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Copper NPs decorated titania: A novel synthesis by high energy US with a study of the photocatalytic activity under visible light

Marta Stucchi [a,b,*], Claudia L. Bianchi [a,b], Carlo Pirola [a,b], Giuseppina Cerrato [c,b], Sara Morandi [c,b], Christos Argirusis [d], Georgia Sourkouni [e], Alberto Naldoni [f], Valentino Capucci [g]

[a] University of Milan, Via Golgi 19, 20133 Milan, Italy
[b] Consorzio INSTM, Firenze, Italy
[c] University of Turin & NIS Inter-departmental Centre, Turin, Italy
[d] National Technical University of Athens, School of Chemical Engineering, 15780 Athens, Greece
[e] Clausthaler Zentrum für Materialtechnik, Agricola Str. 2, 38678 Clausthal-Zelelrfeld, Germany
[f] CNR – Istituto di Scienze e Tecnologie Molecolari, Via C. Golgi 19, Milano 20133, Italy
[g] GranitiFiandre SpA, Castellarano (MO), Italy

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A B S T R A C T

The most important drawback of the use of TiO_2 as photocatalyst is its lack of activity under visible light. To overcome this problem, the surface modification of commercial micro-sized TiO_2 by means of high-energy ultrasound (US), employing $CuCl_2$ as precursor molecule to obtain both metallic copper as well as copper oxides species at the TiO_2 surface, is here. We have prepared samples with different copper content, in order to evaluate its impact on the photocatalytic performances of the semiconductor, and studied in particular the photodegradation in the gas phase of some volatile organic molecules (VOCs), namely acetone and acetaldehyde. We used a LED lamp in order to have only the contribution of the visible wavelengths to the TiO_2 activation (typical LED lights have no emission in the UV region). We employed several techniques (i.e., HR-TEM, XRD, FT-IR and UV–Vis) in order to characterize the prepared samples, thus evidencing different sample morphologies as a function of the various copper content, with a coherent correlation between them and the photocatalytic results. Firstly, we demonstrated the possibility to use US to modify the TiO_2, even when it is commercial and micro-sized as well; secondly, by avoiding completely the UV irradiation, we confirmed that pure TiO_2 is not activated by visible light. On the other hand, we showed that copper metal and metal oxides nanoparticles strongly and positively affect its photocatalytic activity.

1. Introduction

Titanium dioxide is almost the most used semiconductor for several applications in the field of photocatalysis; since 1972 [1] up to now, the attention given to this material is constantly increased.

One of the most important drawbacks of TiO_2 is its band gap (3.0 eV for rutile and 3.2 eV for anatase), which limits the light absorption to the UV wavelengths. In terms of environmental applications and considering the strong need to improve the quality of the environments using "green" techniques, the possibility to render TiO_2 active and working under visible light is crucial [2]. TiO_2 can be successfully applied on building materials obtaining products that have a very impressive impact on the air quality of the indoor environments [3,4]. However, as these latter are illuminated often by LED lights, TiO_2 needs to be able to absorb the visible wavelengths (>400 nm) and be activated in the absence of UV-A radiation. The combination between TiO_2 and noble metal nanostructures has shown very promising results for enhancing the semiconductor's visible light absorption, because increases the absorption through LSPR (Localized Surface Plasmon Resonance) and promotes the charge separation more than charge transfer [2,5,6]. For examples, the presence of surface deposited gold nanoparticles promotes charge transfer process [2,7], and Pt–Cu species supported on anatase show very good results in the alcohol oxidation under sunlight [8].

The use of copper ions has recently attracted much attention because of many important factors. Firstly, comparing it with other metals, such as silver or gold, it is absolutely less expensive and

* Corresponding author at: University of Milan, Via Golgi 19, 20133 Milan, Italy.
E-mail address: marta.stucchi@unimi.it (M. Stucchi).

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more abundant [9]. Secondly it affects the properties of TiO_2 decreasing the electron-hole recombination and improving the photocatalytic activity [10]. In particular, not only copper in its metal form, but also in the Cu(I) and Cu(II) species (including Cu_2O and CuO) can serve as electron mediator extending the adsorption to the long wavelength region, in particular because of the formation of an heterojunction with TiO_2 that promotes the charge separation [9].

Metal nanoparticles (M-NPs) and metal oxides (MO) can be prepared by means of the sonoelectrochemical technique, as the decoration of the metal oxides is usually realized by means of sonication (US) in solutions where ceramics or substrates powder are dispersed [11].

Recent advances in nanostructured composite materials have been led by the development of new synthetic methods, and the sonochemical one [12] has been proven to be a useful tool for generating novel materials [13]. In this sense, sonochemistry can be a new, economical and green method for the synthesis and decoration of metallic particles on various ceramic substrates. Ultrasonic irradiation can act on shape and size of the inorganic metal nanoparticles, thanks to the extreme conditions attained during bubble collapse, have been exploited to produce nanoscale metals, metal oxides, and nanocomposites [14]. The first report on the use of ultrasound for fabrication of noble metals was in 1987 by Gutierrez et al. [15], while for this work the experimental procedure is based on to the work of Tao et al. [16].

Starting from the very promising possibilities to use US to obtain metal nanoparticles and substrates decoration as well, sonochemistry represents a novel and interesting way to decorate the surface decoration of TiO_2 substrates with M-NPs and MO, in our case copper for all the reasons mentioned above.

We proposed this method to decorate a commercial substrate of TiO_2 in a previous work [17]. In that case, we wanted to prove the efficiency of the sonochemical route for TiO_2 decoration with different metals, choosing as most interesting molybdenum, rhenium, tungsten and copper. TiO_2 decorated with copper didn't show good results in term of photocatalytic activity. However, several publications about the very good and promising properties of copper nanoparticles to modify TiO_2, enhancing its photoactivity, in particular under solar and visible light, have been published in the recent years [18,19]. For this reason, we investigate here the influence of copper loading on the photocatalytic activity of TiO_2 catalysts. In addition, the distribution and morphology of metal and metal-oxides NPs on the TiO_2 surface are studied for different amount of metal precursor used during the synthesis procedure.

As in the work mentioned above, the TiO_2 substrate employed in the present contribution is commercial and micro-sized. Although TiO_2-nanopowders exhibit the best performances, a micro-sized support is not dangerous for health, easier to handle, and more suitable for a surface decoration [20].

Samples of Cu-metal and metal-oxides decorated titania, prepared using high energy US, were synthesized, considering copper amounts in the range 1–75 wt.%. Moreover, because of (i) the very few studies on the photocatalytic performance of Cu NPs in respect to his quantity and (ii) the need to find photocatalytic materials able to work under visible light, some tests on their photoactivity for the abatement of VOCs molecules in the gas phase were performed, investigating both the impact of the copper amount and the importance of the power of the irradiation. Photocatalytic activity of TiO_2-based materials were tested though the degradation of acetone and acetaldehyde.

Acetone is one of the most common indoor air pollutants and its photocatalytic degradation has been extensively studied. For this reason, it is suitable to study the efficiency of different types of TiO_2 [21,22]. Different mechanisms can contribute to the overall acetone photo-oxidation reaction, and in all of them acetaldehyde is formed as by-product [23]. Moreover, both acetone and acetaldehyde are hydrophilic and polar pollutants that usually are present and ubiquitous in indoor environments.

2. Materials and methods

TiO_2 (1077 by Kronos) is a commercial and micro-sized sample produced by Kronos® company. It consists of pure anatase having an average particles size of ~110 nm; the surface area is $12\ m^2\ g^{-1}$ and it has a band gap of 3.2 eV. The precursor compound for copper is $CuCl_2{\cdot}2H_2O$ (⩾99% Sigma Aldrich), which was purchased and used without further purification, as all the other reagents used for the preparation described below. The investigation on the photoactivity performance of each sample was performed using acetaldehyde (ACS Reagent, ⩾99.5% Sigma–Aldrich) or acetone (Chromasolv plus, for HPLC, ⩾99.9% Sigma–Aldrich) as reference pollutant molecules.

2.1. Synthesis of copper NPs-decorated TiO_2

The experimental procedure was based on the work of Tao et al. [16] followed by some variations in order to ensure the decoration of copper particles on the titanium dioxide substrates. For the preparation of copper NPs decorated TiO_2, two different solutions were prepared. The first solution (A) contains L-ascorbic acid, CTAB, H_2O and Kronos 1077 TiO_2 respectively, and the second one (B) contains the copper precursor ($CuCl_2 * 2H_2O$), NH_3 to adjust the pH and water.

L-ascorbic acid acts as reducing agent on the copper precursor molecules, while CTAB, which acts as surfactant, plays a crucial role on the morphology and size of the final product; indeed, it has been proved that at low concentration of CTAB, particles have less regular morphology and a broader size distribution.

The solution obtained from the mixture of the solutions A and B was then treated by ultrasounds. A Bandelin SONOPLUS HD 3200 utilizing a 200 W US generator and a sonication extension horn (US frequency: 20 kHz) of 13 mm diameter generating US are employed [16], setting up a power of $50\ W\ cm^{-2}$ and maintaining the temperature at 62 °C; sonication continued for 2.5 h. At the end, the sample is centrifuged in order to remove the solvent and it is washed with water.

Ultrasound is fundamental both for the formation of nanoparticles from the precursor, as to obtain a good distribution on the TiO_2 support surface. Indeed, ultrasonic irradiation speeds up the diffusion of solute in the reaction system, as well as it influences the selective adsorption of the surfactant on copper, inducing elongation or compression in defined directions, affecting the particles morphology. Moreover, the use of US allows working in conditions that do not require high temperatures or extreme settings, in order to make the reaction faster.

Six samples with different copper content were prepared. The percentage of copper was calculated, comparing the weight of TiO_2 and $CuCl_2{\cdot}2H_2O$, as shown in Table 1.

XRD spectra were collected using a PW 3830/3020 X' Pert Diffractometer from PANalytical working Bragg- Brentano, using

Table 1
Composition of the samples.

Sample	TiO_2 (1077 by Kronos)	$CuCl_2{\cdot}2H_2O$
K_1	2 g	0.02 g
K_5	2 g	0.1 g
K_10	2 g	0.2 g
K_20	2 g	0.4 g
K_40	2 g	0.8 g
K_75	2 g	1.5 g