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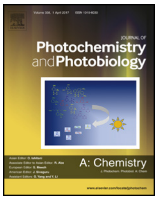

Invited feature article

Visible light photocatalytic activity of macro-mesoporous TiO_2-CeO_2 inverse opals

Roberto Fiorenza[a], Marianna Bellardita[b,*], Tarek Barakat[c], Salvatore Scirè[a], Leonardo Palmisano[b]

[a] Dip. Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy
[b] DEIM, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy
[c] Laboratory of Inorganic Materials Chemistry (CMI), University of Namur (UNamur), 61 rue de Bruxelles, B-5000 Namur, Belgium

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ABSTRACT

Macro-mesoporous TiO_2 inverse opal materials were synthesized and they were tested as photocatalysts under visible light irradiation. The influence of cerium oxide addition towards the Rhodamine B (RhB) photodegradation activity was evaluated. Structural, textural, spectral and surface properties of the TiO_2-CeO_2 inverse opal nanocomposites were studied by XRD, XPS, SEM, TEM, N_2 adsorption-desorption, Diffuse Reflectance UV–vis and Photoluminescence spectroscopies.

Compared to commercial TiO_2 anatase, the macro-mesoporous TiO_2 inverse opal exhibited six times higher kinetic rate constant in the RhB degradation under visible light irradiation. The good photocatalytic activity was related to the peculiar structure of this material, providing higher active surface area and enhancement of the mass transfer phenomena due to a very significant porosity. A positive effect of ceria addition was observed in terms of increased photocatalytic activity (73% of RhB degradation after 120 min of irradiation) when the amount of the CeO_2 was low (up to 3% wt). Moreover the TiO_2-3%CeO_2 exhibited the lowest photoluminescence band intensity among all samples, indicating that the best efficiency in the charge carriers separation occurs in this catalyst. The presence of Ce^{3+} species was favoured for small amounts of cerium oxide, resulting in a positive effect on the photoactivity. The mutual interaction between Ti and Ce metal cations promotes an easier charge transfer on the surface, accelerating in particular the Ce^{4+}/Ce^{3+} redox process that is beneficial for the oxidation reactions. On the contrary the use of high amounts of cerium oxide (>5% wt) led to a progressive agglomeration of CeO_2, thus increasing the crystal size of TiO_2-CeO_2 particles (from 27 to 33 nm) and favouring the coverage of TiO_2 active sites.

This work reports the preparation and some photoactivity tests of some visible light responsive nanomaterials for an efficient solar energy utilization.

1. Introduction

Toxic organic species download into wastewater can cause dangerous pollution of the environment. Dyes, for instance, are visible even at low concentrations and their complex chemical structure consisting of conjugated aromatic compounds can make very difficult the absorption of sunlight and the dissolution of oxygen [1–3]. Moreover about 15% of the world production of dyes is lost during the colouring process and is released with wastewater deriving from the textile industry [4]. Their presence in wastewater is very dangerous for the aquatic ecosystem because source of contamination, eutrophication and perturbations of the aquatic environment. The international environmental standards are becoming more strict (ISO 14001, 2015), and various Advanced Oxidation Processes (AOP) effective for the abatement of organic pollutants, such as dyes, have been proposed [5].

Heterogeneous photocatalysis represents an intriguing method for the purification of water as most of the organic pollutants can be transformed into less toxic species. This oxidative photoprocess presents numerous advantages such as the mild experimental operating conditions and eco-compatibility [6,7].

During the last decades, TiO_2 has been considered as the most promising photocatalyst for the abatement of organic pollutants both in liquid-solid and gas-solid systems or for green organic syntheses [8–12].

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* Corresponding author.
E-mail address: marianna.bellardita@unipa.it (M. Bellardita).

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It is well known that when a photon with energy higher than the band gap energy (E_g) impinges a semiconductor surface, a separation of electron and hole occurs. The electron is excited from the valence band to the conduction band and a positive hole remains behind. These charge carriers can move to the surface inducing the decomposition of adsorbed chemicals. The photocatalytic activity of a semiconductor is principally dependent on three factors [8,9]:

a. the light absorption properties;
b. the light excited charges (electron-hole pairs) transport rate;
c. the electron-hole recombination rates on the surface.

As the light absorption is the first step of photocatalytic process, it is crucial for the solar light-based technology. It is possible to increase the photocatalytic efficiency by improving light absorption and the path length of photons before their recombination, namely by means of a structure effect other than a chemical composition effect. Hierarchically macro-mesoporous TiO_2 structures have been reported to exhibit a significant light harvesting effect by means of macrochannels which allow a better penetration of light inside the photocatalyst [13–15].

Recently, the TiO_2 inverse opals have been intensively studied in photocatalysis because they showed an enhanced photocatalytic activity due to their hierarchical porous morphology which implies a high active surface area and an easier mass transportation [16–18]. One of the key properties of macroporous inverse opal materials is their structure. They are called photonic crystals (PC) and possess a periodic dielectric contrast which gives rise to very high potentials responsible for the increase of the path length of the light [19–21]. In these materials coherent Bragg diffraction inhibits the propagation of photons with certain energies along a particular crystallographic direction and this phenomenon is responsible for the stop-band reflection. Notably the range of reflected back energies depends on the periodicity and the dielectric contrast of the photonic crystal. Photons propagate with reduced group velocity at the wavelengths which correspond to the edges of the stop-bands, and they are called ‘slow photons’. The latter can be responsible for the enhancement of light absorption if their energy is compatible with the absorbance of the material, inducing formation of a high number of electron-hole pairs, and stimulating eventually the photocatalytic activity [22–25].

Obviously, the peculiar structure of the TiO_2 inverse opal possesses prominent advantages. However, the photocatalytic efficiency of TiO_2 nanomaterials still faces many challenges when exposed to a straightforward irradiation of sunlight due to two main drawbacks, namely the wide intrinsic band gap of TiO_2 and the fast electron-hole recombination [26,27]. Thus, many studies have been addressed to reduce the charge recombination by introduction of additional chemical species. A promising strategy to enhance the photocatalytic activity of TiO_2 is the coupling of TiO_2 with other metal oxides such as SiO_2, SnO_2, ZnO, Bi_2O_3 or $BiVO_4$. Such combinations were effective to abate harmful organic chemicals with high rates [28–33]. In particular the combination of $BiVO_4$ and ZnO with TiO_2 inverse opal enhanced the photoactivity for the degradation of RhB in water both under visible and UV light [32,33].

Moreover, nanocomposites of TiO_2 with CeO_2 have received great attention due to their *f* and *d* electron orbital structures and UV light absorbing ability. The high electrical conductivity along with their high thermal stability, and the large oxygen storage capacity of CeO_2 are beneficial factors for the photocatalytic activity of TiO_2 [34–37].

To the best of our knowledge, there are no manuscripts dealing with 3-dimensionally ordered macroporous TiO_2-CeO_2 photocatalysts, although the TiO_2-CeO_2 system has been reported in many works. Due to the paramount importance of CeO_2 both as catalyst and photocatalyst, and the peculiar properties of the opal inverse structures, preparation, characterization and testing of a set of TiO_2-CeO_2 samples with an inverse opal structure were carried out and presented in this manuscript. On the basis of the above considerations, this work aims (i) to study the influence of cerium oxide on the chemico-physical properties of TiO_2 inverse opal, and (ii) to determine the performance of the TiO_2-CeO_2 inverse opal nanocomposites for the photodegradation in water of a model dye molecule, i.e. RhB. As there is a great interest in the use of visible (Vis) or solar light, the degradation of RhB was carried out under Vis irradiation.

2. Experimental

2.1. Catalyst preparation

TiO_2 inverse opal was prepared via a templating strategy using polystyrene (PS) spheres, according to the method previously reported in the literature [32,33,38,39].

Polystyrene spheres were synthesized by emulsion polymerization without adding a surfactant. A solution of NaOH (1 M) was used to wash styrene (20 mL) three times with the aim of removing the polymerization inhibitor and then added to 160 mL of distilled water. The obtained mixture was stirred under Argon atmosphere and heated to 70 °C. Subsequently, $K_2S_2O_8$ (0.16 g) was added to begin the polymerization. The mixture became cloudy after 30 min, and after 5 h the polymerization was stopped by turning off the heating and opening the flask. A dispersion of PS beads in water was obtained, and it was self-assembled by drying at 40 °C for 5 days to form an opal structured template with spheres whose diameter was about 300 nm. The spheres were then infiltrated with the solution containing the Ti precursor (titanium isopropoxide). This mixture was first dried overnight at room temperature and then calcined at 550 °C for 12 h (heating ramp 2 °C/min) to remove the template and to crystallize TiO_2 with an inverse opal structure (IOS).

A commercial sample of TiO_2 anatase (Sigma Aldrich prod. Nos. 637254) was used for the photocatalytic activity comparison.

The wet-impregnation method was used for the preparation of TiO_2-CeO_2 catalysts; different aliquots of cerium nitrate solutions were added to the already formed TiO_2 inverse opal material. The slurry obtained by drying at 100 °C for 24 h was calcined at 300 °C for 3 h (heating rate 2 °C/min). Samples were prepared with different concentrations of cerium oxide (from 1 to 25% weight percentages). The bare CeO_2 used in this work was prepared according to Ref. [40], by precipitation with KOH (0.1 M) from water solution of $Ce(NO_3)_3 \cdot 6H_2O$. The resulting solid was subsequently filtered and calcined at 300 °C for 3 h.

2.2. Catalyst characterization

Morphological properties of the powders were observed by scanning electron microscopy (SEM) using a Jeol JSM-7500F instrument and by transmission electron microscopy (TEM) using a JEOL JEM 2100F instrument operating at 200 kV.

X-ray powder diffraction (XRD) analyses were carried out with a PANalytical X'pertPro X-ray diffractometer using a Cu Kα radiation. Diffraction peaks of crystalline phases were compared with those of standard compounds present in the JCPDS Data File.

Textural properties of the samples were estimated via adsorption-desorption of N_2 at −196 °C using a Micromeritics Tristar 3000 after outgassing at 120 °C overnight.

Visible-ultraviolet reflectance spectra were recorded using a UV–vis spectrophotometer (Perkin Elmer Lambda 35 UV–vis