



Perspective

Photoactive materials based on semiconducting nanocarbons – A challenge opening new possibilities for photocatalysis

Siglinda Perathoner^a, Claudio Ampelli^a, Shiming Chen^a, Rosalba Passalacqua^a, Dangsheng Su^b, Gabriele Centi^{a,*}

^a Dept.s MIFT and ChiBioFarAm, Section Industrial Chemistry, University of Messina, INSTM/CASPE and ERIC aisbl, V.le F. Stagno D'Alcontres 31, 98166 Messina, Italy

^b Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

ARTICLE INFO

Article history:

Received 2 November 2016

Revised 11 January 2017

Accepted 12 January 2017

Available online 28 January 2017

Keywords:

Nanocarbon

Carbon-type photocatalysts

Semiconducting nanocarbons

Carbon nano-dots

Water splitting

CO₂ photoreduction

ABSTRACT

This perspective paper introduces the concept that nanocarbons and related materials such as carbon dots are an interesting intrinsic photocatalytic semiconducting material, and not only a modifier of the existing (semiconducting) materials to prepare hybrid materials. The semiconducting properties of the nanocarbons, and the possibility to have the band gap within the visible-light region through defect band engineering, introduction of light heteroatoms and control/manipulation of the curvature or surface functionalization are discussed. These materials are conceptually different from the “classical” semiconducting photocatalysts, because semiconductor domains with tuneable characteristics are embedded in a conductive carbon matrix, with the presence of various functional groups (as C=O groups) enhancing charge separation by trapping electrons. These nanocarbons open a range of new possibilities for photocatalysis both for energetic and environmental applications. The use of nanocarbons as quantum dots and photo-luminescent materials was also analysed.

© 2017 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

1. Introduction

The concept of “solar-driven chemistry and energy” indicates the radically new possibility to develop the future of chemistry and energy, the latter in terms of vectors for energy storage and transport, based on new sustainable and low-carbon processes which minimize the use of fossil fuels. This is one of the hottest areas for energy chemistry [1] and key element of this concept is to enable the direct use of renewable energy to drive the processes. Photocatalysis is clearly a critical element for this scope and in fact, the interest on this area has been rapidly growing recently. For example, the papers using as keyword “photocatalysis” increased of about one order of magnitude in the last ten years. Few selected examples of reviews on photocatalysis published this year are reported in refs. [2–9]. In spite of the large interest, the range of photoactive materials used for photocatalytic applications is limited, with TiO₂ being still one of the most used. The need to enlarge to visible-light region the photo-activity has significantly stimulated the search of new semiconductor materials [10–16], although sta-

bility and performances of these novel visible-light active semiconductors is still often an issue.

Another direction in which active research in photocatalytic materials is oriented, both for environmental and energy-related applications such as water splitting and reduction of CO₂, is to improve the photocatalytic properties by preparing hybrid materials, particularly with carbons [17–23]. In most of the cases, however, the carbon component has mainly the function of a modifier to enhance charge collection or transport, or to mediate charge transport, rather than playing a direct role as photo-active component. There is, however, a growing interest on carbon nitride/graphene (g-C₃N₄/graphene) hybrids [24], nanocarbon-type photosensitizers [25], use of nanocarbon-based photocatalysts [26,27], development of photoresponsive carbon nanomaterials containing azobenzene moieties [28], hybrids between conjugated polymers and carbon nanotubes as photoactive layers in solar cells [29], nanocomposites of porphyrins and nanocarbon materials for photoinduced electron transfer and light energy conversion [30]. We may comment, however, that in spite of the fast growing knowledge on the preparation of these materials, the use of carbon-based photo-active materials is still limited and sometimes not based on a rational design, differently from the use of nanocarbon materials as catalysts or electrocatalysts [31–40]. We will use here the concept of nanocar-

* Corresponding author.

E-mail address: centi@unime.it (G. Centi).

bons to define the broad area of carbon materials having performances depending on the nano-dimension, such as graphene, carbon nanotubes-CNTs [31].

The aim of this concise perspective paper is to analyse the possibilities offered by nanocarbons as *intrinsic photoactive materials*, thus not as modifiers to enhance the properties of another photoactive material. An example is the addition of nanocarbons to semiconductors such as TiO₂ to collect better photogenerated electrons and to limit charge recombination [41–47]. We may note that the realization of these hybrid carbon-semiconductor materials leads to more complex phenomena, often not considered or only in part. The interface contact between the semiconductor particles and the nanocarbons often determines the behavior, because the intrinsic properties of titania or other semiconductors result modified from this interaction [17]. There are various additional aspects to consider. The intrinsic properties of the nanocarbon influence the electron-transfer and may introduce radiative paths (carrier trapped centers and electron-hole recombination centers) and/or strain-induced band gap modifications [48]. The nature of the TiO₂/nanocarbon interface (which in turn strongly depends also on the specific nature of nanocarbon, particularly the presence of defect sites) determines these effects. Richter and Schmuttenmaer [49] have shown that low mobility in polycrystalline TiO₂ nanotubes results from a single sharp resonance arising from exciton-like trap states, with a similar effect expected in TiO₂-CNTs nanostructured films. The inverse processes of electron injection into the conduction band of TiO₂ can occur [50]. Without a detailed characterization of these aspects, it is not possible to make reliable conclusions whether a carbon-semiconductor hybrid results in enhanced or worse performances [17].

These aspects are scarcely studied, particularly in relation to nanocarbon-semiconductor (TiO₂) hybrids, although they are critical for a rational design of these photoactive materials [17,35]. A further relevant mechanism of modification of the photobehavior is related to C-doping of TiO₂ nanocrystals [51,52]. Further aspects which may influence (in a positive or negative way) the photocatalytic performances are related to:

- The enhancement of the light harvesting capability of a semiconductor by dispersion on the nanocarbons; in addition, nanocarbons offer an effective way for an efficient dispersion of the semiconductor preventing from agglomeration, reducing grain boundaries between semiconductor particles and also providing a hierarchical structure for an efficient light harvesting, and eventually for easy access from gas/liquid phase components (in photocatalytic reactions) or an electrolyte (in dye sensitized solar cells).
- The role of nanocarbons, due to their thermal conductivity, in maintaining more uniform temperature of the semiconductor-nanocarbon hybrid upon irradiation; this is an aspect typically not considered, but which is important.
- The role of nanocarbon in acting as sinks for electrons, enhancing the lifetime of charge separation. Fermi levels of the nanocarbons are generally below the conduction band of the supported semiconductor nanoparticles. In some cases, depending on the specific characteristics of the nanocarbons, however, the Fermi level may also result above that of the semiconductor; there is an obvious effect of the size and shape of semiconductor nanoparticles, which in turn may be influenced from the interaction with the nanocarbon; also these aspects are not usually considered.
- Nanocarbons may induce the adsorption of chemicals which may enhance the photocatalytic activity or quench it.
- Charge creation upon illumination of the semiconductor creates a double layer in solution which affects the transfer rate of molecules across it and in turn influences the reactivity and

in some cases also the selectivity (for example, when relatively stable charged species forms, like carbon dioxide anion radical in the photoreduction of CO₂); the presence of charge delocalization in hybrid carbon-semiconductor materials influence in principle these aspects, which, however, were not studied in literature.

Therefore, the interaction of semiconductors with nanocarbons induces modification of the intrinsic properties of the semiconductor particles (band gap, charge carrier density, lifetime of charge separation, non-radiative paths, etc.) and of the surface properties, which determine positive or negative changes in the reactivity, but often not rationalized, because the points remarked above are not considered or only in a very limited extend. The consequence is that there are not simple relations between addition of nanocarbons and performances of the hybrid carbon-semiconductor materials. For this reason, often quite contrasting data exist in literature on nanocarbon-semiconductor hybrid materials [17,35].

Although these aspects are important, we will instead focus attention in this perspective paper on another important question, also scarcely investigated: the use of nanocarbons as intrinsic photoactive materials (semiconductor materials, quantum dots or photoactive materials). Some of these aspects are present also in carbon-semiconductor nanohybrids, such as antenna centers to capture the light, systems for charge transport and separation, catalytic centers for the reaction [35,53].

1.1. Nanocarbons as promoter of the photocatalytic behavior

The nanocarbons may act as a co-catalyst in promoting the photocatalytic behavior. One effect is related to the change in the adsorption modes of the molecules to be converted photocatalytically. For example, the planar adsorption of an alkylaromatic compounds through π -bonds of the aromatic ring gives rise to different products with respect to when a vertical interaction through the alkyl group occurs. Sites near the catalytic centers may modify the chemisorption mode or stabilize some of the reaction intermediates. They have thus a large influence on the catalytic reactivity. Nanocarbons, with the presence of graphitic zones and different modalities of adsorption with respect to oxides or metal particles, offer great possibilities to control and improve the reactivity and selectivity, even this aspect was not extensively examined in literature. In addition, nanocarbon-semiconductor hybrids provide a better (hydrophobic) microenvironment that enhances the local concentration of organic species in aqueous solutions.

Another relevant aspect for the role of nanocarbons as co-catalysts, also not often considered, is the possibility to stabilize reactive oxygen species. CNT characteristics (diameter, chirality, number and type of defects, functionalization, etc.) determine the production of reactive oxygen species during irradiation, and these species may influence the photocatalytic behavior [54]. This could explain why highly defective CNTs show high photocatalytic activity [55]. Several recent studies have been focused on hybrid nanocarbon-semiconductor materials and their use especially in the photocatalytic removal of pollutants both in liquid and gas phase. Eder [50] and Vilatela and Eder [56] have discussed various examples of use of these materials for the photocatalytic treatment of waste streams. The enhancement of photocatalytic properties of TiO₂ by nanohybrids with CNTs, fullerene, graphene and other nanocarbons have been discussed by Leary and Westwood [57], while Inagaki [58] has reviewed the promotion of the photocatalytic performance of TiO₂ by carbon coating. The application of semiconductor-carbon nanomaterials for the photo-oxidation of pollutants has been discussed in detail by Amal and co-workers [59], while the use of graphene-TiO₂ hybrid nanomaterials as photocatalysts for the photo-degradation of pollutants and micro-

Download English Version:

<https://daneshyari.com/en/article/6530194>

Download Persian Version:

<https://daneshyari.com/article/6530194>

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