I.O.S.U.D. University Politehnica of Timisoara
Doctoral School of Engineering studies

OXIDES AND DIFFERENT CONFIGURATIONS OF TiO_2 - ZnO BASED CORE/SHELL NANOCOMPOSITES FOR THE USE IN SOLAR ENERGETICS APPLICATIONS

Synthesis

Author: Carmen Valentina IRINA-MOISESCU (b. Vasile)

Supervisor: C.S.I.PhD Physics Ioan GROZESCU

Oxide semiconductors, a category that includes zinc oxide ZnO and titanium dioxide, TiO_2 have received increased attention in recent decades due to their photocatalytic properties, useful in many applications [1-2], and these include solar energy.

Semiconductor is a substance (a compound or a solid material) which under certain conditions can conduct electrical current by applying an external continue electrical voltages. A semiconductor material has a conductivity of electricity between that of an insulator (almost zero) and a good conductor [3].

Semiconductors of typeII-VI are composed of elements from groups II and VI of the periodic table. In these structures, the unit cell comprises fouratoms of typeII at the corners of a tetrahedron, and each of these atoms is surrounded by four atoms of type VI and more anatom oftype VI is coordinated by four atoms of type II.

Semiconductors of type II-VI or $A^{II}B^{VI}$, where A is a bivalent element and B is a hexavalent element, have activation energy in the range of 1-3 eV [7], low electrical resistivity and direct electronic band-band transitions [8].

The semiconductor behavior of a material is heavily influenced by temperature. At low temperatures, semiconductors are insulators, and at high temperatures they become good conductors. Semiconductor category includes a wide variety of substances, including oxides.

Zinc oxide, ZnO can be considered as an "old" semiconductor which drew attention of its researchers due to its properties. It was studied and widely used since 1935 [9] and continues to attract attention, by finding new applications. However, being a direct band gap semiconductor of type II - VI (or $A^{II}B^{VI}$,) with a n-type conduction, ZnO is called by some scientific community "material of the future". At normal temperature and pressure, the most binary semiconductor-type II-VI, ZnO, based have a wurtz crystalline structure.

Titanium dioxide (TiO_2,) has been subject to thorough and diversified research motivated by its value in use. Since 1964 appeared several scientific publications focused on the issue this material [41]. Today TiO_2, is used in more applications and can be considered an almost ideal semiconductor due to its high stability, electrochemical [41], catalytic and good photocatalytic properties [43-44], or because of high dielectric constant. TiO_2, is a wide direct band gap range semiconductor which iseasy obtainable and handling, is non-toxic and less expensive [45]. In unprocessed natural state presents three crystalline forms: anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic) [46].

The union of two semiconductors in a core-shell type structure (core / shell) leads to a semiconductor endowed with unique properties. Type core/shell semiconductor with nano particle size below 100 nm, have been studied a lot by researchers in the field due to the transition from micro to nanoparticles, leading to important changes in physical and chemical properties of a material. The core/shell nanomaterials contain at least two semiconductor materials in a structure of "onion" [87]. The ability to adjust the optical properties of the core semiconductor (such as wavelength fluorescence quantum yield, lifetime), but also aepitaxial type growth of the shell of another semiconductor, have led to a growing number of chemical synthesis, the purpose of these nanomaterialsis to be used in various applications.

This thesis, entitled **Oxides and different configurations of TiO_2 - ZnO based core/shell nanocomposites for the use in solar energetics' applications**, is structuredin two parts. Part I includes Chapters 1-4 and is focused on the theoretical study of semiconductor ZnO, TiO_2 respectively core/shell type semiconductor. Part II comprises chapters 5-9, where personal results are presented as a consequence of obtaining and characterize of these semiconductors, but also their testing in solar energetics.

Chapter 1 provides general considerations on nanomaterials ZnO, TiO_2, namely the core/shell type.

Chapter 2 presents the theoretical description of methods of synthesis and characterization of nanocrystalline powders and core/shell typesystems.

In **Chapter 3** describes methods of deposition and characterization of thin films.

Chapter 4 is dedicated to ZnO, TiO_2, applications, respectively core/shell typesystems. In this chapter are described dye-sensitized solar cells, operation, and components of such cells. Proper functioning of these solar cells is closely related to favorable weather conditions spread of solar radiation or radiation.

To climatological a certain territory is necessary to develop a study on meteorological data over a longer period of time. in Romania, this study can be done using data from the national network of weather stations that fall within the competence of **National Meteorology Administration (ANM).**

Chapter 5 presents their contributions on the synthesis of zinc oxide usingvarious methods such as: precipitation, sol-gel and hydrothermal method. The degree of crystallinity, the morphology, size, optical and electrical properties, the obtained nanomaterials shape were studied by different methods of characterization.

Chapter 6 provides experimental data to obtain nanometricTiO_2, powders by sol-gel and hydrothermal method. It is also presented the influence of heat treatment and precursors on the formation of metastable phases and particle size nanocrystallineTiO_2,

Chapter 7 describes how by two methods of synthesis, precipitation and hydrothermal method, we obtained hetero structures such core/shell which are composed of ZnO and TiO_2, oxide semiconductors with wide band gap (3.37 eV or 3.2 eV). We obtained heterostructure type core/shell ZnO/TiO_2, where ZnO is the core and $TiO_2$is the shell, and heterostructure type core/shell TiO_2,/ZnO, whereTiO_2 is core, and ZnO is the shell.

Chapter 8 presents the results obtained during the testing of nanomaterials prepared and characterized sentence for carrying dye-sensitized solar cells with the semiconductor nanocrystalline powders of ZnO and TiO_2, and heterostructures type core/shell ZnO/TiO_2,TiO_2,/ZnO.

The efficiency of these cells sensitized with the dye is influenced by various factors such as the characteristics of the dye, the time of immersion in the dye, electrolyte, etc. Otherwise in making solar cells we varied as a parameter, and then analyzed the current-voltage curve and thus the efficiency of these cells.

We got better quantum efficiency for solar cells with TiO_2, semiconductor layer to the semiconductor layer of ZnO. This result we attributed to the interaction between the atoms of Zn with the molecules of the dye, when complexes Zn^{+2}/dyeare formed. This reaction led to the formation of inactive molecules which have limited dye electron transport and reduced efficiency of solar cells made.

We achieved higher photocatalytic efficiency for heterostructures type core/shell as semiconductor when the outer layers of material used have band gap larger than that of the inner layer.

Chapter 9 presents general conclusions drawn from the results, while highlighting the original contributions.

The bibliography includes 315 bibliographic references.

Materials and tools used in the characterization and testing of structures with nanoscale dimensions obtained in the thesis

The reactants used for samplessynthesis are:

- $Zn(NO_3)_2*6H_2O$ (zinc nitrate hexahydrate) 99% purity, purchased from Merck
- $Ti\{OCH(CH_3)_2\}_4$ (titanium isopropoxide) of 97% purity, purchased from Sigma-Aldrich

Synthesized powders were characterized by:

- X-ray diffractometer X'Pert Pro MPD type
- Scanning electron microscope type Inspect S
- The transmission electron microscope type Twin Tecnai G2 XT/200 kV
- UV-vis-NIR spectrophotometer type Lambda 950

• Infrared spectrometer withFourier transform type Vertex 70
• Spectroflourimeter type Perkin-Elmer LS 55

Thin films deposition method:

• doctor blade

As electrode in the dye sensitized solar cell was used:

• FTO glass - purchased from Sigma-Aldrich, coated with conductive tin oxide film (SnO_2) doped with fluorine (F), with a thickness of 2 mm, the resistance 7Ω /cm^2 and 80-82% transmission (visible)

The solar cells were sensitized with three organic dyes which costs are reduced:

• C343
• N719
• Ru620

Dye-sensitized solar cell cathode was:

• glass substrate covered with the film of conductive tin oxide doped with fluorine, SnO_2: F (glass slide FTO), on which was deposited platinum by thermal decomposition of a solution of hexachloroplatinic acid (H_2PtCl_6) in burntisopropanol at 450°C for 15 minutes

Liquid electrolyte, the role of mediator, used in making dye-sensitized solar cells:

• iodide-triiodide redox couple (I^-/I_3^-) - solution composed of 0.5 M lithium iodide (LiI), 0.05M molecular iodine (I_2), 5 ml of acetonitrile (CH3CN) and optional 20% polyethylene glycol (PEG).

As a light source of the dye sensitized solar cell was used:

• Xenon arc lamp - the measurement was performed under AM 1.5 illumination, sunlight simulator with a power density of 100 mW/cm^2 applied to an open circuit voltage.

The voltage and current intensity of the dye-sensitized solar cells were made using:

• Multimeter, type *ADCMT 7352E Digital Multimeter,* connected directly to a PC