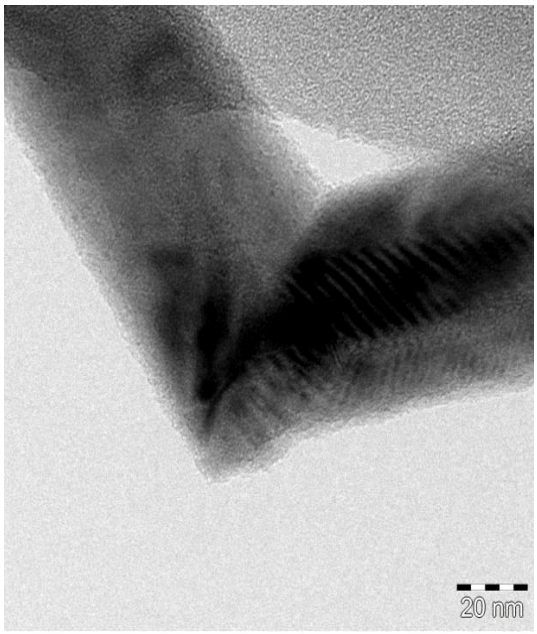
Synthesis, Characterization and Surface Modification of Titanium and Zinc Oxide Nanostructures for Nanotoxicity, Visible Light Emission and Photocatalytic Studies



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Babam Abdullah Mesut Arslan

Annem Serife Arslan

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ve

Yusuf Sami Arslan icin

Abstract

Size dependent quantum confinement and differential characteristics of the anisotropic ZnO and TiO_2 nanomaterials have attracted huge interest in the quest of new functional materials. In order to synthesize ZnO QD's for visible light emission applications, surface modulation for stability in dispersions and defect control at the surface is vitally important. Therefore long alkyl chain group (e.g. oleate) and biological molecule cysteine were used as vectors to regulate reactivity of the ZnO QD's and their visible light emission. Sol-gel chemistry serves as a versatile tool for the fabrication of controlled synthesis of quantum dots and to modify their properties for emission applications such as cell labeling, cell toxicity, solid-state light emission and to understand size/property correlation. High temperature liquid phase synthesis methods, namely heating up and hot injection method were applied toward the synthesis of anisotropic ZnO and TiO_2 nanoparticles. Using different ligand concentrations and reaction conditions, semiconductor nanostructures of unusual geometrical shapes were synthesized and characterized. Hexagonal crystal growing habit of ZnO provided unusual geometrically distorted examples of the hexagonal geometry that have not been reported so far in the literature. Furthermore, TiO_2 nanostructures with significant absorption in visible range of the solar spectrum were obtained by hot injection method and nitrogen doping. The rapid injection and decomposition of Ti-precursor and amine enabled to produce self assembled ball like and multibranched structures with remarkable visible range absorption. Utilization of different concentrations for the precursors provided the possibility of band gap engineering for the anisotropic TiO_2 nanostructures.

Zusammenfassung

Größenabhängige ZnO und TiO_2 anisotroper Nanomaterialien haben ein enormes Interesse bei der Suche nach neuen Funktionalisierten hervorgerufen. Für die Herstellung von ZnO Nanoteilchen „Quantum Dots“ für die Emission sichtbaren Lichts sind Veränderungen der Oberfläche - für die Stabilität in Dispersionen - sowie eine Kontrolle an der Oberflächen vorhandenen Defekte von wesentlicher Bedeutung. Zu diesem Zwecke wurden ZnO Nanopartikeln durch Einbringung von langkettige Alkyl-Gruppen (z. B. Oleate) sowie biologisch relevante Molekülen wie Cystein modifizierte, um die Reaktivität der ZnO „Quantum Dots“ und deren Emission seigen von sichtbarem Licht zu regulieren. Sol-Gel Prozesse dienen dabei als vielseitige Werkzeuge zur gezielten Synthese von Nanoskaligen Materialen und zum Modifizieren der Eigenschaften für die jeweiligen Anwendungen wie zum Beispiel für die Emission wie die Markierung von Zellen, Photokatalysator und UV- Absorber. Hochtemperaturmethoden in flüssiger Phase wie gezieltes Aufheizen und „Hot Injection“ wurden in dieser Arbeit, zur Synthese Kristallbau ZnO und TiO_2 Nanopartikel angewendet. Durch Verwendung unterschiedlicher Ligandenkonzentrationen und Reaktionsbedingungen konnten Halbleiter-Nanostrukturen in ungewöhnlichen geometrischen Formen erzeugt und charakterisiert werden. Die Kontrolle der Kristallwachstumprozesse von ZnO Nanostrukturen ermöglichte es, ungewöhnliche Morphologien zu erzeugen, die bisher in der Literatur noch nicht beschrieben wurden. Des Weiteren wurden TiO_2-Nanostrukturen durch die „Hot injection“-Methode erhalten, die eine signifikante Absorption auf Grund einer N-dotierung in sichbaren Bereich aufweisen. Die äußerst schnelle Injektion und spontane Zersetzung des Ti-haltigen Präkursors in Gegenwart eines Amins erlaubte die Darstellung selbstangeordneter Kugelartiger und verzweigter Standformiger Sternförmiger Strukturen mit bemerkenswerten Absorptionen im Bereich des sichtbaren Lichtes. Das Nutzen unterschiedlicher Präkursor-Konzentrationen ermöglicht den gezielten Aufbau anisotroper TiO_2-Nanostrukturen mit variabler Bandlücken.

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Abbreviations and Symbols

QD	Quantum Dot
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
HR-TEM	High Resolution Electron Microscopy
°C	Degree Celcius
EDX	Energy Dispersive X-Ray Spectroscopy
XRD	X-Ray Diffraction
FT-IR	Fourier Transformed Infra Red
UV –Vis	Ultraviolet- Visible
Raman	Raman Spectroscopy
EPR	Electron Paramagnetic Resonance Spectroscopy
NMR	Nuclear Magnetic Resonance Spectroscopy
DLS	Dynamic Light Scattering
FIB	Focused Ion Beam
PL	Photoluminescence Spectroscopy
μ	Prefix for Micro (1.10-6 m)
AFM	Atomic Force Microscopy
ppm	Parts per million
NP	Nanoparticle
NR	Nanorod
Eg	Band Gap Energy
eqv	equivalent
eV	electron volt
g	Gram
hv	Insident Photon Energy
Θ	Theta (diffraction angle)
h	hour-s
JCPDS	Joint Committee on Powder Diffraction Standards
V_{asym}	Asymmetric stretching mode
V_{sym}	Symmetric stretching mode
Mol	Mol amount
TGA	Thermogravimetric analysis
λ	Wavelength
nm	suffix for nanometer (1.10^{-9} m)

1 Introduction

1.1 Nanomaterials: Opportunities and Challenges

Among various metal oxide structures ZnO and TiO_2 have found wide spread applications due to their structural[1-4], electronic[5-7] and surface properties[8-10]. Generally metal oxide nanomaterials have already begun to effect fundamental characteristics of future materials due to their unique, easy to manipulate and novel performances. Industrial applications of these metal oxides, require established synthesis strategies for scaled up production and detailed investigations of nanoparticles on possible toxicological effects on the living organisms. It is widely experienced that metal oxide nanomaterials, due to nanoparticle anisotropy, quantum confinement effects and surface reactivity need broad attention by an interdisciplinary (the chemical, physical,biological, material science) society. Detailed investigation of these properties, enable the synthesis of programmable nanomaterials which having specific material characteristics like particle size<10 nm, or selectively elongated facets of nanoparticles for better catalytic efficiency[11-12]. Since optical and morphological control leads to control of the light emission or defect oriented new properties, extremely sensitive synthesis methods are required to develop long term stable nanostructures. In addition to that catalytic or photocatalytic properties can be improved by fine control over shape and morphology during the selected synthetic methods. Higher yields for photovoltaic or water splitting features have been already observed for a variety of metal oxide nanostructures[13-14]. On this basis, control of the synthetic methods for anisotropic nanomaterials, real time toxicologic observation of as-synthesized nanomaterial effects on the immune system of the living organisms which related to surface modification and their energy and clean environment applications such as photocatalysis applications have been aimed as main platform for the greener and cleaner energy solutions[15-18].

1.2 Scope

In this thesis the scientific focus was on the liquid phase room and high temperature synthesis of anisotropic ZnO and TiO_2 nanostructures through Hydro-solvothermal (HS), Hot Injection (HI) and Heating Up (HU) methods. A control over nucleation process that can be tuned by controlling the processing conditions (precursor concentration, temperature) as well as by extrinsic factors (addition of surfactants, seeded growth) is expected to deliver reproducible

synthetic materials for controlled synthesis of functional nanomaterials. In this context, the specific objective of this doctoral thesis research were;

i) Synthesis of ZnO, TiO_2 nanostructures by decomposition of different metal-organic precursors (Figure 1) followed by intrinsic encapsulation of as-formed nuclei by suitable ligands to control their shape, band gap and size

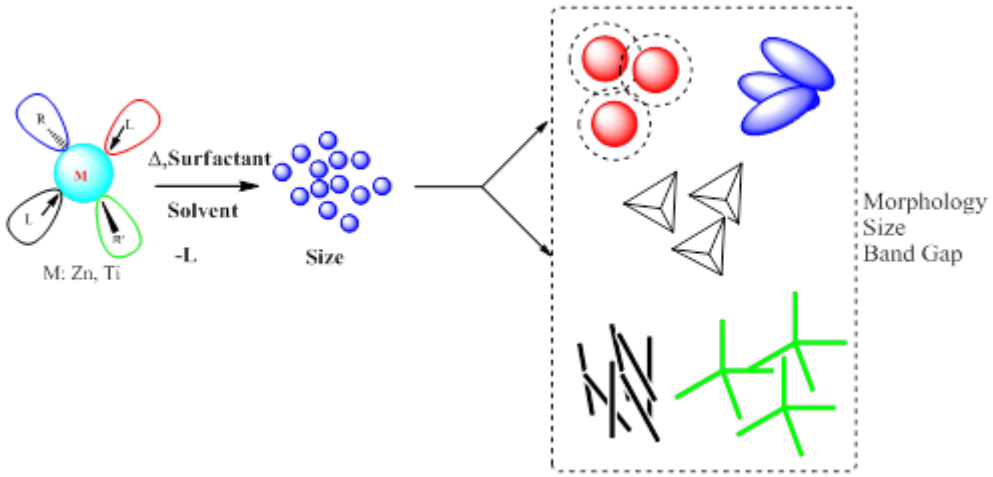

Figure 1 General ZnO and TiO_2 nanostructure synthesis

ii) Development of a library of inorganic-organic core-shell morphologies to produce Ligand@ZnO-TiO_2 nanostructures (Figure 2) with ligand shell and with different surface chemistry for the aim to obtain water dispersable ZnO-TiO_2 nanoparticles required to carry out cell tests and incorporate them into different polymer matrices

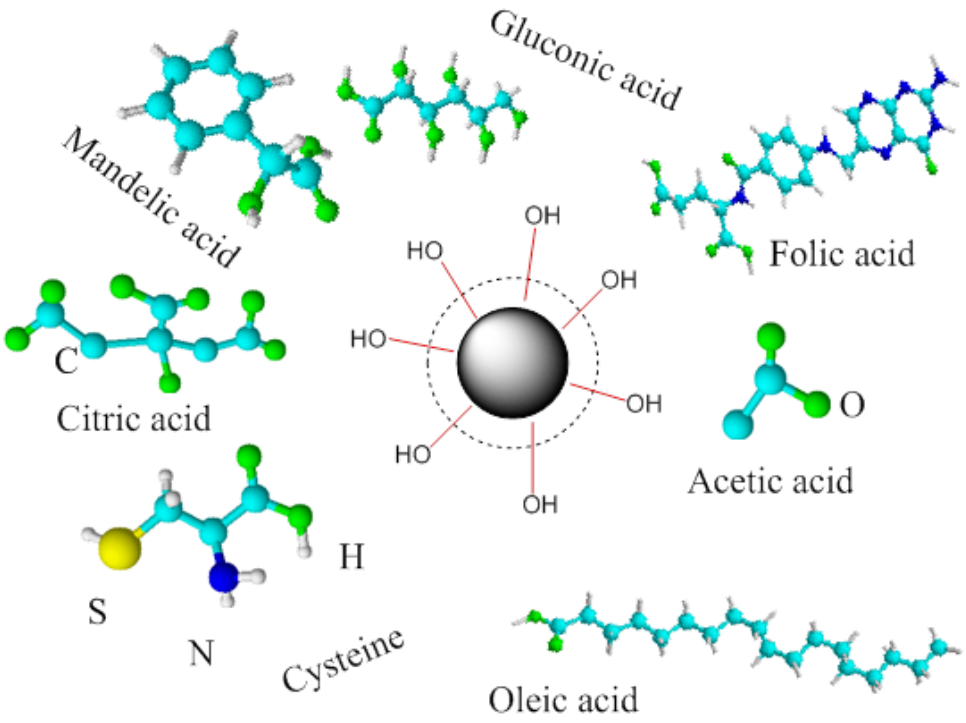

Figure 2 Ligand library for the surface modification and core/shell protection of the nanoparticles.

iii) Phase transfer studies as the ZnO nanoparticles synthesized in organic solvent need to be transferred to aqueous and protic (e.g. alcohol) reagents to undertake evaluation of their functional properties. Within this project it was necessary to investigate the optical (emission) properties, photocatalytic behaviours and cell toxicological influence of the substituted ligands

iv) Incorporation of the ZnO and TiO_2 to various polymer or hybrid structures to synthesize nanocomposites based on the chemical anchoring of metal oxide nanocrystals in polymer matrices by appropriate combination of coupling chemistry. By this anchoring it is aimed to obtain superhydrophilic, broadband antibacterial, selective UV absorptive, blue to red solid state visible light emitting, biodegradable or inorganic organic nanocomposites and modulation of the photocatalytic activity and cytotoxic control have been targeted (Figure 3).

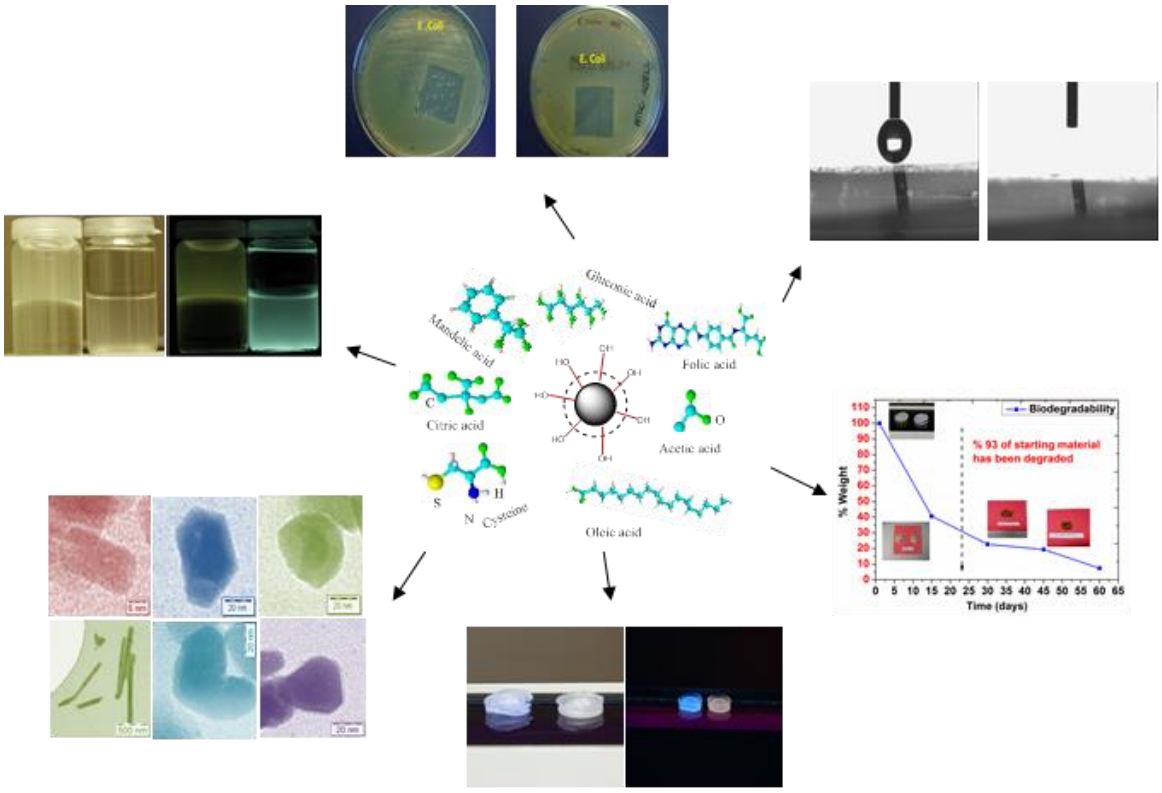

Figure 3 Several applications of ZnO and TiO_2 nanostructures.

v) Multi-morphological nanoparticles of ZnO and TiO_2 by controlling the nucleation and growth environment. Further, the influence of surface capping agents (surfactants) will be investigated to achieve a kinetic control over the evolution of particle databases. It is known that low metal ion concentration and low degree of supersaturation promotes the formation of acicular (needle like) structure that show unique properties due to their single crystalline nature and high aspect ratio.

2 State-of-the-Art: Nanostructure Synthesis

2.1 General Concepts of Nanostructure Fabrication

Controlled synthesis of nanomaterials is achieved basically by two methods which describe their starting point to reach the final form of the nanostructures. Bottom-up method starts from a well designed molecular complex and Top-down uses a miniaturization process to fabricate the nanostructures[19].

2.1.1 Bottom-up and Top-down method

In Top-down approach, macroscopic structure can be miniaturized by applying appropriate etching and/or re-such as lithographic techniques[20], UV light applications[21], e-beam method[22], nano imprinting lithography[23], ball milling[24] and mechanic attrition[2-26]. This method found wide range applications in the commercial manufacturing processes for example electronics and daily life materials (Figure 4)[27-30].

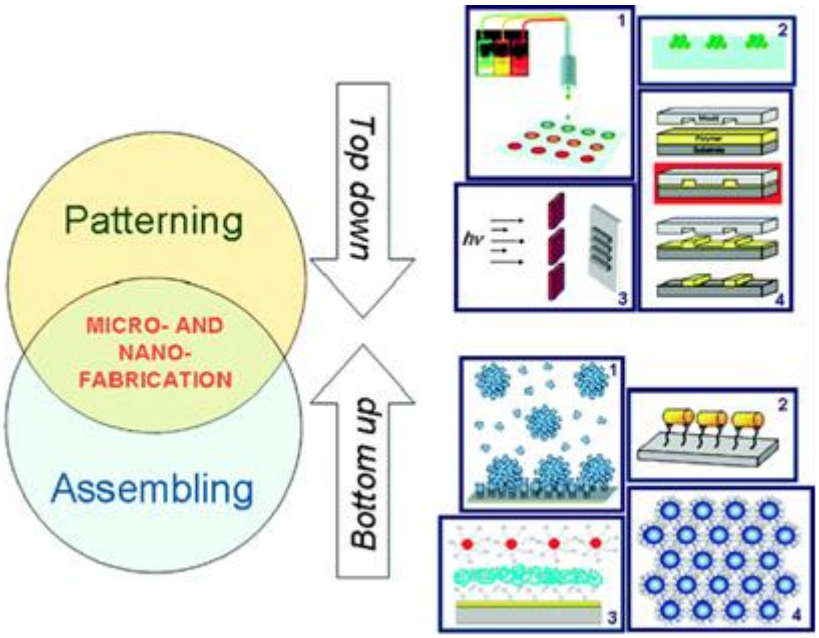

Figure 4 (taken from ref.19) Scheme of complementary "top-down" and "bottom-up" approaches for fabrication of micro- and nano-structures. For the bottom-up strategies: (1) host–guest chemistry, (2) covalent immobilization onto substrate, (3) electrostatic layer-by-layer deposition, (4) self-assembly . For the top-down strategies: (1) ink jet printing, (2) capillary assembly , (3) photolithography , (4) nanoimprinting lithography [1].

On the other hand, bottom-up approach is mostly used in the fabrication of nanostructures which requires atomic precision and well characterized beginning conditions and components such as designed molecular precursors. Several subclasses of this method are present such as supramolecular self-assembly[31], surface directed ordering at interfaces (liquid crystals; LC) [32], Langmuir–Blodgett (LB) synthesis method[33], chemical vapour synthesis[34], liquid phase methods [35-36] (hot injection, microwave), combustion methods[37-38].

2.2 La-Mer theory for the nanoparticle formation: Nucleation and Growth

Solution based production of nanocrystals follow two important steps; a) nucleation and b) growth of the nanocrystals. These processes are widely investigated and formulated.

La Mer and coworkers studied nucleation and growth of sulphur based structures and developed a theory which covers the formation of nanocrystals from homogeneous, supersaturated conditions. According to their mechanism synthesis of the colloid structure should be arranged in a way that the concentration of initial species increases rapidly and rising above the required saturation concentration for a short period of time so that the fast burst of nucleation occurs with the formation of a large number of nuclei in a short time. Particle growth is extremely fast and therefore lower the concentration below the nucleation level slowest step in the growth process.

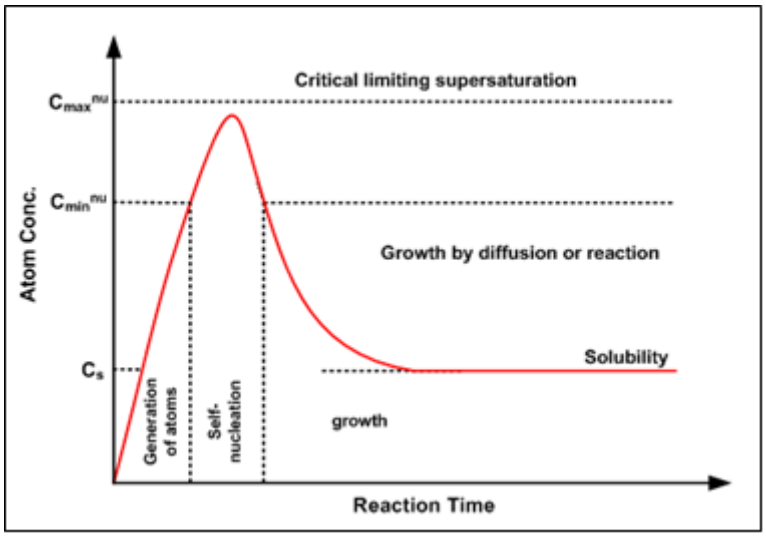

Figure 5 Schematic diagram illustrating La Mer's condition for stable nucleation[39].