



Mix and match metal oxides and nanocarbons for new photocatalytic frontiers



Michele Melchionna^a, Maurizio Prato^{a,b,c}, Paolo Fornasiero^{a,d,*}

^a Department of Chemical and Pharmaceutical Sciences, INSTM, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

^b Carbon Nanobiotechnology Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia-San Sebastian, Spain

^c Basque Foundation for Science, Ikerbasque, Bilbao 48013, Spain

^d ICCOM-CNR, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy

ARTICLE INFO

Article history:

Received 7 January 2016

Received in revised form 1 April 2016

Accepted 6 April 2016

Available online 6 May 2016

Keywords:

Hybrid photocatalysts

Metal oxides

Nanocarbons

Carbon nanotubes

Graphene

ABSTRACT

Hybridization of metal oxides with nanocarbons has become a very fertile soil of research, given the synergy of the two phases that results in most cases in an improved photo-catalytic performance. Despite the mechanism is still uncertain, it has been established that the presence of a nanocarbon can retard recombination of the photo-excited electrons and holes. The improved activity critically depends on the method of synthesis, which should be designed as to have the maximum C-metal oxide contact. Much research has been conducted on graphene and carbon nanotubes, but other carbon structures are slowly coming to surface. The vast majority of reports focuses on photo-degradation of organic contaminants, but application to energy related fields is becoming more and more popular.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Semi conducting metal oxides (MOs) are becoming an ubiquitous ingredient into the assembly of efficient heterogeneous photo-catalysts for the vast majority of catalytic transformations. Their ability to absorb light and form separated charge states is at the core of photo-catalysis. Many combinations of metal oxides with other components have been reported in order to alleviate inherent drawbacks, such as the fast recombination of photogenerated charge carriers (electrons and holes), the specificity towards absorption of UV radiation, and the stability towards photo-corrosion. In recent years it has become evident that introducing the concept of nanoscale into the catalyst design leads to a considerable improvement of the efficiency of the catalysts. Among the various components that can be mixed with metal oxide to improve catalytic performance, carbon nanostructures (CNSs) have acquired a very prominent role. The unique properties of CNSs have already been exploited in many scientific areas, including catalysis [1,2]. Upon a tailored synthesis of organic/inorganic nanocomposites (or nanohybrids) based on CNSs and MOs, the properties of the

two phases can synergistically combine to result in systems with improved photocatalytic performance. In this brief review, we give a critical outlook on the state-of-the-art MOs/CNSs catalysts which are currently enjoying incessant interest for photocatalytic applications, discussing promises and shortcomings of this fascinating field. The review will focus on the use of binary systems, only skirting the more complex multi-component catalysts, which however are emerging as the future dominators in this area of research.

2. Carbon nanostructure and their potential use in catalysis

As mentioned above, the properties of carbon nanostructures are ideal for exploitation in catalytic applications. They offer a wide choice linked to the specific morphology one intends to use, and also some of the properties vary across the different nanocarbon employed. One first problem is the ease of processability of the specific CNS. For instance, carbon nanotubes (CNTs) have been most widely investigated, but their dispersibility in liquid phase is not straight forward, and requires a pre-functionalization step to improve their dispersion. However, such functionalization step, that in most cases is based on simple oxidation protocols [3,4], reduces by much the electronic properties of the CNTs, by partial disrupting the polyaromatic framework [5]. Therefore, a correct balance has to be made between the degree of oxidation for more stable dispersions and the importance of the electronic

* Corresponding author at: Department of Chemical and Pharmaceutical Sciences, INSTM, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy.

E-mail address: pfornasiero@units.it (P. Fornasiero).

properties required by the specific application. The situation is even more complicated for graphene (G), where the π - π stacking is exacerbated due to the flat structure. As a consequence, in order to uniformly disperse it and thus give access to liquid phase synthesis of nanocomposite, G needs to be strongly oxidized [6], giving rise to a material with reduced electronic properties (i.e. reduced electron conductivity), graphene oxide (GO). After hybridization with the metal oxide, the original properties of G can only be partially restored by a reduction treatment to what is called “reduced graphene oxide” (RGO) [7,8]. When other CNSs are considered, such as for instance carbon nanohorns (CNHs) and nanocones (CNCs), an improved dispersibility is encountered, therefore allowing only minor modification of the nanocarbon prior to hybridization with the metal oxide. Given the unbalanced number of reports between CNTs and G versus other CNSs, we wonder if such considerations would lead to a higher attention towards the exploration of less investigated CNSs. An important aspect to take into account when choosing the CNS is the surface area associated with the morphology. Even when oxidized, CNCs have low surface area relative to other CNSs [9], comparable to that of pristine multi-wall carbon nanotubes (MWCNTs) ($\sim 270 \text{ m}^2 \text{ g}^{-1}$) [10] or CNHs ($300 \text{ m}^2 \text{ g}^{-1}$) [11], while higher surface area are found for single-wall carbon nanotubes (SWCNTs) (above $400 \text{ m}^2 \text{ g}^{-1}$) [12]. However, oxidation treatment can considerably increase surface area by removing the tips of the tubular structure and allowing accessibility to internal channels [13]. Another discriminating factor is the electron mobility, that can drastically vary across the different structures; the highest calculated mobility is for G, with values reaching $\approx 100,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [14]. The last consideration regards the degree of purity of the CNSs, which can be characterized by a great variance, and it also depends on the method of preparation. The choice needs to be made taking into account the cost/performance ratio, with the price of more pure nanocarbon at times overcoming theoretical profit. Typical impurities of CNSs evolve from their preparation procedures and consist of metal catalysts. This can be partially removed by acidic treatments.

These are just some of the observations to be considered when selecting the right carbon nanomaterial for the specific application, including photo-catalysis (Table 1).

3. TiO_2 : setting the case study

Titanium dioxide is certainly the most investigated semiconducting oxide in photo-catalysis on account of its chemical stability, low cost and negligible toxicity [15]. However, it also suffers from some limitations, identified in particular in its wide band gap (anatase 3.20 eV and rutile 3.02 eV [16], brookite 3.29 [17]), which implies very poor utilization of solar light, and the rapid recombination of the photo-excited charge carriers (electrons and holes) in the order of 10^{-9} s. Remedies to such limitations include doping [18–21], synthesis of composites with other semiconductors [22–24] or deposition of metal nanoparticles [25–27]. Combination of TiO_2 with various carbon nanostructures (CNSs) has been widely investigated as a way to improve photocatalytic performance of TiO_2 by exploiting the properties of the CNSs. In particular, a plethora of reports include systems with graphene (G) and carbon nanotubes (CNTs). A first asset is the reportedly increased surface area of the catalyst. However, this is sometimes a controversial matter, as it has been shown that some reported TiO_2 /CNSs composites or hybrids exhibit decreased surface area in comparison to free TiO_2 , especially if thermal treatments are carried out on the samples. Superior performance even at lower specific surface areas is a very important point, because it rules out a merely geometric effect of the CNSs, implying an active electronic participation of the CNSs into the catalysis. In this respect and as a general rule, it

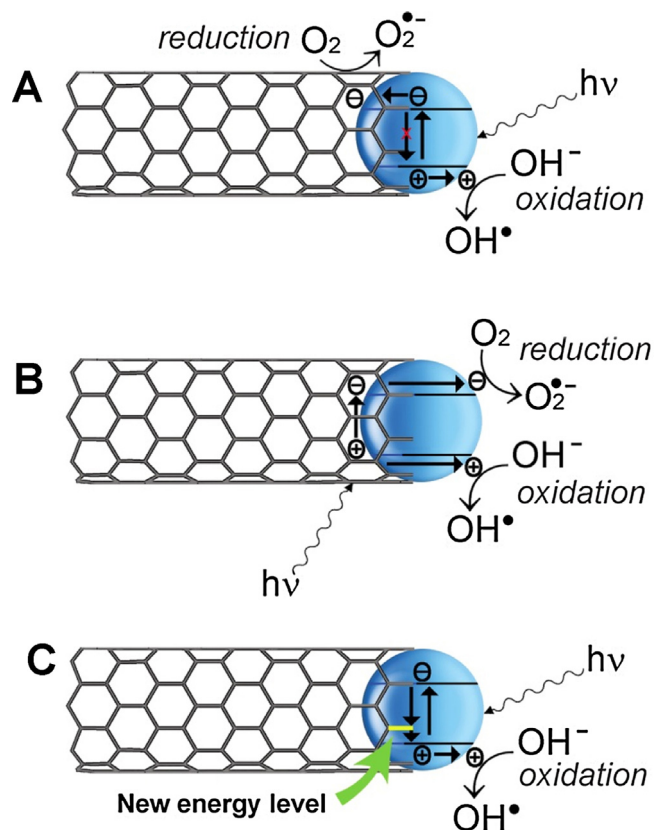


Fig. 1. The three most accredited mechanisms showing the role of carbon nanotubes when combined with TiO_2 (or other metal oxide) for photocatalytic applications. (A) electron scavenger, (B) photosensitizer, (C) introduction of new energy level narrowing band gap (carbon doping).

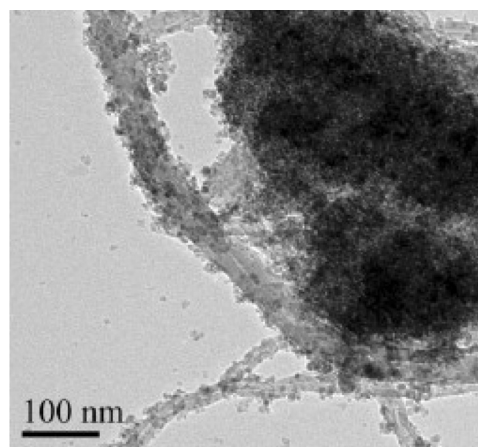


Fig. 2. TEM image of a TiO_2 /MWCNTs composite showing inhomogeneity of the material.

Adapted from Ref. [36] with permission from Elsevier.

would be advantageous to report activity normalized by the catalyst surface area, to emphasize any possible electronic effect by the support [28]. It becomes therefore clear that, apart from surface area considerations, which need to be done carefully, there are additional and more profound advantages for integrating a CNS in photo-catalyst designs.

Despite the proliferation of studies, the TiO_2 /CNSs system still remains too complex to be fully and unequivocally explained. Indeed, the benefits of interfacing TiO_2 with a nanostructured carbon support may evolve from different features of the systems.

Download English Version:

<https://daneshyari.com/en/article/6455312>

Download Persian Version:

<https://daneshyari.com/article/6455312>

[Daneshyari.com](https://daneshyari.com)