Materials Science in Semiconductor Processing ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/matsci

Modification of graphene oxide and graphene oxide–TiO_2 solutions by pulsed laser irradiation for dye removal from water

S. Filice [a,b,*], D. D'Angelo [a], S.F. Spanò [b], G. Compagnini [b], M. Sinatra [b], L. D'Urso [b], E. Fazio [c], V. Privitera [d], S. Scalese [a,**]

[a] CNR-IMM, Zona Industriale Strada VIII n.5, I-95121 Catania, Italy
[b] Dipartimento di Scienze Chimiche, Università di Catania, viale A. Doria 6, 95125 Catania, Italy
[c] Dipartimento di Fisica e Scienze della Terra, Viale F. Stagno d'Alcontres 31, I-98166 Messina, Italy
[d] CNR-IMM, via Santa Sofia n.64, I-95123 Catania, Italy

ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form
22 July 2015
Accepted 24 July 2015

Keywords:
Graphene oxide
Dye adsorption
Methylene blue
Laser irradiation
TiO_2

ABSTRACT

Pulsed laser with visible wavelength (532 nm) allows to modify the properties of graphene oxide (GO) sheets dispersed in water by finely tuning the amount of oxygen functionalities and, therefore, the degree of reduction. In this way both the hydrophilicity and the spectroscopic features of the GO suspension can be changed. This work reports the preparation of reduced graphene oxide (rGO) and mixed solutions of GO or rGO and Degussa P25® titania nanoparticles by pulsed laser irradiation. The produced materials are characterized by scanning electron microscopy, Raman spectroscopy and X-ray photoelectron spectroscopy. Their ability to remove methylene blue from water is investigated by studying the dye decolorization.

1. Introduction

Search for novel, cost effective and efficient materials for dyes removal from water is very important, since these substances are harmful to aquatic organisms and to humans [1]. Recently, graphene and graphene oxide (GO) are drawing much attention as alternative materials for dyes adsorption [2]. Graphene is defined as a flat monolayer of sp^2 bonded carbon atoms, packed tightly into a two-dimensional honeycomb lattice [3]. GO is generally prepared by chemical oxidation of graphite powder resulting in extended graphene sheets decorated with epoxy and hydroxyl functional groups in the basal plane and carboxylic acid groups at the edges [4]. These groups confer high hydrophilicity and negative charge density to GO, favouring the adsorption of cationic species as the methylene blue (MB) azo dye, due to electrostatic interaction [5]. MB can form different aggregates on GO producing maxima of light absorption at specific wavelengths [6].

In this paper, solutions of chemically prepared GO are gradually reduced by pulsed laser ablation in liquid (PLAL) [7]. PLAL, with respect to other reduction methods [8], is more environmentally friendly and allows to tune the density and quality of the oxygen functional groups on GO. In addition, it is tested as new, simple and green method for the synthesis of GO(rGO)–TiO_2 composite materials. The interest for this kind of hybrid materials arises from the photocatalytic activity of TiO_2 for water purification [9,10]. Hybrid compounds containing GO and TiO_2 nanoparticles were realized to get a better dispersion of the semiconductor oxide on a wide surface area and to increase the absorption of light in the visible range [11,12] Anyway, since GO shows higher MB adsorption capacity than other absorbent materials such as carbon nanotubes and activated carbon (see Ref. [5] and references therein), it is important to test also the adsorption properties of the hybrid compounds. In this study we have tested the ability of GO-(rGO-)TiO_2 composites to remove a cationic dye such as MB from water by simple adsorption phenomena. The results highlight the correlation of MB aggregation on GO/rGO surface with the layer charge density of carbon materials.

2. Materials and methods

Natural graphite flakes were purchased from Aldrich. Potassium permanganate, sodium nitrate were purchased from VWR Chemicals. Sulfuric acid (> 95%) was purchased from AnalaR Normapur. Hydrogen peroxide (30 wt% in H_2O), methylene blue

* Corresponding author at: CNR-IMM, Zona Industriale Strada VIII n.5, I-95121 Catania, Italy.
** Corresponding author.
E-mail addresses: simona.filice@imm.cnr.it (S. Filice), silvia.scalese@imm.cnr.it (S. Scalese).

http://dx.doi.org/10.1016/j.mssp.2015.07.073
1369-8001/

(0.05 wt% in H_2O) and P25 titania (> 99.5%) nanoparticles were purchased from Sigma–Aldrich.

GO was prepared by a modified Hummers method and rGO was prepared following the method reported in Ref [7]. Briefly, different solutions of GO at 100 mg/l were irradiated by the second harmonic of a pulsed Nd:YAG laser (532 nm) with a pulse duration of 5 ns a repetition rate of 10 Hz. The laser beam size was around 28 mm^2 and the GO solutions were homogeneously irradiated, without any focusing lens, at a constant fluence of 0.32 J/cm^2 for 15, 60 and 180 min (samples named hereafter rGO15, rGO60 and rGO180, respectively). Aqueous GO–P25 and rGO180–P25 solutions were prepared mixing the GO (rGO180) and P25 with atomic ratio of 1:9 until a final concentration of 100 mg/L. These solutions were irradiated by pulsed laser for 15 min in the same conditions used for GO reduction.

Field emission scanning electron microscope (Zeiss Supra35 FE-SEM) was used to investigate the morphology of the samples.

The adsorption ability of GO and rGO solutions at different concentration (10, 70 and 100 mg/L) was evaluated by measuring the decrease of MB concentration starting from the initial value of $1 \cdot 10^{-5}$ M in water at room temperature. This was done by monitoring the absorbance signal at 664 nm by the Lambert–Beer law using a UV/Vis AGILENT Cary 50 spectrophotometer. The same experiments were conducted for GO–P25 and rGO–P25 solutions. The pH of the solutions was measured by a SevenGO Duo pH-meter of Mettler Toledo, both GO and rGO have pH value of 3.8 while the mixed solutions of GO–(rGO–)P25 show a pH of about 5.

All the solutions were drop casted onto silicon substrates and heated on a hot plate at 120 °C for 1 h to evaporate the water for the following characterizations. The reduction of GO sheets by laser irradiation was verified by X-ray photoelectron spectroscopy (XPS). XPS analysis was performed by using a Thermo Scientific K-Alpha system with a monocromatic Al Kα (1486.6 eV) source. The photoelectron spectra were collected by a CAE analyzer using a pass energy of 200 and 50 eV for the survey and high resolution spectra respectively. A flood gun was used to decrease the effect of surface electrical charging.

Raman scattering has been excited by the 514.5 nm radiation of an Ar^+ laser and analyzed by a Jobin Yvon 450 mm focal length monochromator equipped with a CCD camera detector cooled at 77 K. The incident laser beam was focused by a 100 × objective.

3. Results and discussion

All the samples were investigated by SEM, and the images of the irradiated GO–P25 and rGO180–P25 samples are reported in Figs.1a and b, respectively. The rGO layers appear to be smaller and more irregular than the GO ones; TiO_2 particles are distributed more homogeneously on the surface of rGO than on the GO surface, that remains partially uncovered, as also observed in other SEM images (not shown).

The absorbance spectra of GO and rGO alone or mixed with TiO_2 in water are shown in Fig. 2. In the case of GO a peak at about 230 nm, corresponding to π-π* transitions of C=C bonds and a shoulder at around 300 nm, due to the σ–π* transitions of the C=O bond are visible. After laser irradiation, a redshift of the maximum is observed and the shoulder disappears (Fig. 2). For the mixed GO–P25 and rGO180–P25 solutions, the maximum is shifted to 250 nm and a shoulder at 320 nm is observed due to the presence of the P25 nanoparticles, as clearly shown in the P25 absorbance spectrum reported for comparison in the same figure.

Raman spectra of the samples (Fig. 3) show the characteristic peaks for the graphitized structures [13]: the D band at 1380 cm^{-1} is the same for all the samples while the G band at 1615 cm^{-1} is

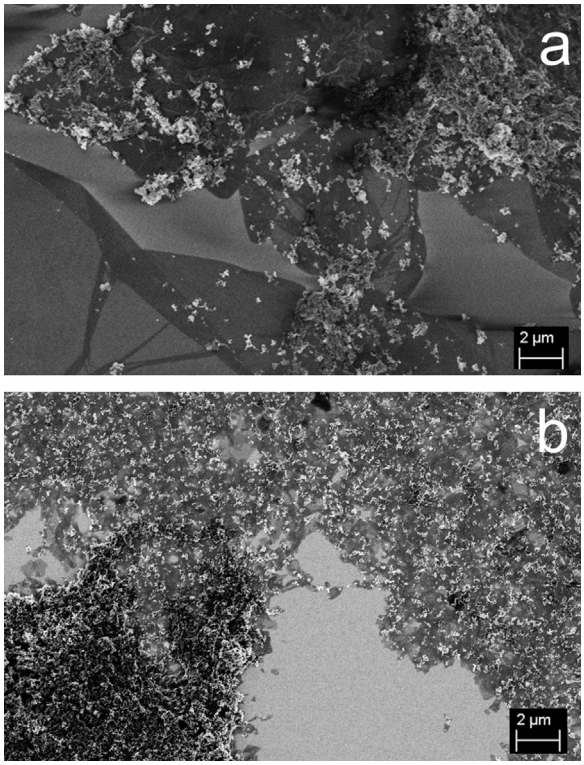

Fig. 1. SEM images of GO–P25 (a) and rGO180–P25 (b) composites obtained by pulsed laser irradiation for 15 minutes.

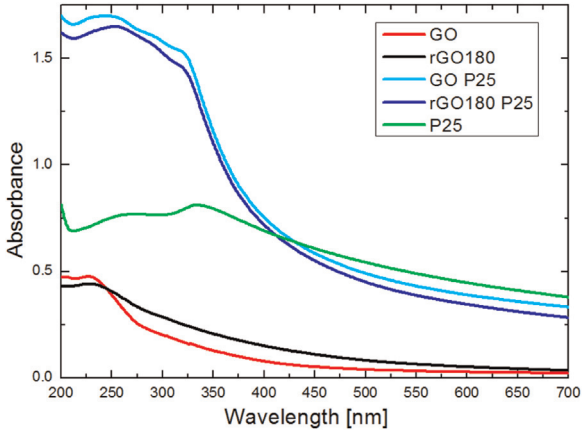

Fig. 2. UV–vis absorbance spectra of 10 mg/l GO and rGO180 solutions, 100 mg/l GO/rGO180–P25 solutions and 90 mg/l P25 solution.

shifted slightly to 1635 cm^{-1} after reduction. This shift can be addressed to a decrease of the number of GO layers and, therefore, to a higher degree of exfoliation induced by laser irradiation [14]. The Raman spectra of the GO–P25 and rGO–P25 composites show three peaks at 400, 523 and 653 cm^{-1} characteristic of anatase phase and the G band is centered at 1633 cm^{-1} and 1638 cm^{-1} for GO–P25 and rGO–P25 respectively. The ratio I_D/I_G is quite the same for all the samples suggesting that the effect of laser irradiation is to change the oxygen content on graphene layers without the formation of new sp^2 domains. In addition it is evident that the TiO_2 peaks are more intense in the composite rGO–P25 than in GO–P25, confirming what is evident from SEM images: TiO_2 nanoparticles cover almost completely rGO sheets, whilst the coverage of GO sheets is only partial.

XPS results are shown in Fig. 4: C1s spectra of GO and rGO180 present two peaks related respectively to sp^2, sp^3 (284.5 eV) and to