Modification of Graphene Oxide and Graphene Oxide-TiO_2Solutions by Pulsed Laser Irradiation for Dye Degradation

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Carbon nanostructures have been already used as high-capacity and selective sorbents for organic solutes in aqueous solutions. In particular, graphene oxide (GO) and reduced graphene oxide (RGO) have been used as scaffold materials for photocatalytic nanoparticles showing higher binding capacity for different water contaminants than free nanoparticles [1]. Furthermore, GO has shown photocatalytic properties and the ability of enhancing the activity of known photocatalysts as TiO_2[2]. Hybrid compounds containing GO and TiO_2 nanoparticles can provide an interesting way to get a better dispersion of the semiconductor oxide on a wide surface area and allows to reduce the charge recombination of the photo-generated carriers in TiO_2. Furthermore, the formation of Ti-C bonds could favour the absorption of light in the visible range [3]. All these effects help to increase the photocatalytic efficiency of TiO_2 [4].

This work reports the preparation of RGO by pulsed laser irradiation for different times starting from a concentrated solution of GO prepared by the modified Hummers method [5]. Theadsorption properties and the photocatalytic behaviour after the reduction has been investigated. Pulsed laser with visible wavelength (532 nm) is suitable to finely tune the degree of reduction and tailor both the hydrophilicity and the spectroscopic features of the final GO suspension [5]. In addition, in this work a pulsed laser irradiation process of mixed solution of GO and RGO with P25 titania for 15 minutes is also used for producingnanocomposite materials.The produced materials are characterized by scanning electron microscopy (SEM) and spectroscopic techniques, such as infrared (IR), Raman and X-ray Photoelectron spectroscopy (XPS). Furthermore, their dye adsorption ability is tested by adding methylene blue (MB) in the solutions and measuring its concentration decrease by UV-Vis absorbance spectroscopy.

Figure 1 reports the SEM images for GO and RGO mixed with P25-TiO_2 nanoparticles. In general, RGO layers appear to be smaller and more irregular than the GO ones; TiO_2 particles are distributed homogeneously on the surface of both GO and RGO, without the formation of big aggregates. In Figure 2 XPS spectra of GO and RGO (after 3h of reductionby laser) are reported: C1s spectra present two peaks related respectively to sp^2, sp^3 (284.5 eV)and to oxygen-containing groups (C-O and C-OH at 286.5 eV, C=O at 288.5 eV and COOH at 289.5 eV) [6].The relative ratio between the intensity of O-related contributions in the C1s peak and the total C1s peak clearly decreases after laser irradiation, indicating a reduction in the oxygen content in RGO, as expected. In the case of GO-P25 and RGO-P25 composites,a lower amount of O-related contributions in the C1s peak, suggesting that, during laser irradiation used to prepare the composites, a further reduction process induced by the presence of TiO_2takes place on GO and RGO.

We have studied the efficiency of GO and its laser reduced forms in the MB adsorption in water: an excellent adsorption capacity is observed for both GO and RGO.The comparison between GO, RGO and the same materials mixed with P25 suggests that reduction of GO can be accelerated by adding TiO_2 and irradiating for 15 min the solution. In Figure 3 we report UV-Vis absorbance spectra of MB in the presence of GO, laser irradiated GO-P25 (on the top), and in RGO solution and laser irradiated RGO-P25 solution (on the bottom). UV-Vis absorbance spectrum of MB for laser irradiated P25-TiO_2 solution is reported in both figures for comparison [7].

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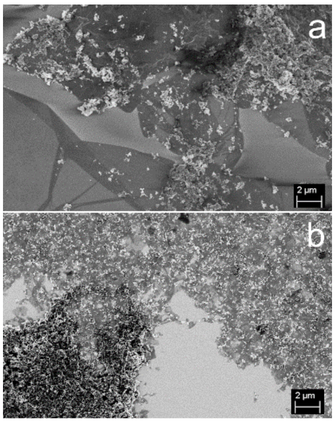

Figure 1: SEM images (on the left) of (a) GO-P25 and(b) rGO-P25

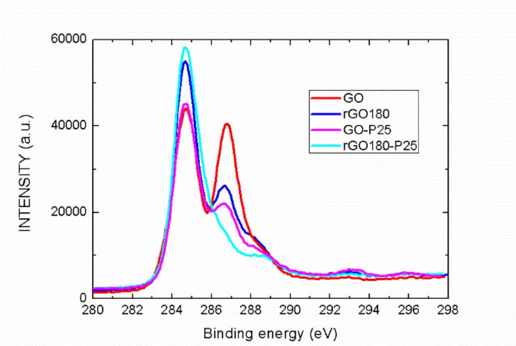

Figure 2: C 1s XPS spectra for GO, RGO and the respective composites with P25-TiO_2.

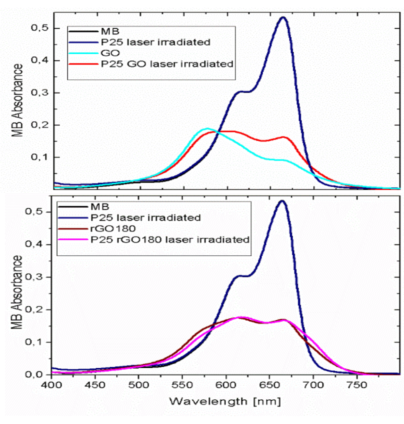

Figure 3: UV-Vis absorbance spectra of MB dye in different solutions (GO, RGO, GO-P25, RGO-P25 and P25 for comparison).