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Serbia*

*in co-operation
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SURFACE MODIFICATION OF ZIRCONIA NANOPARTICLES WITH SELECTED ENEDIOL LIGANDS

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ABSTRACT

The colloidal ZrO₂ nanoparticles were hydrolytically synthesized and characterized using x-ray diffraction and UV/Vis spectroscopy. The surface modification of nanocrystalline particles with selected enediol ligands: catechol (CAT), 2,3-dihydroxynaphthalene (2,3-DHN), anthrarobin (ANT) and quercetin, was found to alter the optical properties of nanoparticles. The formation of the inner-sphere charge-transfer (CT) complexes results in a red shift of the semiconductor absorption onset compared to unmodified nanocrystallites, and a decrease of effective band gap upon increase of the electron delocalization after the inclusion of additional rings.

INTRODUCTION

Widespread interest in the modification of TiO₂ surfaces with organic and organometallic molecules is largely motivated by the application of these materials in photocatalysis and photovoltaics [1]. Similar behavior can be expected from the other non-toxic metal oxides like ZrO₂ which is the subject of this paper. In recent years, much attention has been paid to the preparation of high surface nano-zirconia, not only due to its wide application as a catalyst and catalyst support, but also for its use as an advanced material for structural engineering ceramics, oxygen sensors, fuel cells, and other interesting applications [2]. Zirconia has a large band gap, $E_g = 5$ eV, even larger than TiO₂ ($E_g = 3.2$ eV) and absorbs in far UV region [3]. We hope that sensitization of ZrO₂ crystals and nanoparticles with appropriately chosen molecules, enediol ligands, can lead to a significant red shift of their absorption threshold from the far UV to the visible, thus enabling and improving the absorption of the solar spectrum as well as its possible application as photocatalyst and photovoltaic material.

EXPERIMENTAL

All chemicals used were of highest possible quality (p.a.), Milli-Q deionized water was used as a solvent. The colloidal ZrO_2 dispersions were prepared by forced hydrolysis of $ZrOCl_2$ at $75^\circ C$ for 24 hours with constant steering. After hydrolysis clear dispersion was dialyzed against water until $pH=5$ was reached. Stoichiometric concentration of ZrO_2 was $\leq 0.06 \text{ M dm}^{-3}$. Crystal structure of the obtained zirconia was checked by using X-ray diffraction.

For XRD analysis, obtained colloidal ZrO_2 dispersions were dried on Si-carrier and XRD data were collected in 2θ range of 10° - 60° , with scanning steps of 0.05° . As can be seen (Figure 1), crystal structure of obtained material is not quite developed yet.

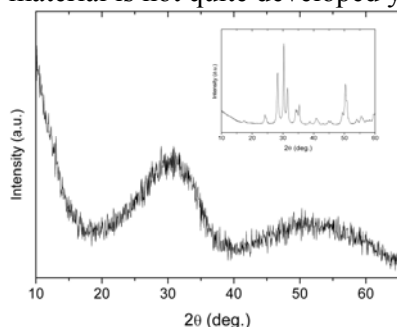


Figure 1. X-ray diffractogram of colloidal ZrO_2 dispersion. Inset: X-ray diffractogram of the same sample sintered at $600^\circ C$ for 3h

Wide peaks and shoulders in diffractogram imply on presence of both amorphous and crystallized material. In order to confirm a formation of ZrO_2 nanocrystals, obtained material was dried at $70^\circ C$, and then sintered at $600^\circ C$ for 3h. XRD data of acquired powder (Inset in Fig 1.) confirmed exclusive presence of ZrO_2 (mixed monoclinic and tetragonal phase).

The surface modification of ZrO_2 resulting in the formation of a CT complex was achieved by the

addition of surface-active ligands (catechol, 2,3-dihydroxynaphthalene, anthrabin and quercetin; structural formulas in Table 1) up to the concentrations required to cover all the surface sites.

The modifications were performed in methanol and allowed to react for 24 h to ensure complete complexation. Absorption spectra of surface modified ZrO_2 nanoparticles were recorded at room temperature in cells with 1 cm optical path lengths using a Thermo Scientific Evolution 600 UV/Vis spectrophotometer.

RESULTS AND DISCUSSION

When ZrO_2 particles are on the nanosize scale, a large fraction of the atoms that constitute the nanoparticle is located on the surface with significantly altered electrochemical properties. Among them, the existing undercoordinated defect sites are the source of novel, enhanced and selective reactivity of nanoparticles toward ligand binding. Upon binding, the new hybrid properties arise from the ligand-to-metal CT interaction due to

orbital mixing between the molecular orbitals of the ligands and the conduction band orbitals of the nanoparticles.

Table 1. Ligands used for modification of ZrO₂ nanoparticles, structural formulas and the effective band gaps (E_g) upon binding

ligand	Structural formula	E _g (eV)
1.	ZrO ₂	5
2. CAT		3.35
3. 2,3-DHN		3.44
4. ANT		1.78
5. Quercetin		2.03

All of the ligands investigated in this work, listed in Table 1, were found to undergo binding at the surface (Fig. 2), inducing new hybrid properties of the surface modified nanoparticle colloids. These hybrid properties arise from the ligand-to-metal charge-transfer (CT) interaction. By extracting the corresponding onset energies from the absorption spectra of surface modified ZrO₂ nanoparticles, the effective band gap energies (E_g = hc/λ) of CAT, 2,3-DHN, ANT and quercetin modified ZrO₂ nanoparticles in methanol were calculated to be: 3.35 eV, 3.44 eV, 1.78 and 2.03 eV, respectively.

CONCLUSION

All investigated ligands (CAT, 2, 3-DHN, ANT and quercetin) form inner-sphere charge-transfer complexes with ZrO₂ nanoparticles (d ~4 nm). The binding of the modifier molecules to undercoordinated surface Zr atoms (defect sites) results in a significant shift in the onset of absorption to the lower energy spectral range. The lowest shift was, as expected, achieved by modification with catechol (enediol with one aromatic ring) and the highest

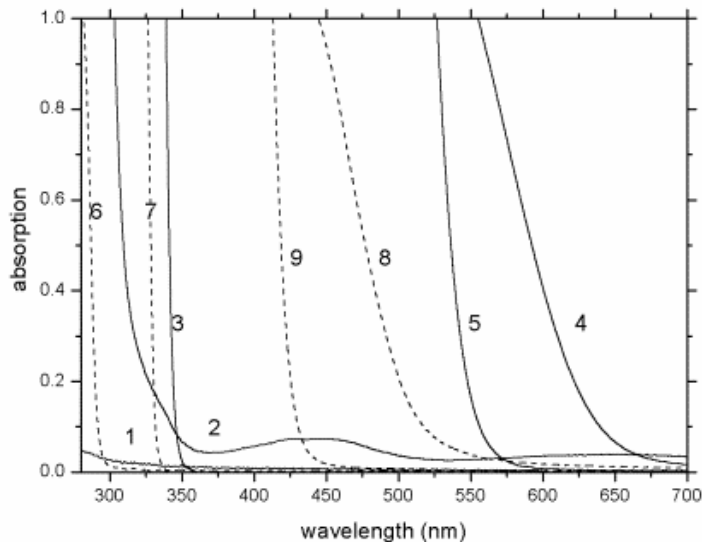


Figure 2. Absorption spectra of bare (1) and surface modified ZrO₂ nanoparticles with different ligands (0.45 mM): (2) CAT; (3) 2,3-DHN; (4) ANT, (5) quercetin. Spectra of pure modifiers are: (6)-(9), respectively.

with anthrabin (three fused aromatic rings) and quercetin (two fused rings with one as substituent), which proves positive effect of extended electron delocalization in modification.

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