



**PHYSICAL CHEMISTRY 2010**

**10th International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry**

Proceedings

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**The Conference is dedicated to the  
100th Anniversary of the academician Pavle Savić birthday  
and  
20th Anniversary of the Society of Physical Chemists of Serbia**

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**21-24 September 2010  
B E L G R A D E**

**ISBN 978-86-82475-17-0**

**Title:** Physical Chemistry 2010. (Proceedings)

**Editors:** S. Anić and Ž. Čupić

**Published by:** Society of Physical Chemists of Serbia, Studentski trg 12-16  
P.O.Box 47, 11158 Beograd, 218, Srbija

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** “Jovan” Printing and Publishing Company; 200 Copies;

Number of pages 16 + 388, **Format:** B5; Printing finished in September  
2010.

**Text and Layout:** “Jovan”

*200 - Copy printing*

*The Society of Physical Chemists of Serbia*

*in co-operation with*

*Institute of Catalysis, Bulgarian Academy of Sciences*

*Boreskov Institute of Catalysis, Siberian Branch of  
the Russian Academy of Sciences*

*Faculty of Physical Chemistry, University of Belgrade, Serbia*

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# PHOTOCATALYTIC ACTIVITY OF TiO<sub>2</sub> NANOPARTICLES MODIFIED WITH DOPAMINE

M. Radoičić<sup>1</sup>, I. Janković<sup>1</sup>, V. Despotović<sup>2</sup>, D. Šojić<sup>2</sup>, Z. Šaponjić<sup>1</sup>,  
B. Abramović<sup>2</sup> and M. I. Čomor\*<sup>1</sup>

<sup>1</sup>*Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia*  
<sup>2</sup>*Department of Chemistry, Faculty of Sciences, University of Novi Sad, Trg D.  
Obradovića 3, 21000 Novi Sad, Serbia*

## Abstract

Photocatalytic activity of bare colloidal TiO<sub>2</sub> nanoparticles (NPs, d~45Å) and surface modified with dopamine was obtained following degradation reaction of herbicide RS-2-(4-chloro-o-tolyloxy)propionic acid (mecoprop, MCP, C<sub>10</sub>H<sub>11</sub>ClO<sub>3</sub>) under UV light irradiation. Results indicated that inner sphere charge transfer (CT) complex is formed on the surface of TiO<sub>2</sub> NPs due to modification with dopamine which induced decreasing of the photocatalytic efficacy of TiO<sub>2</sub> NPs.

## Introduction

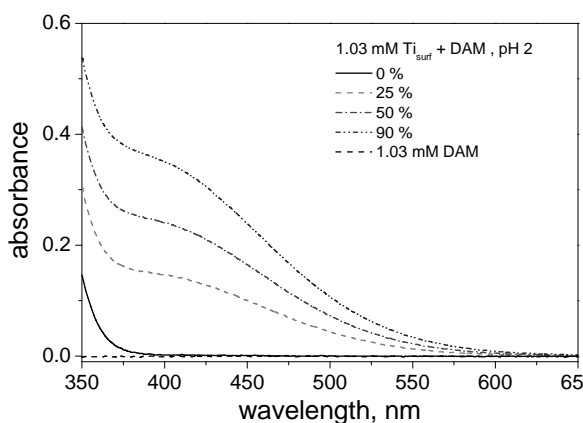
Titanium dioxide is the photocatalytic material which has been studied extensively over the past decade because it is inexpensive, nontoxic, and photostable. The absorption of photons with energy greater than band gap energy of TiO<sub>2</sub> (3.2 eV, λ < 390 nm) promotes electron from the valence band to conduction band, leaving a positively charged hole in the valence band. Most of the charges recombine either radiatively or nonradiatively, while only a small fraction of the charges moves to the surface and react with adsorbed species or be trapped in the midgap surface states [1]. One of the possible ways to minimize charge recombination is to enlarge separation distances before desired redox reaction occurs. This can be done by surface modification of TiO<sub>2</sub> NPs with electron-accepting/donating species [2]. In the nanosize regime, because of the large curvature of TiO<sub>2</sub> particles, the surface reconstruct in such a way that distorts the crystalline environment of surface Ti atoms forming coordinatively unsaturated Ti atoms, coordination change from octahedral (bulk, inside the NP) to square-pyramidal for NP surface. Formation of charge-transfer complex at the surface of NPs can adjust their coordination to octahedral geometry and change the electronic properties of TiO<sub>2</sub> [3]. This type of electronic coupling yields to instantaneous separation of photogenerated charges, the holes localize on organic modifier and electrons delocalize in the conduction band of TiO<sub>2</sub> NPs. In the scope of this work, we wanted to study the effect of fast and enlarged separation distance of photogenerated charges induced by surface modification of TiO<sub>2</sub> NPs and formation of CT complex, on photocatalytic activity of TiO<sub>2</sub> NPs. Photocatalytic degradation of herbicide RS-2-(4-chloro-o-tolyloxy)propionic acid (mecoprop, MCP, C<sub>10</sub>H<sub>11</sub>ClO<sub>3</sub>) was used as model reaction because of its wide use all over the world and usual occurrence in drinking water [4].

## Experimental

All chemicals used were of the highest purity available. All solutions were prepared with triply distilled water. The TiO<sub>2</sub> NPs were prepared by controlled hydrolysis of titanium (IV) chloride (Fluka), as described elsewhere [3]. Particle size was determined using a transmission electron microscope, JOEL CXII. The surface modification of TiO<sub>2</sub> NPs was accomplished by dissolution of Dopamine (3-hydroxytyramine, puriss, Fluka) in TiO<sub>2</sub> colloidal solution. Spectrophotometric measurements were carried out on a Evolution 600 UV-VIS spectrophotometer. Photocatalytic degradation was carried out in a way described previously [4]. The kinetics of MCPP degradation were studied by liquid chromatography- diode array detection, Agilent Technologies 1100 Series, details as in ref. [4].

## Results and Discussion

The absorption spectra of bare and surface modified TiO<sub>2</sub> NPs are presented in Figure 1.

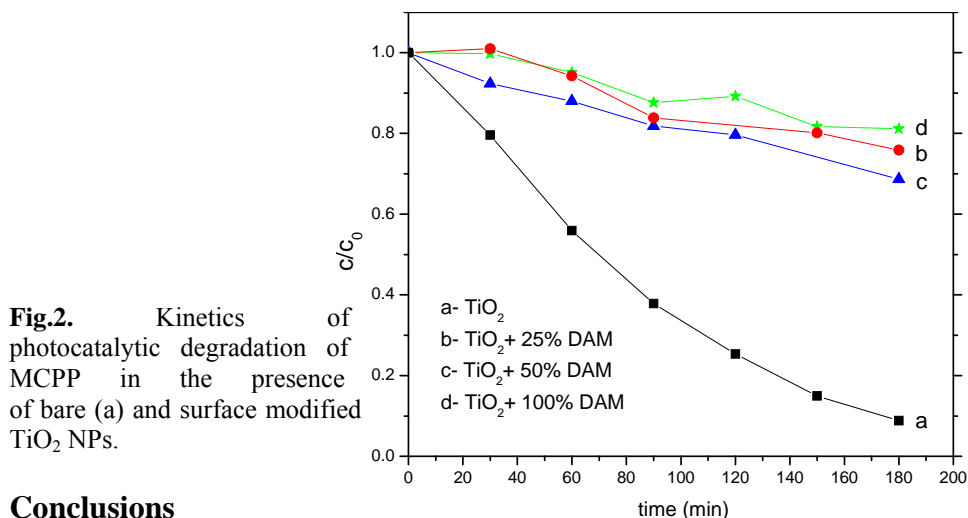


**Fig.1.** Absorption spectra of bare, surface modified TiO<sub>2</sub> NPs and pure Dopamine (DAM), concentrations and surface coverage are presented in inset.

It can be seen that the optical properties of bare TiO<sub>2</sub> NPs are changed due to CT formation with Dopamine. We used three concentrations of Dopamine which produced 25 %, 50% and 90% coverage of surface, undercoordinated Ti atoms (for NPs with  $d \sim 45 \text{ \AA}$ , about 30% of Ti atoms are on the surface).

As can be seen in Fig. 2, MCPP can be decomposed with all applied photocatalysts under UV irradiation. The best results were obtained with bare TiO<sub>2</sub> NPs. Modified TiO<sub>2</sub> NPs showed lower photocatalytic activity, without linear dependence with surface coverage of TiO<sub>2</sub> NPs with CT complex with Dopamine. As the matter of fact, all applied coverages had almost the same photocatalytic activity. One of the possible reasons for such results can be decreased adsorption of MCPP on the surface of modified TiO<sub>2</sub>. This fact must be considered for 50% and 100% of coverage, but even 25 % of coverage reduced photocatalytic activity. The other reason can be based on the nature of the formed CT complex. Namely, all concentration of CT complex on the surface of TiO<sub>2</sub> NPs was capable to extract photogenerated positive holes from TiO<sub>2</sub> NPs. Obviously, extracted holes are not

able to produce OH radicals which can oxidize MCPP and it seems that only electrons from TiO<sub>2</sub> conduction band participate in the degradation of MCPP. As can be seen in Fig. 1, surface modification induced red shift of the absorption onset and charge transfer interaction between the modifier and surface Ti atoms also induced fine tuning of the electrochemical potential of semiconductor NPs indicating changes in oxidizing/reducing abilities. As already stressed in literature [3], TiO<sub>2</sub> conduction band potential is kept constant while valence band potential is moved due to modification, to lower potential and holes extracted through CT complex are not capable to react with MCPP.



**Fig.2.** Kinetics of photocatalytic degradation of MCPP in the presence of bare (a) and surface modified TiO<sub>2</sub> NPs.

## Conclusions

Binding of the Dopamine molecules to undercoordinated surface Ti atoms (defect sites) results in formation of inner-sphere charge-transfer complex, observed by changes in the onset of absorption and effective band gap. Photocatalytic degradation of herbicide MCPP was followed as model reaction for evaluation of photocatalytic activity of applied catalysts. Modified TiO<sub>2</sub> NPs showed reduced photocatalytic activity compared to bare TiO<sub>2</sub> NPs. Observed results can be explained by reduced TiO<sub>2</sub> surface after modification, at which MCPP can be adsorbed and inappropriate potential of holes extracted from TiO<sub>2</sub> NPs in Dopamine molecule, for direct oxidation of MCPP molecule.

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