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PANI-TiO_2 composites: the mechanism behind a green process

Carolina Cionti,[a,b] Cristina Della Pina,[a,c] Daniela Meroni,[a,b] Ermelinda Falletta,[a,c] Silvia Ardizzone[a,b]

[a] Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, 20133, Milano, Italy;
[b] Consorzio INSTM, via Giusti 9, 50121, Firenze, Italy;
[c] ISTM-CNR, via C. Golgi 19, 20133, Milano, Italy;
carolina.cionti@unimi.it

Polyaniline (PANI) is an important member of the family of organic conductive polymers, which holds potential in numerous fields, such as electronics, optics and photovoltaics [1]. In recent years, PANI has received increasing attention for application in wastewater treatment due to its sorption properties enabling the removal of a broad range of pollutants [2,3]. Polyaniline is classically synthesized by oxidative polymerization [4], which involves noxious reagents (aniline as starting compound and persulfates as oxidant) and gives rise to toxic and carcinogenic by-products (such as benzidine and *trans*-azobenzene). A great deal of effort has been devoted to find alternative green routes: in particular, some of us reported a benign synthesis based on aniline dimer ((4-aminophenyl)aniline), H_2O_2 as oxidant and Fe^{3+} as catalyst [5]. However, this procedure yields no control on the polymer morphology, leading to a compact PANI with low surface area and poor dye sorption capability. We have recently developed an alternative green synthesis based on TiO_2 photocatalysis, enabling a morphological control of the polymer [6]. In this work, the reaction mechanism has been investigated in depth via LC-MS, FT-IR and ζ-potential analyses. In the first stage, carried out under UV irradiation, the growth of oligomers from the aniline dimer takes place on the TiO_2 particle surfaces, activated by the photocatalytic generated radicals. In the second step, the addition of H_2O_2 (80% less than in the Fe-catalyzed synthesis) activates the polymer growth, giving rise to the final product. By separating the oligomerization and polymerization steps, polymer composites with high crystallinity and porous morphology could be prepared. The dye sorption capability of the samples was tested toward methyl orange as model for anionic azo dyes: promising results were obtained both in terms of dye removal and product reusability. The creation of PANI-TiO_2 composites opens the door to future applications exploiting the complementary properties of the two materials, such as pollutant removal processes based on combined sorption and photocatalytic degradation.

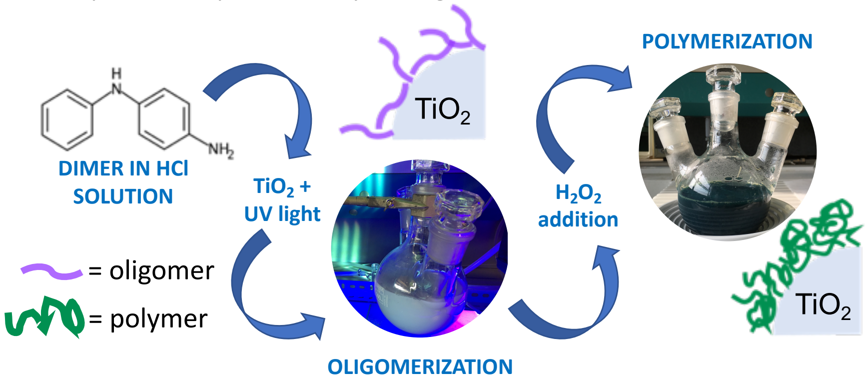

Figure 1. Outline of the reaction mechanism.

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