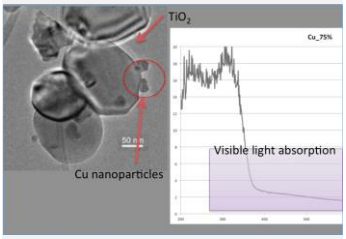
Copper NPs Decorated Titania to Improve the Photoactivity Under Visible Light: a Novel Synthesis by High Energy US.

Marta Stucchi[a,1], *Claudia Bianchi*[a,1], *Carlo Pirola*[a,1], *Giuseppina Cerrato*[b,1], *Sara Morandi*[b,1], *Christos Argirusis*[c], *Georgia Sourkouni*[d], *Alberto Naldoni*[a], *Stefania Vitali*[a,1],*Valentino Capucci*[d]. *(a) Università degli studi di Milano, Dip. Chimica - 20133 Milano, Italy, marta.stucchi@unimi.it. (b) Università degli studi di Torino, Dip. Chimica & NIS Interdept centre - 10125 Torino, Italy. (c) National Technical University of Athens, School of Chemical Engineering, 15780 Zografou-Athens, Greece. (d) Energy Research Centre of Lower Saxony, Am Stollen 19A, 38640 Goslar, Germany. (e) GranitiFiandre SpA, 42014 Castellarano, Italy. (1) Consorzio INSTM, Firenze, Italy.*



Different samples of commercial and micrometer TiO_2 were decorated with copper nanoparticles by means of high-energy ultrasounds, and they were tested on the photodegradation of VOC's in gas phase under visible light, studying in particular the effect of the copper amount first, and also the difference performances using a LED lamp at different irradiation power. The results are consistent with the characterization data, showing an increase of the photoactivity and the absorption in the visible spectra with the increase of the copper amount, but only up to a certain value.

Background

TiO_2 is the most widely investigated photocatalyst because of its suitable properties in term of photo-activity as well as cost, low toxicity and stability; even if TiO_2 needs to have a higher activity to be economically competitive, from a practical point of view alternative materials that are as advantageous as TiO_2 are hard to be found [1]. The recombination of photogenerated charge carriers is one of the main limitations in semiconductor photocatalysis, and the crucial problem related to the practical use of the TiO_2 is its inability to be active under the visible light. Several modification methods were developed in order to accelerate the photoconversion, enable the absorption of visible light, and alter the reaction mechanism or control products and intermediates [2]. Among these latter, metals onto the TiO_2 surface can enhance the electron transfer or the charge separation and improve the formation of the free hydroxyl radicals; another important aspect to take into account is the presence of free electrons that can be excited by light and also the possibility that metals act as an electron sink promoting also in this case the charge separation. The use of copper ions as dopants has recently attracted much attention because these species including Cu_2O and CuO can serve as electron mediator extending the absorption to the long wavelength region[3]. Sonochemistry is a novel and interesting way to obtain surface decoration of TiO_2 materials with metal nanoparticles[4], and in particular it can be used for the preparation of Cu-decorated titania.

Objectives

As very few studies on the photocatalytic performance of Cu nanoparticles (Cu NPs) have been reported so far, different samples of Cu-decorated-TiO_2 were tested in this work regarding the photodegradation of VOC's in gas phase under visible light studying in particular the effect of the copper amount first, and also the difference performances using a LED lamp at different irradiation power. Every sample has been prepared by means of high-energy ultrasounds, according to the procedure usually used for the decoration of SOFC [5]. Different amount of copper were used from 1% to 75% in order to investigate the effect of copper amount in term of photoactivity.

Methods

Samples with different loadings of Copper were prepared with the sonochemical method. The precursor materials were $CuCl_2*2H_2O$ for copper and the TiO_2 was a commercial and micrometric sample produced by Kronos; for each synthesis the US power was set at $50Wcm^{-2}$ at a constant bath temperature of 62°C.

Each sample was characterized by FT-IR analysis, TEM, XRD, and XPS; moreover, the UV-VIS absorption spectra were calculated with the band gap evaluation. The samples show an increasing of the absorption in the visible wavelengths, proportional to the copper amount; the band gap values are very interesting because it is shown that the TiO_2 surface decoration using ultrasounds moves the band gap to lower value. These results are consistent with the photocatalytic tests carried out on the acetaldehyde

photodegradation, in which an increased activity under visible light is reported. In particular, a pirex glass reactor (5L volume) was used to perform each photodegradation reaction: it is directly connected to a Gas-Cromatograph that automatically monitors the internal acetaldehyde concentration over time.

Results

The different copper amount was verified by TEM analysis and the different effect of it can be seen clearly in the absorption spectra, in which the visible light absorption increases proportionally.

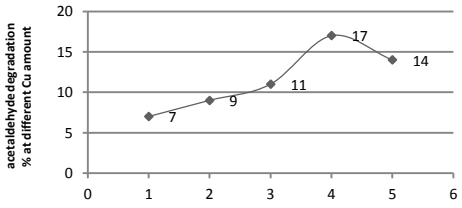


Figure 1. Acetaldehyde degradation at different Cu amount.

However, the copper amount on the TiO_2 surface can have also a negative effect on the photocatalyst performance, in particular because of the overlay of the active sites on the titania surface. This latter concept is consistent with the photocatalytic tests results, in particular for the acetaldehyde photdegradation, in which there is a decrease of the activity over some values of copper quantity. It is important to underline that without any nanoparticles onto the TiO_2 surface, this latter is completely inactive if irradiated just by visible wavelengths.

Conclusion

In this work the effect of the surface decoration of microsized commercial titania with copper NPs is presented. The copper decoration has been studied by means of TEM and XRD analysis, as well as both the absorption spectra and the band gap evaluation have been performed. For the photocatalytic tests, the chosen molecule was acetaldehyde: the best amount of copper in term of photoactivity under visible light was found, demonstrating that a too high quantity of NPs of the TiO_2 surface can affect the activity negatively.

References

[1] T. Ochiai, A. Fujishima, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 13 (2012) 247–262.
[2] J. Lyu, L. Zhu, C. Burda, *Catalysis Today*, 225 (2014) 24–33.
[3] L. Chiang, R. Doong , *Journal of Hazardous Materials*, 277 (2014) 84–92.
[4] M. Stucchi, C.L. Bianchi, C. Pirola, et al., *Applied Catalysis B: Environmental*, *doi:10.1016/j.apcatb.2014.10.004*
[5] P.M. Sakkas, O. Schneider, G. Sourkouni, C. Argirusis, *Ultrasonics Sonochemistry*, 21 (2014) 1939- 1947.