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Enhanced UV- and visible-light driven photocatalytic performances and recycling properties of graphene oxide/ZnO hybrid layers

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ABSTRACT

Light induced catalytic processes have attracted significant attention during the last years for wastewater treatment due to their efficiency in decomposition of organic contaminants. In this study we report the synthesis of graphene oxide (GO)/ZnO hybrid layers with high photocatalytic efficiency using laser radiation. The results show that the hybrid layers exhibit much improved photodecomposition efficiency as compared to pure GO or ZnO both under UV and visible-light irradiation. The enhanced photocatalytic efficiency of the hybrid as compared to the reference pure ZnO and GO layers was attributed to the contribution of GO to the separation and transport of the photogenerated charge carriers. Additionally, under visible light irradiation the organic molecules can act as first sensitizers in the degradation process. The recyclability of the layers was also investigated through repetitive photodegradation cycles under UV- or visible-light irradiation. After consecutive degradation runs, the hybrid photocatalyst layers were still stable and retained high degradation efficiency, ensuring reusability. The photocatalytic activity of the layers was correlated with the gradual change of their chemical structure during consecutive degradation cycles. Owing to the high photodegradation efficiency, reusability, and ease of recovery the synthesised hybrid layers consisting of easily available materials are suitable for environmental purification applications.

1. Introduction

Wastewater contaminants have become one of the most serious environmental problems during the recent years. Organic dyes and pesticides originating both from their production process as well as through their use in various industrial fields as textile, plastic, or agriculture are continuously accumulated into the water reserves [1,2]. Products and wastes of petrochemical industries and mining are also environmental contaminants, classified as hazardous [3,4]. All these organic compounds are toxic and carcinogenic with serious consequences as regards human health and environment. However, due to their high thermal and chemical stability, the removal of organic contaminants from wastewater is complex, requiring a combination of various traditional wastewater treatment procedures [1]. Even so, it is difficult to clean completely wastewaters contaminated with organic pollutants by conventional methods as adsorption, precipitation, physicochemical and biological treatments, or sedimentation since none of these techniques degrade completely the pollutant molecules. Therefore, novel eco-friendly technologies are continuously being developed for the more efficient elimination of organic pollutants. Light induced degradation mediated by non-toxic, low cost, and earth-abundant photocatalytic materials could become one of the simplest and more effective methods for the complete decomposition of organic contaminants in industrial wastewaters [5,6].

Among transition metal oxide semiconductor photocatalysts TiO_2 and ZnO have been the most widely investigated because their high chemical stability, non-toxicity, and low cost [6,7]. However, due to their wide band-gap transition metal oxides absorb only in the UV and near-UV spectral regions, which represent only a small fraction of the total solar radiation. As a consequence, serious efforts were concentrated on the band gap reduction of transition metal photocatalysts with the aim to extend their absorption range towards the visible spectrum. This goal was achieved through doping and co-doping with non-metals [8–11], transition metals [10,11], rare earth metals [12], as well as creation of composites consisting of different metal oxides [10,11]. However, the major drawback of transition metal oxide

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semiconductors is the short photogenerated electron–hole pair lifetime, lowering their photocatalytic efficiency [5,6]. The fast recombination rate of the photogenerated charge carriers was prevented through the addition of electron accepting noble metal nanoparticles [10,13,14] and more recently carbon based nanomaterials [15]. Among the carbon based nanomaterials, graphene has attracted significant attention due to its exceptional electronic properties, and large specific surface area [16]. It was found that in case of semiconductor metal oxide/reduced graphene oxide (RGO) composites, RGO participates in charge carrier separation and transport, contributing also to the formation of reactive radicals, which participate in the degradation process [17–21].

As known, most hybrid transition metal oxides/RGO layer fabrication methods are multi-step processes and imply high temperatures or toxic chemical substances. In this work we report the synthesis of ZnO/RGO nanocomposites through a simple, one step laser technology. Laser based methods and in particular the matrix assisted pulsed laser evaporation (MAPLE) technique, could become an alternative for conventional methods for nanocomposite materials synthesis. MAPLE technique was developed for the immobilisation of organic polymers and bio-organic materials, as a version of conventional pulsed laser deposition commonly used for inorganic thin films growth [22]. However, more recently the technique was applied for processing of nano-entities as carbon nanoparticles (NPs) and gold/carbon nanocomposites [23], SnO_2 NPs [24], CdSe/ZnS core-shell quantum dots [25], CdSe NPs and CdSe/polymer composites [26], CdS quantum dots [27], CNTs [28,29], C_{60} [30], GO [31], TiO_2 NPs/polymer composites [32], rare earth inorganic up conversion phosphor compounds doped with polymers [33], TiO_2 NPs/RGO nanocomposites [34,35], or TiO_2 NPs/RGO/Ag NPs ternary compounds [17,36].

We report the synthesis of highly photoactive GO/ZnO hybrid layers using laser radiation. From the practical application point of view, the main advantage of layered in contrast to powder-like photocatalysts is the easy of recovery from the reaction systems, and recycle them in subsequent degradation processes. The photocatalytic activity of the synthesised ZnO/RGO composite layers was systematically investigated through the decomposition of organic methyl orange (MO) dye pollutant under either UV or visible light irradiation. The photodegradation mechanisms induced by the UV and visible radiations were discussed in detail. The kinetics of the photocatalytic reactions and re-usability of the layers in subsequent degradation cycles were also evaluated. The obtained data was correlated with the structure and chemical bonds between the constituent elements on the surface of the layers after each degradation cycle.

2. Experimental

The MAPLE experimental set-up used for the growth of the rGO/ZnO hybrid layers consisted of a Nd:YAG (λ = 266 nm, τ_{FWHM} = 3 ns, ν = 10 Hz) laser source (Brilliant B, Quantel, France), and a specially equipped MAPLE stainless steel vacuum chamber (Vacuum Projects, Spain). The MAPLE targets consisted on dispersions of GO plates (NanoInnova Technologies, Spain) and ZnO NPs (Sigma-Aldrich, 99.7%) in the concentration range of $1-6$ wt% in distilled water. Reference GO and ZnO layers were obtained from dispersions of 6 wt% GO plates and 6 wt% ZnO NPs, respectively. The dispersions were sonicated and subsequently cooled down until solidification in liquid nitrogen. The double wall target holder filled with liquid nitrogen allowed to maintain the targets frozen during the experiments. The laser fluence incident onto the surface of the MAPLE target was set at 0.2 J cm^{-2}. 10^4 subsequent laser pulses were applied for the deposition of each sample. The experiments were conducted in N_2 atmosphere at 20 Pa pressure. Before each experiment the vacuum chamber was pumped down to a residual pressure of 10^{-2} Pa. (001) SiO_2 quartz plates with 1 × 1 cm^2 surface area were used as substrates, positioned parallel to the target surface at a separation distance of 4 cm.

The chemical composition and bonding states between the elements of the synthesised layers were investigated by X-ray photoelectron spectroscopy (XPS), with the aid of a SPECS XPS spectrometer (SPECS Surface Nano Analysis GmbH) and a Phoibos 150 electron energy analyser. A monochromatic X-ray source (Al Kα, 1486.6 eV) was used for excitation. High-resolution XPS spectra were registered with 0.05 eV steps. The obtained data were analysed using the SDP XPS software, version 7.0 XPS International, Mountain View, CA. The optical transmission spectra of the samples were recorded using a Shimadzu UV-2600 UV–visible spectrophotometer.

The photocatalytic activity of the hybrid GO/ZnO nanocomposite layers was studied and compared with reference GO and ZnO layers. The degradation efficiency was evaluated through the concentration changes of MO aqueous solution in time. The photodegradation experiments were performed under either UV or visible light irradiation, using a LZC-ICH2 photoreactor, from Luzchem Research Inc, Canada. 16 × 8 W lamps with emission wavelengths centered at 360 nm (300–400 nm emission range, LZC-UVA, Hitachi lamp) and 580 nm (420–700 nm emission range, LZC-Vis, OSRAM lamp, Sylvania, USA), were used as lights sources. The samples were immersed in 2 mL MO solutions with 1.25×10^{-5} M (4 ppm) initial MO dye concentration (C_0) in quartz vials, and were stirred continuously during the photodegradation experiments. The absorbance of the MO solution was measured at regular time intervals using a Shimadzu UV-2600 spectrophotometer. The MO dye concentration was calculated from the measured peak absorbance value at 464 nm wavelength, which corresponds to the maximum absorbance of MO in the visible spectral range, applying the Lambert-Beer law.

The photocatalytic degradation efficiencies (η) of the samples were calculated through the expression η [%] = $(C_0 - C) \times 100/C_0$, where C is the MO concentration in the aqueous solution under UV (300–400 nm) or visible light (420–700 nm) irradiation, measured at regular time intervals. The apparent photodegradation rate constant of each photocatalyst, both under UV and visible light irradiation was calculated according to the Langmuir-Hinshelwood pseudo-first order kinetics, $k_{app} = \ln(C_0/C)/t$, from the $\ln(C_0/C)$ plots versus t, the irradiation time [37].

3. Results and discussion

The surface elemental composition and the chemical bonds between the elements of the MAPLE deposited layers were studied by XPS. In Fig. 1 we present the high resolution XPS core level spectra of both a reference GO sample deposited through drop-cast method using a dispersion of 6 wt% GO plates in distilled water (Fig. 1a) as well as GO (Fig. 1b) and composite ZnO/GO layers (Fig. 1c) obtained from MAPLE targets consisting of dispersions of 6 wt% GO plates or mixture of 6 wt% GO plates and 6 wt% ZnO NPs in distilled water, respectively. The C1s spectrum of the reference drop-cast GO sample (Fig. 1a) was deconvoluted in four lines. The line centered at the lowest binding energy, 284.6 eV, corresponds to sp^2 hybridized C atoms of the aromatic rings, while the higher energy lines can be assigned to C atoms directly bonded to O atoms in oxygen containing functional groups of GO [38–40]. The line centered at 285.6 eV was associated in the scientific literature with C-OH hydroxyl groups, whereas the line at 286.5 eV to C-O-C epoxide groups of GO [38–40]. The line centered at the highest binding energy value, at 289.0 eV could include contributions from both carbonyl > C=O and O=C-OH carboxyl groups of GO [38–40]. Similarly, the C1s spectrum of the GO layer deposited by MAPLE was deconvoluted in four lines (Fig. 1b). As can be observed, the intensity of lines corresponding to C–O and C=O bonds are significantly lower as compared to that of the reference GO drop-cast sample, indicating the reduction of GO during laser irradiation, leading to the deposition of RGO layers on the substrate surface. Since the experiments were performed in N_2 atmosphere, simple C–N and double C=N bonds could contribute to the high energy lines of the C1s spectrum, overlapping with the C–O and C=O bonds [17,34]. The N1s spectrum of the layer