

New insights into the Photocatalytic activity of TiO₂/reduced-Graphene Oxide: from the role of the substrate adsorption to the evidence of the electron transfer from rGO to TiO₂

Marco Minella^a, Claudio Minero^a, Fabrizio Sordello^a

^a *Department of Chemistry and NIS Center of Excellence, University of Torino, Via P. Giuria 5, Torino 10125, Italy*
marco.minella@unito.it

The coupling of graphene or reduced graphene oxide (rGO) with a proper semiconductor has been proposed to increase the rates of photocatalytic processes used for the abatement of aqueous pollutants.[1]

In this work we studied the photocatalytic properties of TiO₂/rGO composites through the kinetic analysis of the photocatalyzed degradation of different organic substrates. Different amounts of GO were chemically or hydrothermally reduced onto nanometric commercial TiO₂. The photocatalytic performance of these hybrid materials was compared with that of the pristine supports by measuring the rates of the photocatalyzed transformation of methylene blue (MB), phenol and 2,4-dichlorophenol (2,4-DCP) under different irradiation conditions (UV only, Vis only and UV-Vis light). MB and 2,4-DCP are strongly adsorbed on the hybrids materials.

In the presence of the hybrid catalysts, the degradation of MB under Vis is due to the dye-sensitized photocatalytic mechanism, while under UV-Vis or Vis only there is an additional semiconductor-based photocatalytic mechanism. Conversely, the increment of the rGO loading reduces the rate of photocatalytic transformation rate for the poorly adsorbed phenol and for the adsorbed 2,4-DCP under UV irradiation. Furthermore, negligible degradation rates were observed under Vis for both substrates: the degradation constants for 2,4-DCP are low and it was difficult to discriminate between the Vis-activated photocatalytic process and the residual slow adsorption.

Under UV only irradiation, the presence of the graphenic phase provided an inhibiting contribution to the activity of the material. This could be explained by *i*) a shielding effect of rGO and *ii*) a separation/compartimentation of the substrate since 2,4-DCP is adsorbed on rGO while the main reactive species are generated on TiO₂ surface. The inhibition effect caused by the presence of rGO was lower if UV-Vis irradiation was used and this can be explained considering that a poor, but not null Visible activated degradation was observed.

Among many mechanisms reported on the role of rGO [2], it is inferred that the working mechanism involves electron transfer from photo-excited states of rGO onto the titania, and holes migration from titania to rGO, where adsorbed substrates are oxidized. This last oxidation is possible only if the HOMO has higher energy than the empty states of excited rGO, supposedly for MB and not for phenol/2,4-DCP. Then, reduced graphene oxide is advantageous when substrates are adsorbed and when the charge separation is possible. Alone, or coupled with low working function oxides like SiO₂, rGO could be ineffective.

References:

- [1] M. Minella, D. Fabbri, P. Calza, C. Minero, *Current Opinion in Green and Sustainable Chemistry*, **2017**, 6, 11-17.
- [2] M. Minella, F. Sordello, C. Minero, *Catalysis Today*, **2017**, 281, 29-37.