PBA-capped TiO₂ NCs is characterized by the presence of typical signals of both PBA and residual OLEA ligand molecules. Namely, at 3039 cm⁻¹ the aromatic C-H stretching vibration of pyrene molecule is evident, along with the strong band of the asymmetric -CH₃ stretching at 2956 cm⁻¹ and the strong asymmetric and symmetric stretching of -CH₂- of OLEA at 2923 cm⁻¹ and 2852 cm⁻¹, respectively. In the low wavenumber region of the spectrum of the PBA-coated TiO₂ NCs, the signals of the antisymmetric and symmetric -COO- stretching of PBA, namely ν_{as, CO_2^-} at 1539 cm⁻¹ and ν_{s, CO_2^-} 1434 cm⁻¹, respectively which reasonably superimpose those of the residual OLEA molecules, expected at 1520 cm⁻¹ and 1436 cm⁻¹,¹ can be observed. The difference in $\Delta\nu$ of PBA, estimated as $\nu_{as, CO_2^-} - \nu_{s, CO_2^-}$, which is about 105 cm⁻¹, allows to infer the mode of binding as a chelating bidentate to the Ti⁴⁺ Lewis sites.^{2,3} These findings, along with the presence of the intense band peaked at 844 cm⁻¹, which is assigned to the characteristic out of plane C-H bending of the pyrene aromatic ring and the lack of the free C=O stretching band of the PBA and OLEA molecules, expected at 1691 cm⁻¹ and around 1650-1720 cm⁻¹, respectively¹ allow to conclude that pyrene molecules coordinate the surface Ti⁴⁺ Lewis sites by the carboxylate anions in the form of a chelating bidentate binding.

Fig. S2 reports the SEM and AFM images of the bare CVD graphene transferred on SiO₂/Si. The image shows an almost flat surface exhibiting striations in correspondence of grain boundaries and mechanical lattice deformations of the graphene plane⁴ which bring to wrinkles or folds.

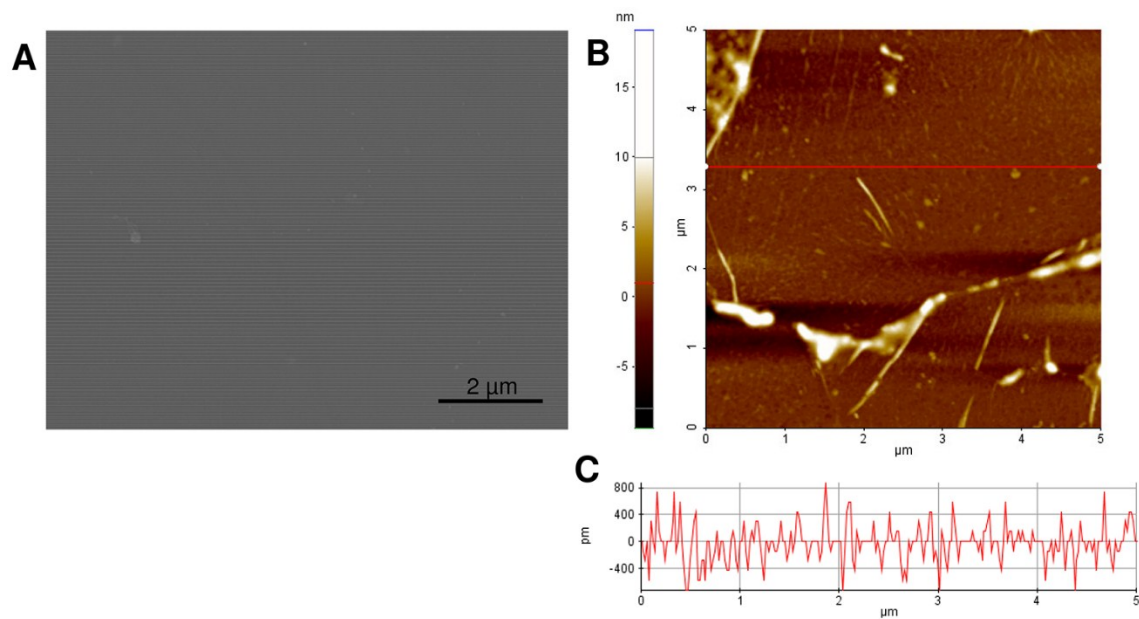


Fig. S2. (A) SEM and (B) 2-D topography AFM images of CVD graphene transferred on SiO₂/Si substrate. In (C) cross sectional line profile recorded along the red line of (B).

Fig. S3 reports the EIS Nyquist plots of the ITO glass modified electrodes investigated in the work and registered in 0.1 M NaClO₄.

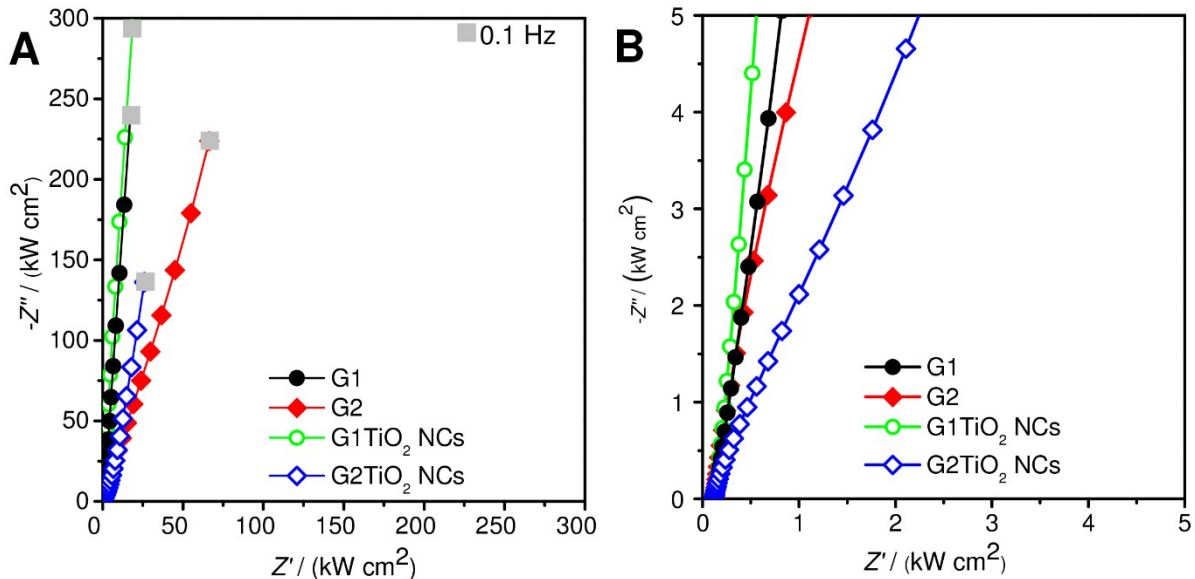


Fig. S3. EIS Nyquist plots of the ITO electrodes modified with monolayer graphene (G1), bilayer graphene (G2) and PBA-TiO₂ NCs functionalized monolayer and bilayer graphene (G1TiO₂ NCs and G2TiO₂ NCs) in 0.1 M NaClO₄.

Figure S4 reports the photocurrent response of the working electrodes formed of PBA surface coated mono (G1) and bilayer (G2) graphene, under illumination with an UV-lamp ($\lambda = 356$ nm) at the bias voltage of 1V in 0.1 M NaClO₄. The graphene electrodes have been functionalized by incubation for 48 h in a diluted solution of the PBA linker, namely 10⁻¹⁰ M. Such a value of concentration of the PBA linker has been selected because it is lower than the critical micelle concentration of pyrene, namely 10⁻⁷ M, being thus pyrene compounds expected in monomer form and not as micellar aggregates⁵

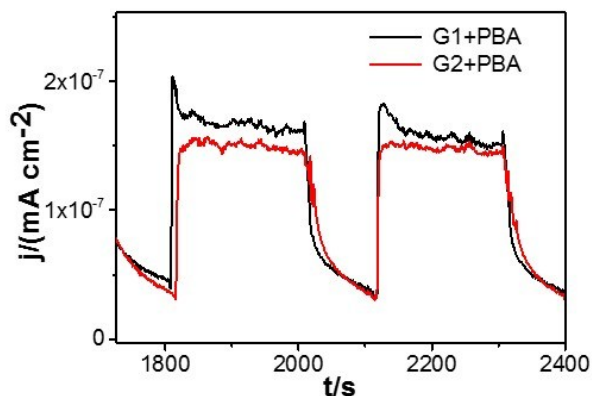


Fig. S4. Photocurrent transient measurements collected under UV-light ($\lambda=365$ nm) irradiation at the bias voltage of 1 V in 0.1 M NaClO_4 of ITO electrodes, modified with the PBA surface coated G1 and G2.

Fig. S4 shows that the photocurrent densities of the PBA coated G1 and G2 are about $0.11 \mu\text{A cm}^{-2}$, hence lower than those of the corresponding samples functionalized with the PBA-coated TiO_2 NCs (panel A of Figure 5) and even lower than those of the bare G1 and G2, namely $0.15 \mu\text{A cm}^{-2}$ and $0.30 \mu\text{A cm}^{-2}$, respectively, attesting for the detrimental effect of PBA in enhancing the photoactivity of the CVD graphene film. Such results comply with the poor photocurrent density signals detected for the graphene electrodes modified by other pyrene compounds.⁶

References

- 1 P. D. Cozzoli, A. Kornowski, H. Weller, *J. Am. Chem. Soc.* 2003, **125**, 14539.
- 2 P. J. Thistlethwaite, M. S Hook, *Langmuir* 2000, 16, 4993.
- 3 M. Nara, H. Torii, M. Tasumi, *J. Phys. Chem.* 1996, 100, 19812.

- 4 M. Ahmad, H. An, Y. S. Kim, Y. S., J. H. Lee, J. Jung, S.-H. Chun, Y. Seo, *Nanotechnol.* 2012, **23**, 285705
- 5 M. Zhang, R. R. Parajuli, D. Mastrogiovanni, B. Dai, P. Lo, W. Cheung, R. Brukh, P. L. Chiu, T. Zhou, Z. Liu, E. Garfunkel, H. He, *Small* 2010, 6, 1100
- 6 S. C. Feifel, K. R. Stieger, H. Lokstein, H. Luxc, F. Lisdata, *J. Mater. Chem. A* 2015, 3, 12188.