UV-INDUCED SYNTHESIS OF POLYANILINE-TiO_2 HYBRIDS: A MECHANISTIC STUDY

C. Cionti[a,b], E. Falletta[a,c], D. Meroni[a,b], C. Della Pina[a,c], S. Ardizzone[a,b]

[a] Department of Chemistry, Università degli Studi di Milano, via Golgi 19,20133, Milan, Italy

[b] Consorzio INSTM, via Giusti 9, 50121, Florence, Italy

[c] ISTM-CNR, via Golgi 19, 20133, Milan, Italy

Polyaniline, an important member of the conductive polymer family, has received increasing attention due to its peculiar pH-dependent properties which open the way to a wide spectrum of applications, ranging from electronics and optics to photovoltaic[1,2]. PANI is traditionally synthesized via oxidative polymerization[3], a process which involves toxic reagents (aniline and persulfates) and leads to carcinogenic byproducts. Aiming to more environmentally friendly procedures, other synthetic strategies have been developed during the years: in particular, some of us[4] have reported a green synthesis involving aniline dimer ((4-aminophenyl)aniline) as starting compound, H_2O_2 as oxidant and Fe^{3+} as catalyst, thus yielding H_2O as only coproduct. Unfortunately, with this eco-friendly process, there is no control on the polymer morphology and the result is a compact PANI with low dye-sorption capabilities. We have recently proposed a new green synthesis in which PANI growth is activated by TiO_2 photocatalysis giving rise to PANI-TiO_2 hybrid systems[5]. The reaction is carried out in two steps: the photocatalytically induced oligomerization of aniline dimer at the TiO_2 surface, and the polymerization step initiated by H_2O_2 addition. In this work, the reaction mechanism was investigated via radical scavenger tests and by a combination of LCMS, FTIR, XPS and ζ-potential measurements. UV light is essential to initiate the reaction, as without irradiation only short oligomers with poor chain-conjugation are formed (Fig.1). Overall, this synthetic method leads to composites stable under UV irradiation in usage conditions, with high specific surface areas (crucial for sorption properties) and enhanced crystallinity, which is beneficial for PANI conductivity. The role of synthetic parameters like reagent ratios and temperature was also investigated; while incrementing the H_2O_2 amount leads to poorer crystallinity and lower surface area, the TiO_2 content in the hybrid can be increased without affecting its morphology and performance. All samples were tested towards the removal of model dye pollutants. The reusability of the nanocomposite and the influence of common interferents were investigated, also via tests in simulated drinking water.

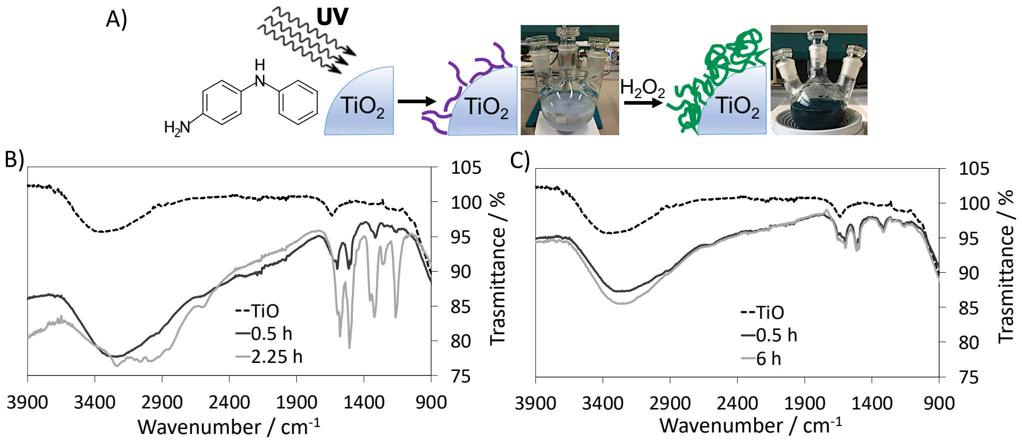

Figure 1. A) Scheme of the reaction pathway. B) and C) FTIR spectra of TiO_2 and of samplings of the oligomerization step with the passing of time under UV irradiation and in the dark, respectively.

References

[1] C.O. Baker, X. Huang, W. Nelson, R.B. Kaner, *Chem. Soc. Rev., 46,* **2017**, 1510.
[2] F. Cui, Y. Huang, L. Xu, Y. Zhao, J. Lian, J Bao, H Li, *Chem. Commun.*, *54,* **2018**, 4160.
[3] H.D. Tran, J.M. D'Arcy, Y. Wang, P.J. Beltramo, V.A. Strong, R.B. Kaner, J. *Mater. Chem.*, *21*, **2011**, 3534
[4] C. Della Pina, M. A. De Gregorio, L. Clerici, P. Dellavedova, E. Falletta, *J. Hazard. Mater.*, **2018**, *344*, 308
[5] C. Cionti, C. Della Pina, D. Meroni, E. Falletta, S. Ardizzone, *Chem. Commun.*, **2018**, *54*, 10702