



PHYSICAL CHEMISTRY 2008

Proceedings

*of the 9th International Conference on Fundamental
and Applied Aspects of Physical Chemistry*

Volume II

The Conference is dedicated to the 200th Anniversary of the University in Belgrade



September 24-26, 2008,
Belgrade, Serbia



PHYSICAL CHEMISTRY 2008

Proceedings

*of the 9th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry*

Volume II

ISBN 978-86-82475-13-2
Title: Physical Chemistry 2008. (Proceedings)
Editor: Prof. dr A. Antić-Jovanović
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia
Printed by: "Jovan" Printing and Published Comp;
250 Copies; Number of Pages: x + 301 (469-770);
Format B5; Printing finished in September 2008.
Text and Layout: Aleksandar Nikolić

250 – copy printing

SURFACE MODIFICATION OF TiO₂ NANOPARTICLES WITH CATECHOL

I.A. Janković¹, Z.V. Šaponjić¹, E. Džunuzović² and J.M. Nedeljković¹

¹*Vinča Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Serbia*

²*Faculty of Technology and Metallurgy, Department of Physical Chemistry and Electrochemistry, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

Abstract

Surface modification of nanocrystalline TiO₂ particles with catechol was found to result in a red shift of the semiconductor absorption compared to unmodified nanocrystallites. The undercoordinated defect sites at TiO₂ surface are the source of novel enhanced and selective reactivity of the nanoparticle toward bidentate ligand binding. Catechol, an enediol ligand, have the optimal geometry for chelating surface Ti atoms, resulting in a five-membered ring coordination complex and restoration of six-coordinated octahedral geometry of surface Ti atoms.

Introduction

Semiconductor nanoparticles exhibit unique properties being different from those of bulk crystals. The electronic, optical, structural and photoredox properties can be greatly varied by changing the particle size without changing the chemical composition [1]. Controlling the nanoparticle size distribution and surface properties opened up the possibility for their application in microelectronics and photocatalysis.

Titanium dioxide is the photocatalytic material being studied extensively because of its inexpensiveness, nontoxicity, and photostability. Unfortunately, the use of TiO₂ for photocatalytic applications driven by solar light is limited by its wide band gap ($E = 3.2$ eV) leading to the absorption of less than 5 % of the available solar spectrum photons. There has been tremendous interest in recent years in developing the way for sensitization of TiO₂ for photoexcitation in the visible region [2]. Optical properties of nanocrystalline TiO₂ can be improved by surface modification with electron-donating bidentate ligands. In this work we report optical characterization of TiO₂ nanoparticles, with average diameter of 4.5 nm, modified with catechol.

Experimental

All chemicals used were of the highest purity available. All solutions were prepared with triply distilled water. The TiO₂ nanoparticles with mean particle diameter of 4.5 nm were prepared by controlled hydrolysis of titanium (IV) chloride (Fluka), as described elsewhere [3]. Surface modification of TiO₂ nanoparticles was accomplished by dissolution of catechol in TiO₂ colloidal dispersion (pH=2). Spectrophotometric measurements were carried out on a Thermo Evolution 600

UV-vis spectrophotometer and on Thermo Nicolet 380 FTIR (Smart Orbit ATR accessory).

Results and Discussion

The absorption spectra of TiO₂ nanoparticles and surface modified TiO₂ with increasing concentrations of catechol are presented in Figure 1. It can be seen that the optical properties of TiO₂ nanoparticles change and the onset of absorption shifts by 1.4 eV to the red, compared to unmodified nanoparticles. This can be explained with the complex formation between catechol and Ti atoms on the surface of 4.5 nm TiO₂ nanoparticles. Similar results were obtained when TiO₂ nanoparticles have been modified with various enediol ligands.[4] It was reported that the coordination of Ti surface atoms changes from six coordinate (octahedral) in bulk to pentacoordinate (square-pyramidal) in small particle colloids. Distortion of bond length accounts for the large curvature of small particles and converts surface into more reactive "corner defects". Upon binding with enediol ligands to the surface sites, the asymmetry of these sites is removed, and the bulk structure of the conduction bands is restored.

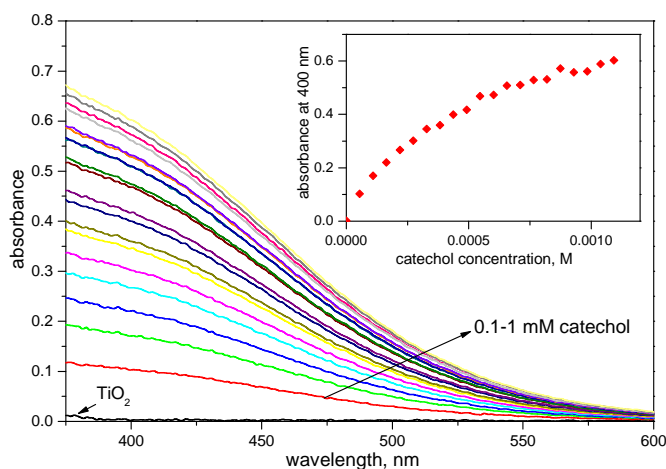


Fig. 1. Absorption spectra of 3.25 mM TiO₂ nanoparticles before and after surface modification with catechol. Inset: A_{400} vs catechol concentration

The binding of catechol ligand follows the Langmuir-type adsorption isotherm (Inset of Figure 1) and from the linear dependence

$$\frac{1}{A_{400}} = \frac{1}{KA_{400}^{\max}} [\text{cat}] + \frac{1}{A_{400}^{\max}}$$

binding constant $K = (2460 \pm 120) \text{ mol}^{-1} \text{ dm}^3$ was obtained.

Using FTIR spectroscopy, we have confirmed bidentate binding of catechol (Figure 2). It is obvious that upon formation of catechol-Ti_{surf} complex infrared spectra different from catechol [5] is obtained. The intensities and the position of the bands corresponding to stretching aromatic ring vibrations $\nu(\text{C}=\text{C})$ are

changed. The bands assigned to phenol OH in-plane bending ($\delta_{\text{inpl}}(\text{PhOH})$, 1100-1200 cm^{-1} region) and stretching vibrations ($\nu(\text{PhOH})$, 1200-1300 cm^{-1} region) lose their fine structure while the band assigned to bending in-plane OH vibrations at 1365 cm^{-1} disappears completely.

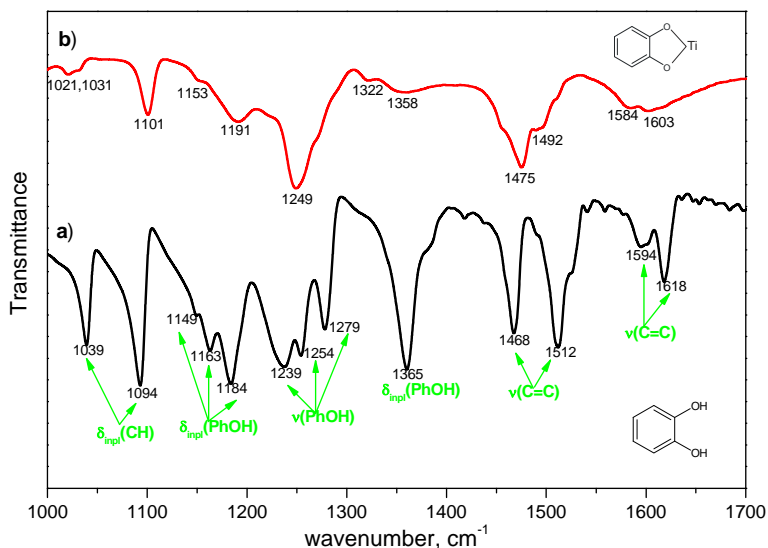


Fig. 2. FTIR spectra of dried samples: a) catechol and b) 0.05M catechol-modified 0.18M TiO_2 at pH 2

Conclusions

Specific binding of catechol modifier to surface "corner defects" on 4.5 nm TiO_2 nanoparticles induces red shift of 1.4 eV in the onset of absorption, compared to unmodified nanoparticles. Formation of bidentate chelating complex is the consequence of an adjustment in the coordination geometry of the Ti atoms near the TiO_2 nanoparticle surface, from octahedral to square-pyramidal in order to accommodate the large surface curvature. Surface modification is alternative method for light sensitisation of large band gap semiconductors.

References

- [1] O.I. Mičić, T. Rajh, J.M. Nedeljković, M.I. Čomor, *Israel J. Chem.*, 1993, **33**, 59-65.
- [2] M.R. Hoffman, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69-98.
A. Hagfeldt, M. Grätzel, *Chem Rev.*, 1995, **95**, 49-68.
- [3] T. Rajh, Z.V. Šaponjić, O.I. Mičić, *Langmuir*, 1992, **8**, 1265-1269.
- [4] T.Rajh, L.X. Chen, K. Lukas, T. Liu, M.C. Thurnauer, D. M. Tiede, *J. Phys. Chem. B*, 2002, **106**, 10543-10552.
- [5] P. Z. Araujo, P. J. Morando, M. A. Blesa, *Langmuir*, 2005, **21**, 3470-3474.