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PHOTOMAT Report Summary

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Final Report Summary - PHOTOMAT (TUNABLE MATERIALS: PREPARATION, CHARACTERIZATION AND INVESTIGATION OF PHOTOCATALYTIC ACTIVITY OF NEW HIBRID MATERIALS)

The PHOTOMAT project aims at developing new materials with tunable properties, combining good mechanical properties and photocatalytic activity. Advanced materials were synthesised, characterised and evaluated for their photocatalytic efficiency in abating pollutants such as emerging pollutants. The ability of the prepared materials to abate pollutants has been checked both when catalysts are dispersed in aqueous solution or coated in a film or membrane. Such investigations involved the evaluation of the role of the major reactive species, the determination of the reaction kinetics and the identification of the major intermediate and by-products at different treatment times.
Different synthetic strategies were followed to achieve this goal. The first approach led to develop and tailor high quality carbon nanoparticles (CNPs) for the production of polymer/ceramic nanocomposites. CNPs include carbon nanotubes (CNTs) and functionalised graphene sheets. CNTs were grown using chemical vapour deposition, whereas functionalised graphene sheets have been synthesised by the rapid thermal expansion of graphite oxide. The latter has been synthesised from natural graphite flakes.
Firstly, we investigated the photochemical stability and the ability of to act as photosensitizer of graphene at different stages of oxidation/reduction. While graphene sheets exhibited a good performance in the removal of pollutants via adsorption (i.e selected dyes), graphene oxide and reduced graphene oxide demonstrated to act as good photosensitized and then these forms were used to obtain composite materials.
CNPs were then modified on the surface using controlled oxidation and diazonium chemistry. These modified CNPs were the core of the further developed composite materials and found interesting application on both basic and applied science. The surface modification of CNTs allowed to control the synthesis of TiO2 nanoparticles (NPs) in situ on graphene sheets. In particular, we showed that by changing surface functional groups we could synthesize NPs with different morphology and exposing different facets to the environment (Figure 1). This allowed us to control the photocatalytic efficiency of the resulting hybrid materials. We were able to prove, for the first time, that functional groups present on the material surfaces, specifically graphene, could control the morphology of TiO2 nanoparticles grown on them. Previously, researchers who wanted to control TiO2 morphology did so using shape controllers in solution. Our results showed, for the first time, that surface functionalities too can induce such selectivity in TiO2 morphology, most likely due to a change in local pH. While this is an important basic contribution, we also showed that the ability to control TiO2 morphology and its coupling to graphene has a deep effect on the efficiency of this material as a photocatalyst. In fact, upon stabilization achieved by adding shape controllers in solution, we showed that only one of the nanocomposites was able to improve the efficiency of TiO2 to photocatalitically degrade the target molecule. As we had hypothesized, this was the composite with the most reducing facets towards reduced GO and the most oxidizing ones towards the solution. This result paves the road for a new generation of hybrid photocatalysts, which achieve better results in pollutants abatement thanks to their carefully controlled architecture.
Surface-modified graphene has also found application in an unexpected field. In fact, graphene functionalized with carboxylic groups demonstrated to be a good candidate in binding the amino groups in proteins, so open the door of its employment in biochemistry applications. A first successful example is reported in the development of a homogeneous multianalyte immunoassay.
A second strategy foresees the preparation of semiconductor/insulator oxides (i.e. TiO2, ZnO, ZrO2) and their doping with non-metal elements (N, S, P, B, F, C), metals (Sc, Pt, Ag and Au) and lanthanides (Ce). Diverse synthesis technique were used (sol-gel, impregnation, precipitation, microwave assisted and hydrothermal) to obtain materials with different morphology and high surface area. Via sol gel and hydrothermal synthesis techniques it was possible to obtain nanostructured materials, paying much attention in the calcination phase avoiding possible sintering processes. Via impregnation techniques micro structured materials were obtained; in these cases the surface area was lower but big crystals have been selected to grow on a particular crystallographic phase. Presence of surface and bulk defects both in the pure and doped samples and their reactivity were checked with EPR, UV-Vis-NIR and luminescence spectroscopy. Spectral response of the synthesized materials were evaluated in terms of the spectral dependences of the quantum yields for the testing photochemical processes. In particular the optimization of the synthesis parameters was one of the goal proposed and actually has been successfully achieved. The overall structural and spectroscopic characterization techniques used allowed to point out the main features of each sample and we were then able to select the most interesting materials (high surface area, crystallinity, lower band gap) to be used for photocatalytic

applications. In particular, the two synthesis ways we selected as the more interesting were hydrothermal and precipitation methods, that are also the most easily transferable to an industrial process, since are simple and low cost processes. Among the synthetized oxidic materials, Ce-doped ZnO was the material that exhibits the best photocatalytic performance. Ce-doped ZnO had shown a high efficiency toward the abatement of both conventional and emerging contaminants (i.e iodinated X-ray agents and sweeteners, scarcely eliminated in water treatment plants) with rates higher that the commercial TiO2 P25, in particular when employing visible light. Due to these interesting performances, this material will be tested also in more complex system. In particular, the following step foresees its use in a pilot waste water treatment plant using solar light.
Finally we combined CNTs, functionalised graphene and semiconductors in UV-cured polymeric films. The carbonious or inorganic fillers were dispersed in the polymeric precursor and the system cured by means of UV light finding the best curable conditions. The homogeneous dispersion of CNTs and graphene filler is an issue of relevant importance in order to obtain advanced materials. In particular, in preparing UV-cured coatings, the main issue was related to the competitive absorption effect of UV-light by the carbonious fillers and the photoinitiators. The cured films were then fully characterized in term of thermal and viscoelastic properties, as well as an accurate morphology investigation. The presence of surface defects and their reactivity was checked as well by optical spectroscopy under ultra-high vacuum conditions and in presence of gas or liquid media with controlled composition.
The obtained results allowed to straightened the knowledge on the UV-curing process of curable formulations containing semiconductors fillers which can strongly interact with the UV-light during curing process. The dispersion of carbonious fillers within polymeric matrices has important relevance in academic investigations as well as for industrial applications. The obtained cured films could find applications as photocatalyst as well as materials with high dielectric permittivity, very important for the high voltage industrial applications. Concerning these applications, the UV-cured films have been demonstrated to be quite good photocatalyst and the crosslinked films containing the gold-functionalized graphene showed important enhancement of electrical conductivity, which could find relevant applications in the electronic industries.
In the last part of the project, we explore different routes to obtain a self-supporting composite material, where our materials can be dispersed. These approaches comprise the use of electrospinning, graphene scaffolds, thermal conductive composites or polydopamine functionalized membranes.
Preliminary results are encouraging. Considering electrospun materials, the resulting films have a very high surface area, since they are made of nanoscopic fibers. The plan is now to use these films as photocatalysts; we believe that they should work better than the previously synthesized membranes, thanks to their high surface area. Furthermore, the polydopamine functionalized membranes showed a good ability in dye removal from waste water.
The materials synthesized and described above have a high potential in further technological applications. As already highlighted the preliminary results just shown could be very interesting in the field of photocatalysis and in the waste water purification. We are highly confident that our material could be employed to improve the quality of the life (for humanity and natural environment) in the next future.

Related information

Result In Brief	New materials to improve water quality
Documents and Publications	final1-publishable_resume-final.docx

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