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Research Article

Synthesis, Characterization and Application to Catalysis of ZnO Nanocrystals

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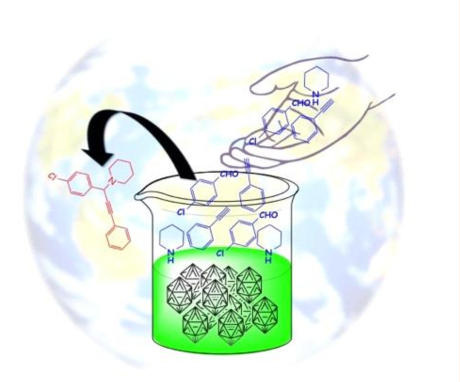
Abstract

Nano-metal oxides gained considerable importance due to their distinct catalytic activities in various organic transformations due to the combination of high surface area and unusually reactive morphologies. ZnO is an important semiconductor material, with a wide range of applications including: pigments, cosmetics, chemical sensors, solar cells and optoelectronics. Additionally, ZnO nanocrystals (NCs) are an eco-friendly, non-toxic, inexpensive and commercially available material, which is starting to be exploited as a potentially economical and highly efficient catalyst for a plethora of organic reactions. Herein, we review fundamentals of ZnO NCs preparation and the recent developments in reactions catalysed by ZnO NCs with special focus on solventless transformations.

Keywords: ZnO, nanocrystals, green chemistry, catalysis, spectroscopy.



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Introduction

The ability to use cheap and stable catalysts in organic synthesis is very important for fine and pharmaceutical chemical industry, which based their production on stoichiometric reactions. However, in order to develop greener and more sustainable production, they must include heterogeneous catalysis in their processes and oxides emerged as one of the most promising options. There is also a growing concern about the influence of organic solvent on the environment as well as on the human body. Although a number of modern solvents, such as ionic liquids and water, are being studied as potential replacements, when possible solventeless reaction is definitely the preferred option because it is generally simpler, cleaner, safer and easier to perform. Thus, there is a growing appetite for catalyzed solventless reactions in fine chemicals and pharmaceutical both from economical and environmental viewpoints.

Metal oxides nanoparticles have an influential role in catalytic organic transformations, especially towards the development of work-ups with as little as possible number of chemical step, as well as to improve effectiveness. Among the most commonly used nano-metal oxides one can highlight: nano-CaO, -TiO_2, -CuO, -ZnO and -MgO. Common characteristics to all of these materials are the low-cost synthesis, high surface area, excellent stability, and efficient recovery. The nanoscale also leads to an increase in catalytic performance due to the growth in the surface free energy.

For example, Kantam and co-workers catalysed the synthesis of organic carbonates with nanocrystalline MgO [1]. They used variety of MgO forms like commercial MgO [CM-MgO], conventionally prepared [NA-MgO], and aerogel-prepared [NAP-MgO]. It has demonstrated that material NAP-MgO, exhibited greater activity and selectivity following 15 min of the experiment of 1-phenylethanol with diethyl. For this sample structure and nature of the reactive centres are responsible for the unexpected catalytic activity. The polyhedral structure allied to high surface reactivity transformed one of the most inert materials known to mankind into a highly reactive catalyst. NAP-MgO proved to be excellent catalyst with all of examined substrates in synthesis of organic carbonates, which were obtained with 100% or nearly 100% selectivity.

ZnO is a semiconductor material, with a wide range of applications including: pigments, cosmetics, chemical sensors, solar cells and optoelectronics [2]. Additionally, ZnO nanocrystals (NCs) is an ecofriendly, non-toxic, inexpensive and commercially available material, which has been extensively studied in the photo-degradation of many organic pollutants, and more recently as a potentially inexpensive and highly efficient catalyst for a plethora of organic reactions, such as Friedel–Crafts acylation, Beckmann rearrangements, synthesis of cyclic ureas from diamines, Biginelli reactions, Hantzsch condensations, Phospha-Michael additions, *N*-formilation of amines, *N*-alkylation of imidazoles, and ring-opening of epoxides [3,4].

Despite the manifold of ZnO catalyzed organic synthesis reactions, the development in the field has been sluggish and restricted to the discovery of new reaction. This is primarily due to the fact that ZnO is an amphoteric material, meaning it gets easily decomposed by both acid and base media. Thus, the application of ZnO NCs, in particular sub-10 nm particles, has not been demonstrated. Secondly, the use of nanoparticles in their natural form, in a continuous flow mode is prohibitive because they cause pressure drops and blockages. Herein, we review the recent developments in the preparation of materials based on sub-10 nm sized ZnO NCs, describe the physical-chemical properties of ZnO, summarize the most promising synthetic routes in which ZnO NCs is being use, and finalize with some comments and future perspectives.

ZnO Physical and Chemical Propertions

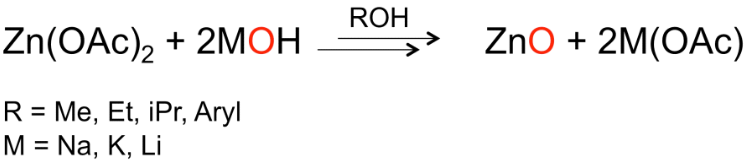
Crystalline ZnO is a thermochromic white powder that changes reversely from white to yellow upon heating. This colour change is caused by oxygen losses from the lattice. ZnO is nearly insoluble in water but soluble in (degraded by) most acids and base (amphoteric oxide). It crystallizes in two main forms hexagonal wurtzite and cubic zinc blende, with the tetrahedral zinc and oxygen centres. For the usually observed wurtzite-type ZnO crystals particular surfaces exist corresponding to lattice planes containing only one type of atoms, either Zn or O. Thus, a ZnO crystal terminated by polar surfaces like the unreconstructed (0001)-surface (Zn^{2+} terminated) and the (0001^{-}) surface (O^{2-} terminated) exhibits a dipole moment along the crystallographic [0001] direction. As with most group II-VI materials, the bonding in ZnO are largely ionic (Zn^{2+}–O^{2-}). This property accounts for the preferential formation of wurtzite rather than zinc blende structure, as well as the strong piezoelectricity of ZnO. Because of the polar Zn-O bonds, zinc and oxygen planes are electrically charged. To maintain electrical neutrality, those planes reconstruct at atomic level in most relative materials, but not in ZnO where its surfaces are atomically flat, stable and exhibit no reconstruction. This anomaly of ZnO is not fully explained yet. Nevertheless, the polar surfaces of ZnO crystal are highly promising templates for use in catalysis and gas sensors owing to the excellent surface/interface properties. The vast number of possible applications of ZnO are based on a set of suitable material parameters: a large direct band gap (~3.3 eV) at room temperature, high absorption coefficient, large exciton binding energy, low cost, low toxicity, and the relatively simple synthesis of different nanoscale morphologies.

ZnO NCs Synthesis and Stabilization

Preparation methods of ZnO NCs

The inherent and unique electronic, optical, and catalytic properties of ZnO NCs are dependent on a variety of factors, including chemical composition, crystallinity, sizedispersion, shape, surface character and surface ligand organization. All these factors are largely determined by the synthetic procedures and therefore much effort has been made to development of new efficient methods for ZnO NCs preparation. While there are manifold of methods leading to micron or submicron sized ZnO NCs, synthesis and stabilization of sub10 nm sized ZnO NCs is particularly challenging. A variety of physical and chemical approaches to ZnO nanomaterials have been developed. The physical methods such as vapourphase oxidation, thermal vapour transport and condensation as well as chemical vapour deposition can lead to ZnO structures of high purity [5]. However they are mostly time and energy consuming and require advanced and expensive equipment. Therefore many efforts have been put into the development of chemical synthetic methods, which not only appear to be cheaper enabling their scale-up but can also provide stable suspensions of ZnO NCs both in organic solvents or water.

The sol-gel method constitutes one of the best choices to obtain ZnO NCs of controlled size and morphology [6]. Generally, this classical inorganic route for the production of ZnO NCs involves the basic hydrolysis of zinc acetate $Zn(OAc)_2$ mediated by an alkaline hydroxide in an alcohol (**Scheme 1**). In this process the solution composition, overall concentration of precursors and temperature has a marked influence on the rate of particle growth and its shape [7].



Scheme 1 Schematic presentation of the ZnO NCs synthesis utilizing zinc acetate

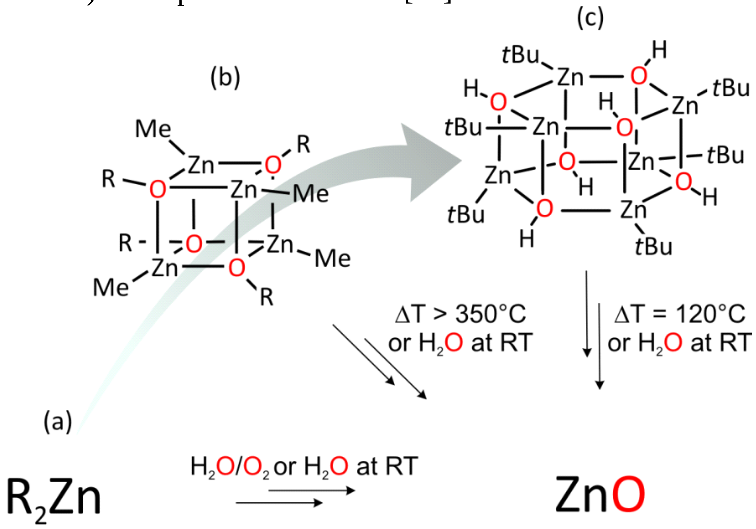
For example, Weller et al. demonstrated that increase of the concentration of substrates by solvent evaporation at room temperature resulted in a particle growth from 3 nm to 5 nm, however without changing the shape of the particles [6c]. The authors also demonstrated that refluxing the concentrated solution for the short time yields rod-like nanoparticles, while the increase in the heating time mainly leads to the significant elongation of the particle along the *c* axis (up to 100 x 15 nm after 24 h). Moreover, the very first stages of ZnO NCs growth can be modulated by the properties of alcohols used as a solvent [8]. For more polar alcohols (ethanol, propanol) the nucleation process is retarded in comparison to that conducted in the presence of longer alkyl chain alcohols (*e.g.*, hexanol). Interestingly, while a variety of zinc salts [$Zn(OAc)_2$, $ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$] can be used as precursors of ZnO NCs, the syntheses utilizing acetate precursor provided NCs with a relatively narrow size distribution probably due to strong ability of carboxylate ligands to stabilize the primary nanoparticles [9].

For sol-gel routes involving inorganic precursors it was found that the resulting ZnO NCs continue to grow after synthesis, even when stored at 0 °C [6b]. Therefore this procedure requires usually the presence of a surfactant, to modulate their growth and solubility. A variety of long chain capping ligands (*i.e.* dodecylamine, trioctylphosphine oxide (TOPO), dodecanethiol, oleic acid or polymers where utilized in order to provide the better stability of ZnO NCs and enabling their purification and/or transfer from parent post-reaction mixtures to other chemical environments. These types of ligands influence also the size, shape and luminescent properties of synthesized NCs. Notably, it is expected that the proper passivation of ZnO NCs surface can provide their increased stability towards acidic species. For example, the reaction system involving $Zn(NO_3)_2$, diethanolamine and oleic acid yield stable blue luminescent ZnO NCs [10]. Despite the fact that synthetic methods based on inorganic salts are convenient, relatively cheap and can lead to nanomaterials with controlled morphology, the usage of ionic species (*i.e.* solvent and metal hydroxides) may modify the chemical and/or physical properties of the final material and requires relatively high temperatures.

An alternative to the above described inorganic routes, the organometallic approach make use of high reactivity of organozinc precursors of the type R_2Zn toward oxygen and/or water as the oxygen sources and enables processing in ambient conditions in aprotic solvents [11]. A controlled hydrolysis and/or oxidation of a precursor, which contains Zn-C bonds, in a solution lead to ZnO nanoparticles. The formation of NCs may be controlled kinetically by changing parameters of the system (i.e. type of organometallic precursor, ligands or surfactants, solvent etc.). The elegant studies of Chaudret et al. demonstrated that the exposition of R_2Zn precursor in a donor solvent toward air at room temperature afforded crystalline ZnO nanoparticles of controlled size and shape (**Scheme 2a**) [12]. The authors showed that the exposure of a mixture of dicyclohexylzinc $(cC_6H_{11})_2Zn$ and a long chain amine as surfactant to air can lead to stable suspensions of spherical, disk or rod shaped ZnO NCs, which exhibited yellow luminescence [12]. It was found that the experiments performed in donor solvents led to the formation of anisotropic nanoparticles, while the usage of toluene or hexane produced more likely isotropic forms of ZnO NCs [12b]. For these systems the introduction of water is crucial for the formation of ZnO NCs in the room temperature. These observations are in line with the results for the anhydrous Et_2Zn/O_2 system, which required relatively high temperatures (~200°C) to the ZnO

NCs formation [13]. Only recently, this strategy was nicely developed by employment of mixtures of Et_2Zn and a zinc dicarboxylates $Zn(O_2CR)_2$ in various molar ratios in toluene which led to ZnO NCs via direct exposure to water vapour or by addition of hydrous acetone [14]. According to the recent studies of Lewiński and co-workers on reactivity of R_2Zn type compounds toward oxygen [15], it is reasonable to assume that in the described reaction system the ZnO NCs are rather the result of hydrolysis of both parent ZnR species and incipient ZnOR species resulting from the Zn-C bond oxygenation.

More advance organozinc precursors for nanoscaled ZnO materials consist of molecular building blocks that contain in the structure zinc and oxygen ions in the correct ratio and are known as *Single Source Precursors*. Amongst them, alkylzinc alkoxides (RZnOR′) with heterocubane structure have received the most attention (**Scheme 2b**), and their ′Zn_4O_4′ heterocubane core has been regarded as a ‘preorganized ZnO’. These alkoxides have been found to yield ZnO either by controlled thermolysis under diverse atmospheric conditions [16] or by reaction with water [17]. While the transformations of ′Zn_4O_4′ alkyl-Zn-alkoxides may yield ZnO NCs of controlled oxygen vacancy, the semiconducting materials obtained by this way are particularly interesting as model systems for investigations on catalytic properties of ZnO nanophases. For example, the temperature treatment (over 250°C) of the crystalline samples of $[MeZnO\textit{i}Pr]_4$ and $[MeZnO\textit{t}Bu]_4$ with various heating rates led to aggregates of nanoparticulate ZnO containing different amounts of oxygen vacancies [16b]. The resultant materials exhibited catalytic activity proved in the synthesis of methanol from CO and H_2. The $[EtZnO\textit{i}Pr]_4$ was also successfully used for the synthesis of ZnO NCs colloids upon heating (up to160°C) in the presence of TOPO [18].



Scheme 2 Development of ZnO organometallic precursors: (a) dialkylzinc compounds, (b) alkylzinc alcoxides, (c) the representative of alkylzinc hydroxide

As for R_2Zn type precursors, the introduction of H_2O to the reaction systems containing [RZnOR'] enabling syntheses of ZnO NCs in ambient temperatures (**Scheme 2b**). The application of a variety of aprotic solvent and surfactants as well as the proper post-synthetic treatment of obtained materials led to the variety of interesting materials based on ZnO nanostructures. For example, the controlled hydrolysis of [RZnOR'] compounds in the emulsion system water-in-oil enables control of the anisotropic growth of ZnO nanoparticles leading to the material of controlled morphology and electronic properties [17d]

Notably, while the thermal decomposition of these type of precursors in the solid state lead to the aggregates of the dense structure, the hydrolytic pathway can lead to aerogels with high surface areas up to 200 m^2g^{-1} [17c,e]. Furthermore the controlled hydrolysis of [RZnOR'] precursors can also lead to metastable long overlooked or even unknown phases of ZnO [17b]. Notably, the synthetic methods providing semiconducting materials with high surface areas and/or unique phases are especially beneficial for applications in catalysis and energy conversion [19].

Another idea to make a profit on the interaction of R_2Zn precursors with water was only very recently developed by Lewiński and co-workers. The authors provided a new family of well-defined precursors, which contain in their molecular structure hydroxide ligands derived from water molecules present in the reaction systems. For example, the direct hydrolysis of $t\mathrm{Bu_2Zn}$ lead to the formation of zinc hydroxide species which crystallize as a drum-like hexamer $[t\mathrm{BuZnOH}]_6$ [20]. As such the $[t\mathrm{BuZnOH}]_6$ can be employed as an excellent example of predesigned ZnO NCs precursor that decomposes smoothly in one step at only 120°C with the formation of wurtzite-ZnO NCs with average size of 5 nm and no carbon impurities (Scheme 2c). The authors argued that such low decomposition temperature of $[t\mathrm{BuZnOH}]_6$ can be rationalized in terms of the presence in the structure of ZnOH groups which can hydrolyze proton-reactive ZnC bonds with a concomitant evolution of an alkane. Further studies confirmed crucial role of ZnOH species in the design of organozinc precursors of ZnO nanoparticles. The investigations showed that the decomposition temperature of mixed alkoxyzinc hydroxides $[(t\mathrm{Bu})_4\mathrm{Zn}_4(\mu_3\mathrm{O}t\mathrm{Bu})_x(\mu_3\mathrm{OH})_{4-x}]$ decreases in conjunction with increasing amount of hydroxyl groups in molecular structure of used precursors [21]. Thus, the Zn-OH groups appear to be desirable feature that lowers the decomposition temperature of reported ZnO NCs precursors in a significant degree. Notably, the latter compounds can be regarded as very attractive hybrid precursor systems consisting of two types of ligands. It is expected that their decomposition can lead *via* various pathways generating a variety structural and electron effects which can be potentially employed for catalytic and photovoltaic applications.

Strategies for solubilisation of ZnO NCs in water

There is a growing demand for new ZnO-nanocatalysts of reactions carried out in water. However, most reports regarding ZnO NCs synthesis provided solutions for ZnO NCs soluble in organic solvents and only few studies were focused on the preparation methods leading to water-stable ZnO NCs.

A common strategy that provides water-solubility to these systems consists in the displacement of the original hydrophobic ligands by the hydrophilic ones [22]. An interesting methodology for surface-functionalization and stabilization of ZnO NCs in aqueous media is based on organosilanes chemistry [23]. For example, the efficient transfer of oleate-capped ZnO NCs to water was achieved through surface functionalization with PEG-siloxane [23b]. In the case of ZnO such strong modification of the NCs surface often results in the alternation of the surface oxygen vacancy state, which may modify their catalytic activity and optical properties.

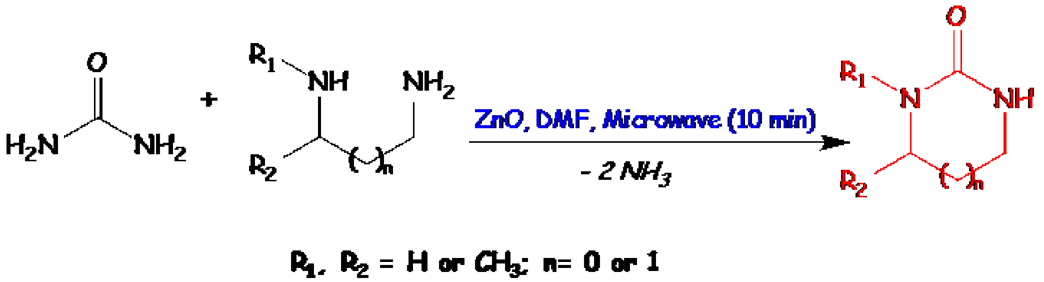
An alternative strategy involves the formation of interdigitated layers of amphiphilic polymers or surfactants. For example, Kahn et al. presented transfer of hydrophobic ZnO NCs (24 nm) to water by encapsulation in ammonium surfactants bilayer with the process efficiency over 60% [24]. In the presented method hydrophilic ligand does not directly interact with the nanocrystal surface preventing quenching of ZnO surface defects. The same group demonstrated synthesis of well-defined nanocrystalline ZnO using organometallic reagents in combination with (amino)-PEG ligands that can be readily dispersed in water as well as in many other polar and non-polar solvents [25]. The described approach enabled the control over the particle size and shape by varying the experimental conditions. Another interesting approach concerns one-pot synthesis of water stable ZnO NCs without introduction of an additional surfactant. In this case, the reaction between zinc stearate (metal precursor) and triethylene glycol (used as a solvent) afford water soluble ZnO NCs with size distribution ranging from 2 to 9 nm stabilized by an ester compound [26].

Aiming at expanding greener organic catalysis, early steps have been made in preparation of water stable sub-10 nm ZnO materials. Therefore, much attention should be paid to the search on new synthetic methods leading to defined water-soluble ZnO NCs and investigation on the organization of molecules (i.e. ligands, surfactants, and solvents) interacting with NCs surface. The latter factors can have strong impact on the surface oxygen vacancy states of ZnO NCs, which vary their photophysical and catalytic properties.

Reactions Catalysed by ZnO NCs

In recent years, ZnO proved to be one of the most useful and multifunctional metal oxides employed as catalyst. ZnO has a wide range of applications in very important organic synthesis such as Knovenagel condensation, synthesis of N-acylosulfoamides and sulfonate esters, Friedel-Crafts acylation, N-formylation of amines, formation of cyclic ureas, preparation of tetrazoles or synthesis of coupling of propargylamines. ZnO has proven to be a good alternative to often-complicated reactions schemes requiring harsh reaction conditions.

ZnO was used as catalyst in the microwave synthesis of cyclic ureas from diamines [27], depicted in **Scheme 3**. Utilization of ZnO resulted in a reduction of reaction temperature and time, and significant increase in product selectivity. This method proved to be an effective replacement to the conventional synthesis, in which very harmful phosgene (applied during the Second World War as a toxic gas, highly suffocating and poisonous, which small of fumes caused the death) or oxidative carbonylation of diamines (dangerous caused by the possibility of explosion) were used, i.e., the reaction become significantly greener by the simple addition of ZnO.

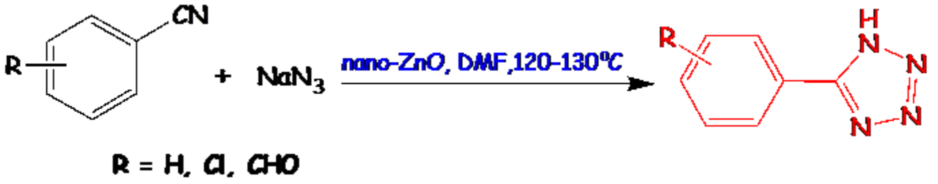


Scheme 3 Scheme for the synthesis of imidazoline-one

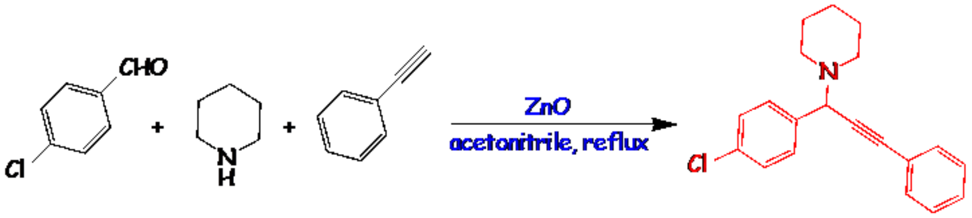
Kantam and co-workers [28] synthesized another class of very important compounds, namely the 5-substituted 1H-tetrazoles. These compounds are widely used in agriculture, biology, medicine, pharmacy, explosives as well as precursors of the various nitrogen-containing heterocyclic compounds such as imidoyl azides. The cycloaddition of an azide with nitrile to obtain 5-substituted 1*H*-tetrazoles dates back to 1901 [29]. Kantam et al. [28] reaction is depicted in **Scheme 4**. They used nano-ZnO as catalyst, nitrile and NaN_3, as reagents (with NaN_3 in slight excess) at 120-130°C, and a variety of solvents (water, DMSO, DMF, NMP, [bmim][BF_4]) and other forms of Zn catalyst (ZnO commercial, $Zn(acac)_2$, ZnBr) but the best yields were obtained when ZnO NCs and DMF or NMP were used as catalyst and solvent, respectively. In these conditions, they obtained 5-phenylotetrazol at a yield of 70-72%. Nano-ZnO material was found easy to recover and reuse. The reaction could also be carried out with heterocyclic structures.

There is a growing demand for solventless reactions in order to reduce the amount of organic waste, protect the environment, and decrease costs. Satyanarayana et al. [30] tested ZnO NCs in organic synthesis of propargylamines. Propargylamine are synthetic intermediates for the synthesis of biologically active of chemicals: β-lactams, conformationally constrained peptides, isosteres. Generally propargylamine are derived from the amination of propargylic halides, propargylic phosphates as well as propargylic triflates. The coupling reactions proposed by Satyanarayana et al. were conducted in one-pot containing the alkyne, amine and aldehyde at 90 °C. When they use nano-ZnO (produced by deposition method) they obtained 91% yield and short reaction time (4h). Differences in the results were explained on the basis of morphology and concentration of the active centers on the surface, i.e., surface area. The catalyst could be recovered by centrifugation and re-used (total 10 times), without significant decrease in activity.

Kantam et al. [31] also prepared propargylamines with ZnO-based materials in acetonitrile (**Scheme 5**). The reaction yield was 25% with commercial ZnO, which increased to 52% when ZnO NCs was used instead. It should be mentioned that the best yields were obtained with Zn dust ca. 95%.



Scheme 4 ZnO NCs mediated preparation of 5-substituted 1*H*-tretazoles



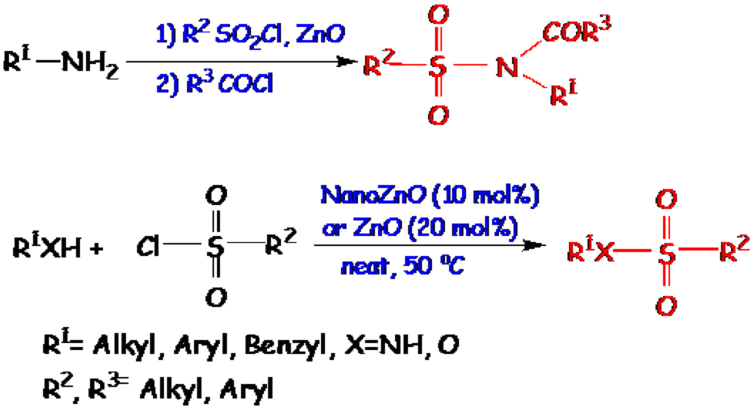
Scheme 5 Synthesis of *N*-[1-(4-chlorophenyl)-3-phenyl-2-propynyl]-piperidine via reaction of 4-chlorobenzaldehyde, piperidine, and phenylacetylene in solvent under reflux

Numbers of researchers have used various forms of ZnO NCs in organic transformation known as Knoevenagel condensation. This is a very simple reaction scheme between carbonyl compounds (aldehydes, malonic acid esters), which yields *α,β*-unsaturated, used in the chemical, pharmaceutical and perfumery industry. Commonly, Knoevenagel condensation catalysed reactions use a base such as piperydine, pyridine, ammonia amines or their salts, in solvent in order to achieve the desired products.

Suresh and Sandhu [32] used ZnO-nanobelts in the preparation of compounds such as 5-arylidine-2,4-thiazolidinediones and 5-arylidine-rhodanines. They synthesized ZnO-nanobelts by chemical precipitation method using zinc acetate and pure ethanol. ZnO NCs was tested in the important Knoevenagel transformation of 4-metoxybenzaldehyde and 2,4-thiazlidinedione with various amount of catalyst, and plurality of carbonyl compounds under solvent-free conditions at 90° C. It was found that catalyst amount played a role reaction effectiveness reaction. High yields (> 90%) were obtained with all the tested reagents at optimal conditions within a few minutes. ZnO-nanobelts prevented the formation of by-products in this solventless reaction. Furthermore the catalyst could be recycled and reused repeatedly, without loss in performance.

Knoevenagel synthesis catalysed by ZnO nanoparticles could yield also coumarins [33]. For this purpose 2-hydroxy aldehydes and various β-dicarbonyl compounds (1:1.25 molar ratio) were used in the presence of 10 mol % ZnO NCs. Reaction was carried out under microwave irradiation or under thermal conditions. These simplified and fast methods gave the desired product in very good yields. As with the previous case, the catalyst was able to recover and reuse with successfully.

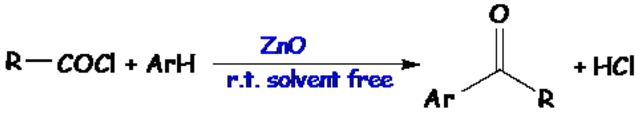
ZnO is also active in the formation of other compounds, such as N-acylosulfonamides and sulfonate esters (**Scheme 6**) [34]. These one-pot syntheses avoid the use of aggressive reagents, and formation of undesirable reaction products. The authors tested two types of prepared ZnO (I type with particle size about 37-47 nm and type II with particle size of 30 nm) and compared the results with commercial ZnO. All tested catalysts were found to be chemoselective. Curiously, the ZnO NCs type I containing the larger particle size yielded the most product in the reaction of $PhSO_2NH_2$ with AcCl. This was related with preferable dispersion of the catalyst in reaction mixture but it demonstrates that not always '*smaller is the best*'.



Scheme 6 Sulfonylation and acylation with ZnO catalyst

Friedel- Crafts acylation plays an important role in organic synthesis, and is often carried out between an aromatic or heterocyclic compound and acylating agent such as acid chloride. To the best of our knowledge, the there is only one published result on the use ZnO in the Friedel-Crafts acylation reaction [35]. They used a simple work-up procedure with just two substrates, and ZnO powder at room temperature. Most of the examined reactions finished within 5-10 min. Interestingly, the reaction occurs only in acid chloride or hydrogen chloride but not in anhydride acid.

Recently, we tested novel ZnO NCs systems in Friedel- Crafts acylation (**Scheme 7**). Only sub-10 nm particles were found active, however the catalyst suffers severe deactivation due to the formation of HCl, an avoidable by-product of Friedel- Crafts acylation. We are currently working on stabilization procedures to enable their application in the future.



Scheme 7 Friedel- Crafts acylation catalyzed by ZnO

Spectroscopy

There is a plethora of spectroscopic methods to determine physical and chemical properties of ZnO NCs, such as Raman, X-ray diffraction, X-ray photoelectron spectroscopy, electron microscopy, electrochemistry methods, to name only a few. However, in this section we would like to highlight emerging methods that can be used to determine the desired properties during material synthesis and catalysis.

The first method is photo-in photon-out X-ray spectroscopy, often carried out at large facilities due to demands for high flux beams. This spectroscopy determines the complete electronic structure with element specificity because X-ray beam is tuned to a specific atom electronic transition. One can carry out the spectroscopy in static or time-resolved mode, depending on the required information. When measurements are carried out around Zn K-edge, true in situ studies can to be carried out due to the large penetration depth of the probe beam [36].

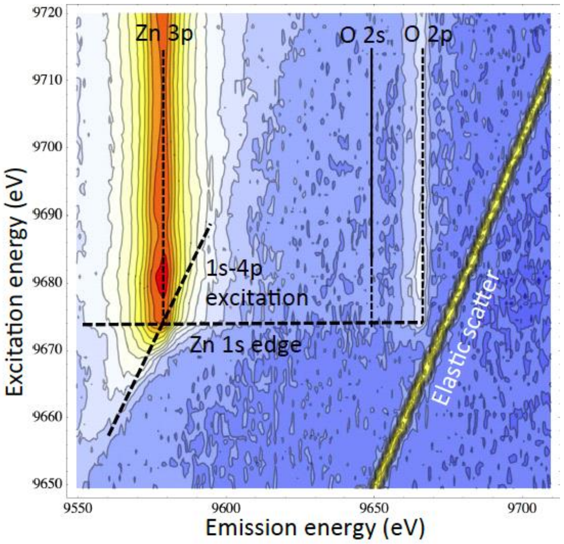


Figure 1 RXES map of ZnO NCs

Sá and Szlachetko demonstrated that resonant X-ray emission spectroscopy (RXES) measurements could determine accurately the electronic of a variety of semiconductors in a variety of morphologies (powders, thin films, single crystal, etc) [37]. **Figure 1** shows the RXES map of ZnO NCs measured at Zn K-edge. There are several parameters that can be extracted from the RXES. We can extract information about occupied electronic states, which corresponds in semiconductor nomenclature to valence band from the nonresonant X-ray emission spectroscopy

(XES) spectrum. The second parameter that can be extracted is the material's unoccupied electronic states or conduction band stricture from X-ray absorption spectroscopy (XAS) spectrum. **Figure 2** shows the XAS and XES spectra extracted from RXES maps for ZnO NCs and Zn metal. Figure 2 reveals no gap XAS and XES signals for Zn metal, which is evident in the ZnO NCs. The gap relates to the direct band gap of ZnO, which is always slightly overestimated because of element scattering contribution. Theoretical calculations of the signals shows that ZnO valence band is composed primarily of O 2p electrons while the conduction band are composed of Zn 4s electronic states.

It is known that ZnO particle size has a direct influence in position of valence and conduction band, i.e., band gap. ZnO band gap increases with the decrease of particle size [38]. Thus, by following in situ the changes on XAS and XES spectra one can determine particle size during material synthesis and/or catalysis. Furthermore, when using sub-10 nm ZnO, the surface contributes largely to the measured signal, which can be used to monitor molecules adsorption and catalytic reactions.

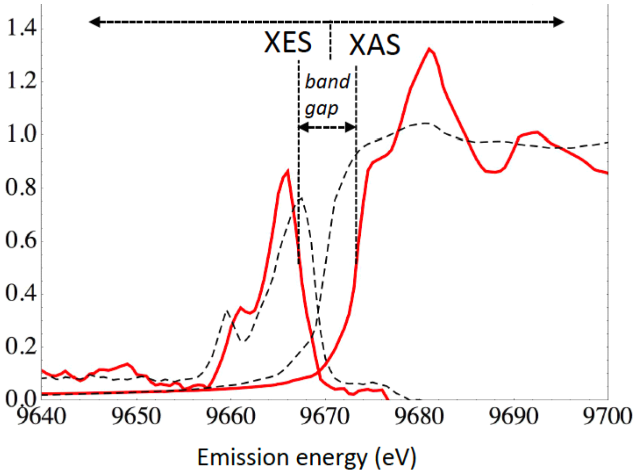


Figure 2 Comparison of XAS and XES signals extracted from RXES map for ZnO (red line) and Zn metal (dashed black line)

Time-resolved fluorescence spectroscopy has been widely used to monitor charge recombination upon band gap excitation. This is of particular importance to the fields of photo-voltaics and photo-catalysis, which is out of the scope of this tutorial review. However, recently Jacobsson et al. [39] demonstrated that UV fluorescence signal upon band gap excitation relates to surface excitons, i.e., oxygen vacancies in ZnO surface. Thus, the signal can be used to monitor adsorption of molecules on nano-ZnO in particular for sub-10 mn size with unprecedented time resolution and chemical speciation.

Interaction of nanoparticles with reactants and solvent is very important in catalysis, in particular for solventless reactions, where reagents also act as solvents. Since reagents adsorption geometry and strength affects the overall catalytic performance, it is important to gather information about these parameters during reaction. As aforementioned, RXES can provide information on what happens in the catalyst electronic structure during molecules adsorption and catalytic reaction but it is equality important to determine what happens at the nanoparticle solvent/reagent interface and beyond. Zobel et al. [40] used X-ray scattering spectroscopy to determine solvent structure around bare and surface modified ZnO NCs. They found that layers of enhanced order existed with a thickness influenced by the size of the molecule-adsorbed and up to 2 nm beyond the nanoparticle surface. These results show that the enhanced reactivity of solvated nanoparticles must include a contribution from a solvation shell.

Comments and future perspectives

Nano-ZnO promises to be an important player in organic synthesis in the nearest future. This was stimulated by the recent demand for greener possesses in this area and the development of synthetic procedures capable of preparing stable ZnO with sub-10 nm size. Additionally, the recent progresses in spectroscopic methods will help massively the development of this area. These new methods provide clues on what happens in, on and beyond the catalytic surface with unprecedented resolution and accuracy.

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