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The fungicidal effect of TiO_2 doped with metallic ions

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Abstract

Incorporating metal ion dopants into the titanium dioxide particles can influence the performance of the photocatalysis. This affects the dynamics of electron-ion recombination and interfacial charge transfer. We might tell there is an optimum dopant concentration to enhance the photocatalytic activity. Metals ions serve as shallow trapping sites for the charge carriers so as separates the arrival time of e- and H+ at the surface. Photocatalytic oxidation is based on the production of several highly reactive short-lived chemical compounds—oxygen-based radicals and ions—that are effective in microorganism disinfection and neutralizing volatile organic compounds. Usually the microorganism is completely destroyed. In this paper we report the effect of TiO_2 that was doped with different metal ions on Aspergillus fungi that was isolated from the wheat. The metals ion that was using like dopants was: silver and platinum. In the powder with TiO_2 the metallic ions appear in different percentage and became from the different precursors organic or non-organic. Our experiments show that the TiO_2 doped with platinum has the better fungicidal effects like TiO_2 doped with silver. It is possible that photocatalytic oxidation could become one of the decontamination methods of the future.

Keywords:

1. Introduction

Nanomaterials have many unique properties and thus have drawn substantial attention in the recent years [1, 2]. TiO_2 was so far extensively used as a photocatalyst for the investigation of conversion of the solar energy into chemical energy and in environmental applications, i.e. the photooxidation of organic pollutants in drinking and residual waters [3, 4].

Recently, among nanomaterials a growing interest has been devoted to TiO_2-based photocatalysts, which are low-cost chemically stable and non-toxic compounds and possess high photocatalytic activity [5, 6]. Incorporating metallic and non-metallic dopant ions into the titanium dioxide particles can influence the performance of these photocatalysts. This affects the dynamics of electron-ion recombination and interfacial charge transfer. Presence of dopant ions shifts the exciting radiation spectrum from UV domain towards the VIS region [7]. The photocatalytic efficiency of nanocrystalline TiO_2 system is strongly influenced by an electronic modification of the catalyst through deposition of metal particles [8–11], surface sensitization [12-15], and selective metal ion doping. Many metal ion dopants for the TiO_2 system have already been investigated by different research groups [17,18]. It has been known that the advantage of the doping of the metal ions in TiO_2 is the temporary trapping of the photogenerated charge carriers by the dopant and the inhibition of their recombination during migration from inside of the material to the surface or the enhanced association of the functionalized organic pollutants to the doping ion surface

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sites. The effect of metal ion doping strongly depends on many factors such as the dopant concentration, the particle size of the nanocrystalline TiO_2, the distribution of the dopants, the d-electronic configuration of doping ions and so on [16].

2. Experimental

Materials

The starting materials used for the synthesis were: titanium isopropoxide (TTIP, Fluka), ethanol, distilled water, silver nitrate (Merk, $AgNO_3$) and hexachloroplatinic acid (Merk, PtH_2Cl_6).

Photocatalyst synthesis

Titanium dioxide doped with metallic ions (Ag, Pt) was obtained directly from precursors by sol-gel method.

Sol-gel (SG) method presumes the mixing of 30 mL of ethanol with 5 mL of TTIP (the precursor for Ti) added by dropwise. After a few minutes of stirring, distilled water was added also in drops. The doping precursors, $AgNO_3$ for TiO_2-Ag synthesis and PtH_2Cl_6 for TiO_2-Pt synthesis, were added after the pH adjustment. The doping precursors amount were 1% and 2% from Ti quantity for both materials (TiO_2-Ag 1%, TiO_2-Ag 2%, TiO_2-Pt 1%, TiO_2-Pt 2%).The solution was continuous stirred for one hour and the obtained materials were filtered, washed and dried at 60ºC.

The thermal treatment for both materials was achieved for 2 hours at 500ºC temperature.

Materials characterization

Phase characterization of the doped photocalysts was carried out by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE X-ray diffractometer with Cu Kα radiation in θ:2θ configuration. The particles size and morphology were determined by Scanning Electron Microscopy (SEM) using an Inspect S PANalytical model and the energy dispersive X-ray analysis detector (EDX).

Direct isolation techniques of fungi and prepare inoculum

The term "direct is applied to techniques involving the simple transfer of a mould from its natural habitat to a pure culture situation in the laboratory [22]. The fungal inoculum was prepared by adding 90 mL of sterile distilled water with two drops of Tween-80 into a plate with 10 grams of wheat. We prelevate 1 ml of suspension and cultivated in Sabouraud medium.

After the transfer we wait five days for the mould to grow and form a colony. It developed separated colony and we made a fungal inoculum with Aspergillus spores [22] . We verified the fungicidal activity of TiO_2 powder doped with metallic ions – platinum 1% and 2% and silver 1% and 2% on *Aspergillus niger*. In our experiment we used the dilution plating method.

The level of yield spores dilutions was 10^{-3}. For every dilution with powder of doped TiO_2 and for the witness we cultivate 4 Petri dishes. For testing the effect of TiO_2 doped with metallic ions we take the Petri dishes under UV light at 254 nm six time 10 minutes and half of hour pause, and in the same time for observe the effect of UV light without the TiO_2 powder. The manner of irradiation of the sample without powder was the same. After the irradiation the Petri dishes was take on the thermostat for 5 days at 25^0C.

3. Results and Discussion

In figures 1 and 2 are presented the XRD spectra of TiO_2 doped with Ag (1% and 2%) and Pt (1% and 2%). The peaks of anatase TiO_2 corresponding to 2θ ~ 25.2º, 37.87º, 48.01º, 53.81°, 62.67°, 75.07° [19, 20] appear for both doped TiO_2.

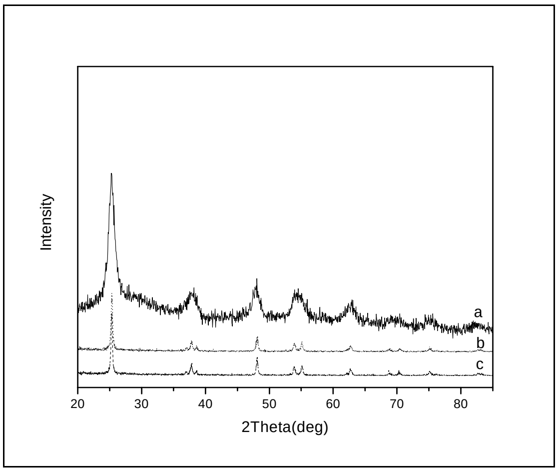


Figure 1. XRD patterns of TiO_2-Ag; a- undoped TiO_2, b- TiO_2-Ag 2%, c-TiO_2-Ag 1%

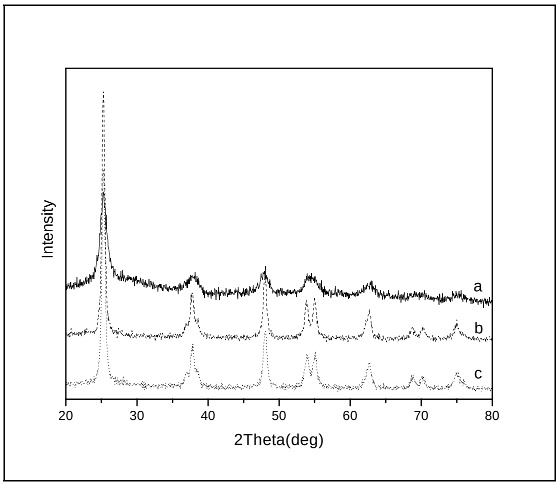
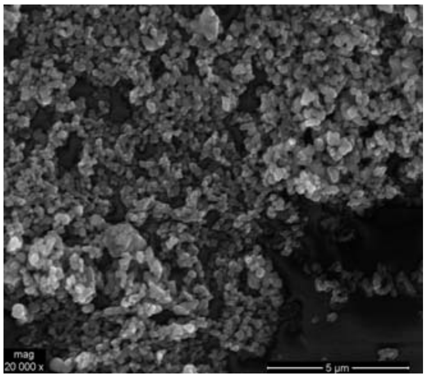


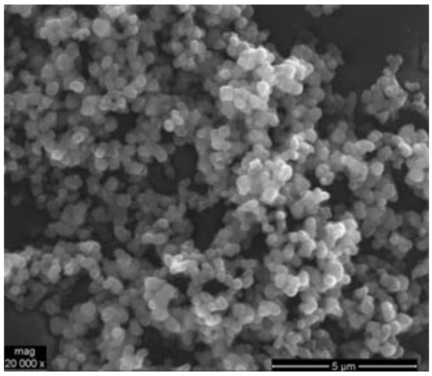
Figure 2. XRD patterns of TiO_2-Pt; a- undoped TiO_2, b- TiO_2-Pt 1%, c-TiO_2-Pt 2%

It can be seen that the peaks corresponding to Ag and Pt are not found, because they are uniformly distributed in the crystalline network of the titanium dioxide.

Figures 3 and 4 show the surface morphology of the TiO_2-Pt (1%, 2%) and TiO_2-Ag (1%, 2%) determined by using SEM.

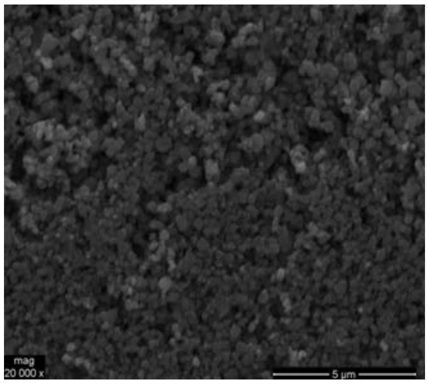


(a)

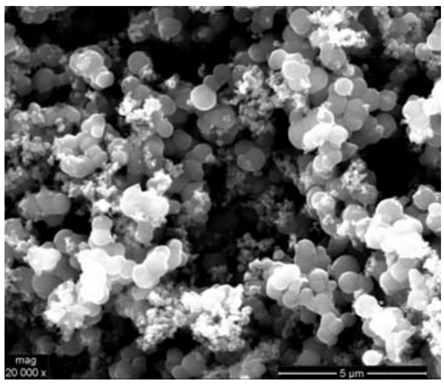


(b)

Figure 3. SEM morphology of: a) TiO_2-Pt 1% and b) TiO_2-Pt 2%



(a)



(b)

Figure 4. SEM morphology of: a) TiO_2-Ag 1% and b) TiO_2-Ag 2%

Particles of doped TiO_2 obtained by sol-gel method present nanospherical morphology, highly agglomerated (Figs. 3, 4). The nanosphere dimensions are between 20-40nm.

The energy dispersive spectroscopy (EDAX) was performed only to identify the ions dopants (Ag, Pt) in titanium dioxide structure (Figs. 5 and 6).

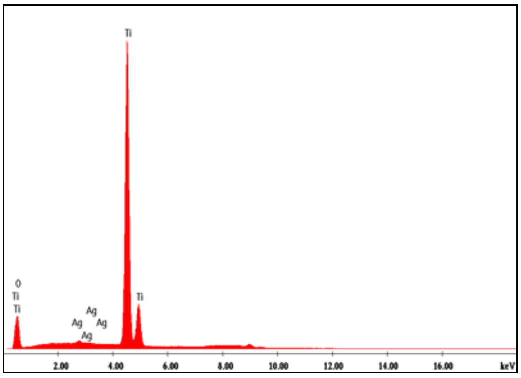


Figure 5. EDX spectra for TiO_2-Ag (1% and 2%)

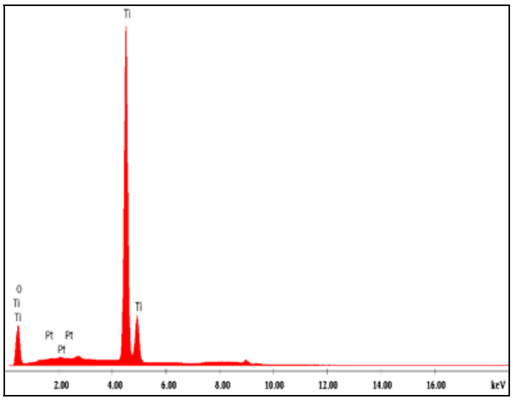
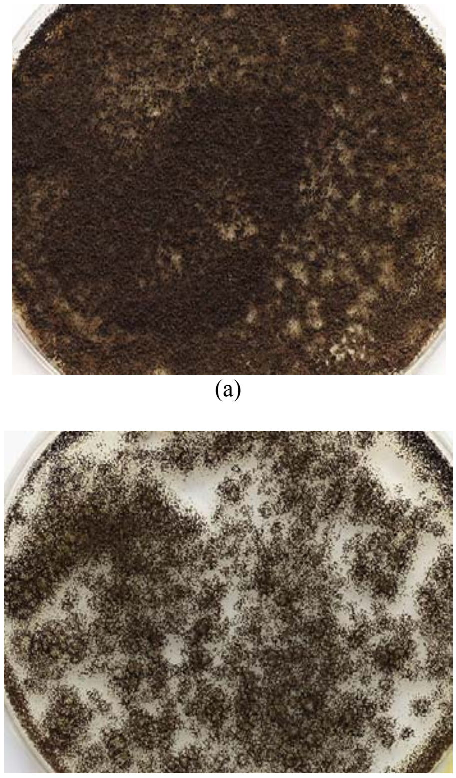


Figure 6. EDX spectra for TiO_2-Pt (1% and 2%)

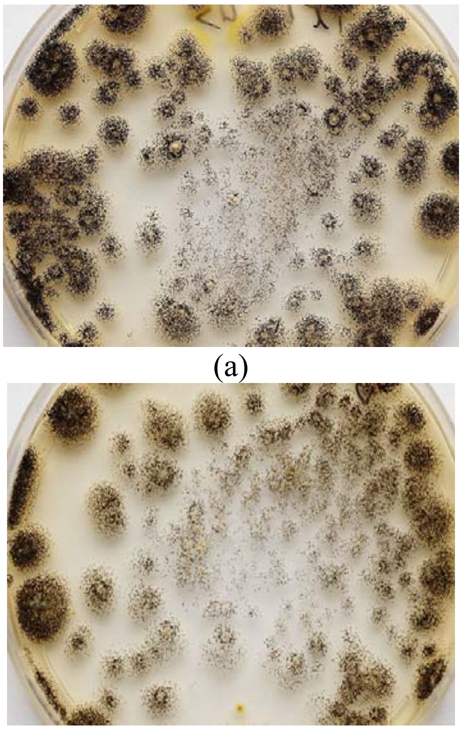
After obtaining the powder and the microbiologic experiments, in every day we made observation. We observe the moment of apparition of the hyphae, their aspects, the sporulation, the most efficient compound TiO_2 metallic ions doped, the more efficient work conditions for obtained the best results, we tried to determine the spores viability to the second generations. We present in the next images the aspect of fungi colony in Petri dishes – the witness without and UV treatment and the of fungi colony in Petri dishes with powder after treatment with UV.



(a)

(b)

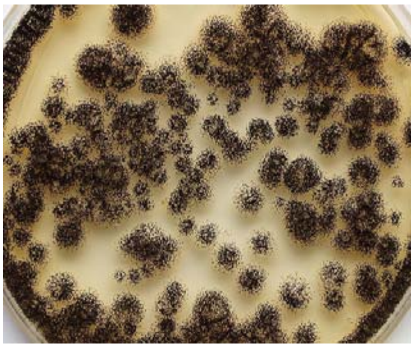
Figure 7. *Aspergillus niger* – (a) witness (b) after UV exposure



(a)

(b)

Figure 8. *Aspergillus niger* after the treatment with TiO_2 doped with platinum (a) 1% (b) 2% and UV exposure



(a)

(b)

Figure 9. Aspergillus niger after the treatment with TiO_2 doped with silver – a) 1% b) 2% and UV exposure

After examined the photos, we can see the difference of development of fungi colony in the Petri dishes in the same work conditions. This is the reason because we conclude that the difference of fungal cells viability is due of the presence of TiO_2 powder and it dopant – platinum and silver, the dopant concentration (1% or 2%) and the time and modality of exposure to UV light. The intermittent exposure to UV light leads to better results.

4. Conclusion

Nanocrystals of TiO_2 doped with silver and platinum (1% and 2%) have been prepared by sol-gel method.

The XRD results showed that the TiO_2 nanocrystals were in the anatase form.

The SEM images reveal that the particles of doped TiO_2 obtained by sol-gel method present nanospherical morphology, highly agglomerated, and the nanosphere dimensions are between 20-40 nm.

The fungi cell alteration in culture media is due to the photocatalytic effect of TiO_2 that was doped with platinum and silver and to the production of free oxygen radicals with pronounced fungicidal effect.

The fungicidal effect depend of the concentration of dopand – the better results obtained to the 2% comparing with 1% for the same dopant.

Comparing the fungicidal effect of the dopant when the other work conditions was the same could see that using the platinum leads to better results.

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