ZnO-BASED NANOMATERIALS FOR ORGANIC POLLUTANTS REMOVAL FROM WASTEWATER

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ABSTRACT. This paper presents a comprehensive literature overview on synthesis, morphology and properties of ZnO nanoparticles, metal-doped ZnO nanomaterials and ZnO-supported zeolite nanocomposites and their application for organic pollutants removal from wastewater. ZnO is among semiconductor photocatalysts widely explored and used for treatment of harmful contaminants in wastewater, due to its low toxicity, reasonable price, facile synthesis and tunable morphologies. However, some drawbacks arise from its wide band gap and fast recombination rate of photogenerated electron/hole pairs, which might be overcome by synthesis of ZnO doped with metals. Such materials demonstrate enhanced photocatalytic activity in comparison with pure ZnO. The relatively poor adsorption capability of ZnO and difficulties in recovering and recycling of nanoparticles provoke the development of nanocomposites of semiconductor nanoparticles supported on zeolites and other substrates. Thus, the adsorption ability and selectivity of nanomaterials ZnO-zeolite for dyes and toxic metals elimination are also discussed.

Keywords: ZnO, ZnO-based nanocomposites, zeolites, photocatalytic activity, adsorption capability.

НАНОМАТЕРИАЛИ НА ОСНОВАТА НА ZnO ЗА ОТСТРАНЯВАНЕ НА ОРГАНИЧНИ ЗАМЪРСИТЕЛИ ОТ ОТПАДЪЧНИ ВОДИ

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РЕЗЮМЕ. В тази статия е представен литературен обзор върху синтеза, морфологията и свойствата на наночастици от ZnO, ZnO дотиран с метали и нанокомпозити ZnO-зеолити, и тяхното приложение за отстраняване на органични замърсители от отпадъчни води. ZnO е полупроводник и фотокатализатор, който е широко изследван и използван за третиране на опасни вещества в отпадъчни води, поради неговата ниска токсичност и цена, лесен синтез и промяна на морфологията на материала. Обаче, от неговата широка забранена зона и бързата рекомбинация на фотогенерираната двойка електрон/дупка възникват определени недостатъци при използването му, които могат да се преодолеят чрез синтез на ZnO, дотиран с различни метали. Такива материали показват по-висока фотокаталитична активност в сравнение с чистия ZnO. Относително слабата адсорбционна способност на ZnO и трудностите при отделянето и рециклирането на наночастиците пораждат интерес към разработването на нанокомпозити от полупроводникови наночастици, нанесени върху зеолити и други подложки. Ето защо, адсорбцията и селективното задържане на багрила и токсични метали от нанокомпозити ZnO-зеолит са също дискутирани в статията.

Ключови думи: ZnO, нанокомпозити, зеолити, фотокаталитична активност, адсорбционна способност.

Introduction

The implementation of nano-sized materials in the past years has gained a tremendous popularity in many aspects of modern technology – electronics (Liu et al., 2015), medicine and life sciences (Mirzaei et al., 2017), environmental protection (Hoffmann et al., 1995) and sustainability (Oskoei et al., 2016). The list of different materials (metals, metal oxides, sulfides, carbides, etc.) in nanoscale that has been applied as photovoltaics (Aissat et al, 2015), dyes for bioimaging and target drug delivery as well as photocatalysts, is really long and constantly increasing. The used nanomaterials vary in composition depending on the intended application – polymer, metal, oxides and halides. Special interest has been paid to semiconductor metal oxides nanoparticles and their use in the environmental protection and water treatment (Zhang et al, 2012; Lee et al., 2016). The ever increasing demand for fresh drinking water is an issue worldwide. The most affected areas are countries with limited supply of natural water resources like Africa and Arabian Peninsula. The applications of cost effective methods at large scale for water treatment are most desired and widely investigated. In this aspect, as a promising candidate appears the method of photocatalysis, which is based on photo-induced generation of electron-hole pair in the semiconductor nanoparticles and formation of strong oxidizing species that are able to oxidize and decompose organic pollutants in the wastewater. The potential of photocatalysts depends on the type of semiconductor, particle's size, surface area and morphology of material, pH of the media as well as the characteristics (wavelength, intensity) of the light source used for irradiation.

In order to be applied in practice the photocatalytic material should be efficient, cost effective and environmentally friendly. One of the preferred choice for photocatalyst is ZnO. It is cheap and non-hazardous material which is very efficient in degradation of organic contaminants under UV radiation (Moezzi et al., 2012; Kolodziejczak-Radzimska et al., 2014).

Here we present a review on different methods for synthesis of ZnO nanoparticles, metal-doped ZnO nanomaterials and ZnO-supported zeolite nanocomposites, their morphology, properties and applications for organic pollutants removal from wastewater.

ZnO nanoparticles

ZnO is n-type II–VI semiconductor material with band gap of 3.37 eV and high exciton binding energy (60meV). Nanosized ZnO materials has gained popularity in the recent years due to their versatile use in different areas like biomedicine (Steffy et al., 2018; Zhu et al., 2020), environmental protection (Daneshvar et al., 2007), cosmetics, optics and electronic.

ZnO nanoparticles (ZnO NPs) are very promising candidates for large scale application purposes because they are inexpensive to manifacture, non-hazardous and easily synthesized. One of their advantages is that they have been categorized by the U.S. Food and Drug Administration (FDA) as GRAS (generally recognized as safe) metal oxide nanoparticles (21CFR182.8991).

ZnO NPs raise particular interest as a photocatalyst and antibacterial agent since nanoparticles have suitable band gap width for UV light excitation and a large surface area due to the small size of the nanoparticles, which strongly depend on the synthesis method (Ahmed et al., 2017; Kumar et al., 2019). It is reported that ZnO NPs have been applied for disposal of Gram-positive (Bacillus megaterium, Bacillus pumilus and Bacillus cereus) and Gram-negative (Escherichia coli) bacteria resistant to all other type of eradication techniques (Nagajyothi et al., 2014).

Major impact on the efficiency of ZnO NPs as a photocatalyst has their size, shape and surface morphology, which makes the method for their synthesis very important. The ability to tune and control NPs properties by controlling their size and shapes is of great importance when method for preparation is developed. (Basnet et al., 2020).

A different shapes of ZnO NPs have different morphologies like nanoflake, nanoflower, nanobelt, nanorod and nanowire (Ong et al., 2018). The methods for their preparation can be summarized in two major divisions – chemical and biological. The chemical methods usually involve a controlled precipitation of zinc salt while biological methods are based on the use of plant extracts (from different parts such as leaves, roots, rhizomes, bark, fruits, flowers) and microbes (Basnet et al., 2018).

The so-called wet chemical methods include hydrothermal, sol-gel, precipitation, microemulsion, solvothermal, electrochemical deposition process, which are among most popular approaches. The precipitation methods developed for preparation of ZnO NPs in solution use zinc salts like $Zn(NO_3)_2$, $ZnCl_2$, $Zn(CH_3COO)_2$, $Zn(C_2O_4)$ and precipitation agents like NH_4OH, NaOH and KOH for formation of $ZnO/Zn(OH)_2$, followed by further annealing at high temperature in order to improve the crystallinity of the ZnO NPs. At such conditions a wurtzite hexagonal structure is often formed. A capping agent can be added to improve the control over the size and shape of the obtained ZnO NPs.

The precipitation method is very attractive because it is cost effective, uses non-toxic solvent (as water), allows good control over the obtained NPs during the precipitation. The addition of surfactants with various structures, for example sodium dodecyl sulphate (SDS) (Juabrum et al., 2019) and cetyl trimethyl ammonium bromide (CTAB) (Sun et al., 2003), amino acids (Wu et al., 2008), polymers (polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) (Tachikawa et al., 2011; Vidyasagar et al., 2016) and polysaccharides (starch) (Vidhya et al., 2015), would not only restrict the NP size but also would prevent aggregation of the obtained NPs and would stabilize them in the dispersion (Vijayakumar et al., 2020). That's why the synthesis of NPs is often carried out in the presence of surfactants in the reaction media.

ZnO nanoparticles have a lot of applications that were listed above but two of them attract our interest – their photocatalytic and antibacterial activity. ZnO is very effective photocatalyst used in treatment of water and degradation of model organic compounds (dyes) like methylene blue, reactive black, congo red as well as some pharmaceutical and agricultural pollutants like furosemide, glyphosate-based herbicide, tartrazine, diclofenac and others.

Páez et al. (2019) have reported removal of a glyphosate-based herbicide from water using ZnO nanoparticles. They have applied a method of controlled precipitation where acidified water solution of zinc acetate $Zn(CH_3COO)_2$ as Zn precursor and ammonium hydroxide (NH_4OH) as precipitant were mixed at room temperature and constant stirring. This method resulted in ZnO NPs with uniform particle size (<100 nm), spheroidal morphology and formed soft agglomerates with well-defined wurtzite structure. The material was successfully tested for removal of the herbicide glyphosate (Monsanto herbicide Roundup 747 SG) without UV irradiation. The decrease in herbicide concentration was monitored by using UV–Vis absorption spectroscopy. Removal from 70% to 90% was calculated depending on the ratio glyphosate to ZnO NPs in herbicide solution, indicating the nanomaterial as very effective sorbent. The equation for removal of glyphosate by ZnO NPs followed kinetics of a pseudo second order reaction (chemisorption process).

ZnO-doped nanoparticles

A drawback of ZnO as a photocatalyst is its wide band gap (3.2 eV) which requires UV light for generation of electron-hole pair and activation of photocatalytic process, as well as the fast recombination rate of photogenerated electron/hole pairs, which hinder the catalytic efficiency. The lowering of its band gap would allow a sunlight photo-induction and would provide very cheap and convenient way to use ZnO in sun-driven devices and settings.

The band gap of semiconductors can be altered by introduction of a new energy states. The incorporation of metal ions in ZnO structure causes the formation of additional energy level, either within or beyond the band gap of ZnO, which decreases the recombination of electron/hole pairs since the metal ions act as an electron trap, thus reducing the band gap energy. This results in more effective separation of electron/hole pairs and enhancement of photocatalytic activity under visible light (Nouri et al., 2014; Sitthichai et al., 2017).

There are different types of dopant that has been used for ZnO NPs, like alkali metals, alkaline earth metals, transition metals and post-transition metals (Adam et al., 2020; Chandekar et al., 2020). The effect of each type of dopant is different, but they generally improve the optical and electronic

properties of the ZnO NPs. The most studied dopants are Mg, Fe, Co, Ni, La and some others. Precipitation method is very suitable for preparation of doped ZnO nanostructures since it allows to use conditions and synthesis schemes applied and already known for pure ZnO NPs.

Metal oxides are also used as dopants, for example V_2O_5-ZnO nanostructures. Authors have reported a facile sol-gel method for successful preparation of ZnO and V_2O_5-ZnO nanostructures that had flake-type structure of V_2O_5-ZnO obtained from ZnO nanorods (Shukla et al., 2018). It was found decrease in the band gap from 3.28 eV for ZnO to 2.64 eV for V_2O_5-ZnO detected by UV-Visible spectroscopy. The authors applied the V_2O_5-ZnO nanomaterial for methylene blue (MB) dye photodegradation which showed improved photocatalytic efficiency of the composite under visible light irradiation.

Other interesting and promising results were reported for the preparation of Ag/ZnO photocatalysts by the deposition of Ag on the surface of the ZnO by a simple immersion reduction method (Wang et al., 2021). The Ag load in the material was controlled by the concentration of Ag ions, immersion time and the amount of the reducing agent. A decrease in the band gap of the Ag/ZnO compare to the ZnO was observed due to the surface plasma resonance effect caused by Ag modification. The Ag/ZnO NPs were tested in the decolorization of Rhodamine B where they showed improved photocatalytic efficiency under UV irradiation.

ZnO-zeolite nanocomposites

For development of methods for water treatment and environmental protection non-expensive, non-toxic, abundant and easy-recyclable materials are needed.

ZnO is excellent material for utilization in photocatalytic process but the inconvenience in practice is caused by the fact that it forms very fine suspension which makes it hard to retrieve from the treated water media. Some techniques like thin films or membrane impregnation have been use in order to secure the easier handling of the photocatalyst.

Other approach is preparation of composite materials where ZnO is combined with a suitable substrate. In this aspect a very good candidate is the natural zeolite. It is abundant in the nature and non-expensive. The zeolite itself has been used for water treatment for heavy metal ions removal and it is expected that it would demonstrate a synergetic effect with ZnO NPs.

In the literature, there are a few general approaches for preparation of such composites – by impregnation, by precipitation and by ion-exchange.

Karimi-Shamsabadi et al. (2017) report the preparation of photo-catalyst NiO-ZnO doped onto nano zeolite X (NZX) and its use in the photocatalytic degradation of Eriochrome Black T (EBT) and Methyl Orange (MO) under UV-light irradiation. The method used for preparation of nano-zeolite crystals was hydrothermal crystallization. The composite was prepared by Ni(II) and Zn(II) ions exchange on zeolite in an aqueous solution and following by calcination at 450 °C. Thus, the formed catalyst NiO-ZnO-NZX showed significantly enhanced photo-degradation activity when tested towards EBT and MO. This activity was attributed to the synergistic effect of mixed p–type NiO and n–type ZnO oxides. It was reported that about 80% of photodegradation of EBT and MO dyes was achieved in 90 min under UV light irradiation, confirmed by spectrophotometry and chemical oxygen demand (COD). The factors that affected the degree and rate of degradation efficiency were pH of solutions, Ni^{2+} and Zn^{2+} loading onto NZX, dosage of photocatalyst, and initial EBT and MO concentrations. Mohammadi et al. (2020) report a composite based on novel ZnO-magnetic/ZSM-5 material with high adsorption capacity and magnetic separation capability which was tested on the adsorption of disperse blue 56 dyes. It was found that the optimal conditions for dye removal process were as follows adsorbent dosage 0.015 g, pH 3, stirring time 15 min and initial dye concentration 10^{-5} M for maximum removal percentage (>91.0 %). The benefit of the composite ZnO-magnetic/ZSM-5 was its magnetization saturation value equal to 3.2 emu/g. This is a good indication that magnetically separation technologies can be used in its utilization, marking it as an efficient recoverable adsorbent. The authors reported that ZnO-magnetic/ZSM-5 in their experiments can be used up to 3 times without noticeable diminishing of adsorbent activity (yield of removal) and no obvious decrease of magnetic intensity. Kinetic and isotherm models of disperse blue 56 can indicate pseudo first-order model and the Freundlich isotherm based on high R^2 (0.980) and R^2 (0.989), respectively. The maximum adsorption capacity of disperse blue 56 obtained based on the Langmuir model was 6.23 $mg.g^{-1}$. Other authors have engaged Faujasite X zeolite in their studies as a support for ZnO nanoparticles, incorporating them into its 3D channels and supercages. This type of zeolite was chosen because its structure naturally limits the growth of ZnO NPs and ensure control over their size. The method for preparation was via impregnation of the zeolite in aqueous solution of $Zn(NO_3)_2$ with different concentrations and subsequently calcination under O_2 flow. BET analysis showed a difference in N_2 adsorption–desorption which is an indication that ZnO is inside the zeolite structure. A blue-shift of the emission band in PL spectrum was detected which was attributed to the quantum size effect of ZnO NPs inside the Faujasite X matrix.

Cheng et al. (2012) also have chosen the method for impregnation and in situ formation of composite material. They have selected a simple route for incorporation of ZnO in mesoporous ZSM-5 zeolite. A commercial H-ZSM-5 (Si/Al = 50) initially treated with NaOH solution has been used in the experiment. This was meant to evoke a partial desilication which would lead to a large number of intracrystal mesopores. After this pre-treatment the ZnO nanoparticles were successfully incorporated in the mesopores using wet impregnation method. By different modern methods for characterizations (XRD, UV–visible absorption spectra, TEM and N_2 adsorption) authors were able to establish the location of ZnO nanoparticles. It was found that only mesopores can be loaded (about 15%) with ZnO NPs with average size of 20 nm, while micropores remained unchanged and cannot be loaded.

By using similar technique Lim and Ryu (2009) have reported the preparation of ZnO/TMA-A zeolite nanostructured composite. Applying anion exchange method then a hydrothermal method a nanoparticles ZnO were obtained into TMA-A zeolite. Its structure and morphology was confirmed by XRD, SEM and HR-TEM, respectively. Since it was of essence to obtain ZnO NPs with controlled size and properties, a study on the optimal heat-treatment condition for oxidation of zinc was conducted. It indicated that temperature range from 500 to 550 ^oC was appropriate for crystal ZnO/TMA-A zeolites formation. The ZnO NPs with size 5–10nm were well

distributed among 100–150nm nanoparticles of TMA-A zeolite. The microstructure and crystalline analyses revealed that ZnO NPs were evenly incorporated into TMA-A zeolite nanostructure. The XRD analyses have shown the sodalite cage size of 12.389 Å for ZnO/TMA-A zeolite sample treated at 500 ^{o}C.

Li M. et al. (2013) have reported the preparation and enhanced antimicrobial properties of nano-ZnO-supported zeolite filled polypropylene random copolymer (PPR) composites. Nano-ZnO-supported zeolite particles were prepared by chemical precipitation of ZnO on zeolite suspended in zinc chloride solution and following addition of 1mol/L NaOH under constant stirring. After separation and washing of the product it was dried in vacuum oven for 1 h, in muffle furnace at 200^{0}C for 4h and 500^{0}C for 2 h, respectively. After detailed analyses (fluorescence and UV–Vis spectra, inductive coupled plasma and scanning electron microscopy) it was demonstrated that ZnO with flower-like morphology was formed on the surface of zeolite particles. The composite PPR filled with nano-ZnO-supported zeolite was prepared by mixing them at 170 ^{0}C and stirring with 50 rpm for 7min. These inorganic-organic composites were tested for antimicrobial activity. It was demonstrated that nano-ZnO-supported zeolite filled PPR composites show higher antimicrobial activity to the S. aureus and E. coli than the PPR composite filled with corresponding amount of only nano-ZnO. A great advantage for the application of this nano-ZnO-supported zeolite composite is that the nanostructured content does not significantly influence the mechanical properties of PPR composites. This is a good indication that PPR composites with high antimicrobial activity and mechanical stability can be obtained by using nano-ZnO-supported zeolite as functional filler for PPR.

Alcantara-Cobos et al. (2020) reported the preparation and subsequent testing of ZnO nanoparticles (nanZnO) and a zeolite-ZnO nanoparticles composite (Ze-nanZnO) for the removal of Tartrazine. The method they used was chemical precipitation for both nanoparticles and nanocomposite which is facile, cheap and easily to scale-up. The procedure they employed consists of contacting clinoptilolite type zeolite with a zinc acetate solution, then adding drop wise NaOH solution (1 mL/min) and stirring the mixture for 2 h and reflux. The ZnO nanoparticles-zeolite composite (Ze-nanZnO) was washed with deionized water and ethanol, dried at 80 ^{0}C and calcined at 300 ^{0}C. The same procedure was used for ZnO nanoparticles (nanZnO) preparation. These materials were tested for the removal of tartrazine from aqueous solutions by an adsorption combined with photocatalysis process. The experiments have shown that the adsorption of Tartrazine onto nanZnO follows a fast decrease of the concentration while the adsorption onto the composite Ze-nanZnO was slower. The following process of degradation of tartrazine applying both materials under ultraviolet light irradiation seems to be a highly efficient process for both of them, 87 and 81% degradation were observed for nanZnO and Ze-nanZnO respectively. Strictly speaking the first material shows better efficiency than the second, but first material is difficult to remove from the aqueous solution after the process. The results from the mineralization process were obtained by measuring the total organic carbon (TOC) at different contact and irradiation times. The estimated degradation of the tartrazine was between 85 and 90%, noting that higher degradation was observed using Ze-nanZnO as catalyst compared to nanZnO. It was estimated that nanZnO affects “Lactuca sativa” species, but judging by the results the material produces “low toxicity” to this species.

Du G. et al. (2017) demonstrated the preparation of efficient photocatalyst by immobilization of zeolitic imidazolate framework-8 (ZIF-8) derived ZnO on Zeolite A. This type of organometallic compounds known as metal–organic frameworks (MOFs) are hybrid structures consisting of inorganic connectors and organic linker molecules (Jiang Z. et al., 2013). In the case of zeolitic imidazolate framework-8 (ZIF-8), inorganic connectors are Zn(II) ions and organic linker molecules are 2-methylimidazole ligands. By applying the sonochemical synthesis the authors used pre-prepared zeolitic imidazolate framework-8 (ZIF-8) as precursors and zeolite A as support to successfully obtain ZIF-8@Zeolite A (ZIF-8@Z). The following calcination at different temperatures lead to formation of ZnO@Z photocatalysts at different temperatures by removing the organic functional groups of ZIF-8. The prepared photocatalyst, ZnO@Z was studied for application in the degradation of rhodamine B (RhB) aqueous solution under UV light irradiation and ZnO@Z showed higher photocatalytic activity than simply ZnO derived from ZIF-8. This observation can be attributed to the synergistic effect between ZnO and Zeolite because since zeolites are sorbents and can adsorb RhB dye. This prolongs the contact time with catalysts and increase its efficiency. The most active nanocomposite ZnO@Z was obtained by calcination at 550 °C for 5 h and demonstrated the highest photocatalytic efficiency (99.4 %).

Heidaria Z. et al. (2020) reported the synthesis of novel ZnO nanorods over ion exchanged clinoptilolite (ZnO/ICLT) by sonoprecipitation. This material was investigated and found efficient as a catalyst for the photocatalytic degradation of the drug furosemide (FRS). The composite’s enhanced photocatalytic activity was attributed to its higher surface area (due to decreasing the particle size) in comparison to ZnO NPs prepared by conventional precipitation method. By the means of various analyses (TEM, EDX, BET, UV-visible spectroscopy techniques, XRD, etc.) was shown that the average particle size of ZnO in ZnO/ICLT prepared by sonoprecipitation was 20.5 nm, while without sonication the size increases up to 34.8 nm. Additionally, the sonication during the precipitation process prevents the agglomeration of nanoparticles. The effects of different parameters such as amount of ZnO on the zeolite, catalyst dosage, initial FRS concentration, pH of reaction media on the photocatalytic degradation were studied. It was found that the maximum degradation rate of FRS was achieved by using 15 wt% ZnO on ICLT, catalyst loading of 0.75 mg.L^{-1} at pH 7. It was shown that ICLT has a synergetic effect on ZnO photocatalytic ability as calculated from Langmuir–Hinshelwood equation for photocatalytic degradation over 15%ZnO/ICLT, which has twice higher value than the one for ZnO photocatalysis. The good photocatalytic activity of 15%ZnO/ICLT makes it an excellent candidate for nanophotocatalyst in wastewater treatment applications.

Nezamzadeh-Ejhieh A. et al. (2014) reported also the use of natural zeolite clinoptilolite as a support for ZnO and its photocatalytic degradation of 4-nitrophenol. Nano-sized powder clinoptilolite was prepared via planetary ball mill mechanical method. The ZnO NPs were synthesized by ion exchange of nano-clinoptilolite in a 0.1 M zinc nitrate aqueous solution for 24 h followed by calcination at 450 ^{0}C for 12 h, thus forming the nanocomposite material ZnO/natural clinoptilolite

(ZnO/NCP). The photocatalytic tests of ZnO/NCP in the degradation of 4-nitrophenol under UV light irradiation prove the efficiency of the catalyst. The results from the experiments showed that the photodegradation rate of 4-nitrophenol was affected by a few parameters such as the initial 4-nitrophenol concentration, the pH of solution and the amount of catalyst. The process of photocatalysis was accelerated by addition to the system of an electron acceptor, namely hydrogen peroxide and potassium bromate, the latter was the more effective one. The comparison of photodegradation efficiency of the composite ZnO/NCP and pure phases of ZnO or zeolite, showed the enhanced activity of the composite and the advantage of a combination between zeolite and ZnO.

Conclusions

ZnO is a very promising material with enormous potential in terms of large scale processes for water treatment and practical usage. Its high efficiency in photocatalytic degradation of dyes, pharmaceutical products and herbicide combined with its low cost and simple synthesis marks it as an excellent candidate for integration in advanced and environmentally friendly technologies and settings for water treatment and remediation. Keeping in mind that ZnO has also good antibacterial properties which is advantageous combination when speaking of clean water. One of its disadvantages is that ZnO requires UV light irradiation (its band gap is 3.2-3.3 eV) to operate as effective photocatalysts, which can be easily overcome by doping ZnO with metals. Such incorporation of metal ions into the ZnO lattice leads to formation of additional energy levels that narrow the band gap and makes possible the activation of photocatalyst by sun light. This is a major leap since it will significantly lower the cost for processes when doped ZnO is applied. However, technically speaking the small size of ZnO and ZnO-doped NPs causes difficulties in catalyst removal from the treated water, so it is more convenient if ZnO NPS are attached on suitable support. Good candidate is a zeolite (synthetic and natural) because it is non-toxic material with good sorption properties and high surface area due to its micro porosity. It has been shown that ZnO supported zeolite nanocomposites have a high photocatalytic efficiency in degradation of different organic compounds demonstrating synergetic effect between ZnO and zeolite.

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References

Adam, R.E., Alnoor, H., Pozina, G., Liu, X., Willander, M., Nur, O. 2020. Synthesis of Mg-doped ZnO NPs via a chemical low-temperature method and investigation of the efficient photocatalytic activity for the degradation of dyes under solar light. – *Solid State Sciences,* 99, 106053.

Ahmed, S., Chaudhry, A.S.A., Ikram, S. 2017. A review on biogenic synthesis of ZnO nanoparticles using plant extracts and microbes: A prospect towards green chemistry. – *Journal of Photochemistry and Photobiology B: Biology,* 166, 272-284.

Aissat, A., Ghomrani, M.A., Belil, W., Benkouider, A., Vilcot, J.P. 2015. The doping effect on the properties of zinc oxide (ZnO) thin layers for photovoltaic applications. – *International Journal of Hydrogen Energy*, 40 (39), 13685–13689.

Alcantara-Cobos, A., Gutierrez-Segura, E., Solache-Ríos, M., Amaya-Chavez, A., Solís-Casados, D.A. 2020. Tartrazine removal by ZnO nanoparticles and a zeolite-ZnO nanoparticles composite and the phytotoxicity of ZnO nanoparticles. – *Microporous and Mesoporous Materials*, 302, 110212.

Basnet, P., Chatterjee, S. 2020. Structure-directing property and growth mechanism induced by capping agents in nanostructured ZnO during hydrothermal synthesis—A systematic review. – *Nano-Structures and Nano-Objects*, 22, 100426.

Basnet, P., Inakhunbi Chanu, T., Samanta, D., Chatterjee, S. 2018. A review on bio-synthesized zinc oxide nanoparticles using plant extracts as reductants and stabilizing agents. – *Journal of Photochemistry and Photobiology*, 183, 201-221.

Chandekar, k.v., Shkir, M., Khan, A., Al-Shehri, B.M., Hamdy, M.S., AlFaify, S., El-Toni, M.A., Aldalbahi, A., Ansari, A.A., Ghaithan H. 2020. A facile one-pot flash combustion synthesis of La@ZnO nanoparticles and their characterizations for optoelectronic and photocatalysis applications. – *Journal of Photochemistry and Photobiology A: Chemistry,* 395, 112465.

Cheng, X., Meng, Q., Chen, J., Long, Y. 2012. A facile route to synthesize mesoporous ZSM-5 zeolite incorporating high ZnO loading in mesopores. – *Microporous and Mesoporous Materials*, 153, 198–203.

Daneshvar, N., Rasoulifard, M.H., Khataee. A.R. 2007 Removal of C.I. Acid Orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder. – *Journal of Hazardous Materials*, 143(1–2), 95–101.

Du, G., Feng, P., Cheng, X., Li, J., Luo, X. 2017. Immobilizing of ZIF-8 Derived ZnO with Controllable Morphologies on Zeolite A for Efficient Photocatalysis. – *Journal of Solid State Chemistry*, 255, 215-218.

Heidaria, Z., Alizadeha, R., Ebadia, A., Oturan, N., Oturan, M.A. 2020. Efficient photocatalytic degradation of furosemide by a novel sonoprecipited ZnO over ion exchanged clinoptilolite nanorods. – *Separation and Purification Technology*, 242, 116800, 1-13.

Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W. 1995. Environmental applications of semiconductor photocatalysis. – *Chemical Reviews*, 95 (1), 69–96.

Jiang, Z., Li, Z.P., Qin, Z.H., Sun, H.Y., Jiao, X.L., Chen, D.R. 2013. LDH nanocages synthesized with MOF templates and their high performance as supercapacitors. – *Nanoscale*, 5(23), 11770-11775.

Juabrum, S., Chankhanittha, T., Nanan, S. 2019. Hydrothermally grown SDS-capped ZnO photocatalyst for degradation of RR141 azo dye. – *Materials Letters*, 245, 1-5.

Karimi-Shamsabadi, M., Behpour, M., Babaheidari, A. K., Saberi, Z. 2017. Efficiently enhancing photocatalytic activity of NiO-ZnO doped onto nanozeoliteX by synergistic effects of p-n heterojunction, supporting and zeolite nanoparticles in photo-degradation of Eriochrome Black T

and Methyl Orange. – Journal of Photochemistry and Photobiology A: Chemistry, 346, 133–143.

Kolodziejczak-Radzimska, A., Jesionowski, T. 2014. Zinc oxide-from synthesis toapplication: a review – *Materials*, 7, 2833–2881.

Kumar, M.R.A., Ravikumar, C.R., Nagaswarupa, H.P., Purshotam, B., Gonfa, B.A., Murthy, H.C.A., FSabir, F.K., Tadesse S. 2019. Evaluation of bi-functional applications of ZnO nanoparticles prepared by green and chemical methods. – *Journal of Environmental Chemical Engineering*, 7(6), 103468.

Lee, K.M., Lai, C.W., Ngai, K.S., Juan, J.C. 2016. Recent developments of zinc oxide based photocatalyst in water treatment technology: a review. – *Water Research*, 88, 428–448.

Li, M., Li, G., Jiang, J., Tao, Y., Mai, K. 2013. Preparation, antimicrobial, crystallization and mechanical properties of nano-ZnO-supported zeolite filled polypropylene random copolymer composites. – *Composites Science and Technology,* 81, 30–36.

Lim, C. S., Ryu, J.H. 2009. Synthesis and characterization of TMA-A zeolite nanocrystals incorporating ZnO nanoclusters. – *Journal of Crystal Growth*, 311, 486–489.

Liu, M., Li, K., Kong, F., Zhao, J., Yue, Q., Yu, X. 2015. Improvement of the light extractionefficiency of light-emitting diodes based on ZnO nanotubes. – *Photonics and Nanostructures - Fundamentals and Applications,* 16, 9–15.

Mirzaei, H., Darroudi, M. 2017. Zinc oxide nanoparticles: biological synthesis and biomedical applications. – *Ceramics International*, 43, 907-914.

Moezzi, A., McDonagh, A.M., Cortie, M.B. 2012. Zinc oxide particles: synthesis,properties and applications. – *Chemical Engineering Journal*, 185–186, 1-22.

Mohammadi, R., Feyzi, M., Joshaghani, M. 2020. Synthesis of ZnO-magnetic/ZSM-5 and its application for removal of disperse Blue 56 from contaminated water. – *Chemical Engineering and Processing - Process Intensification*, 153, 107969.

Nagajyothi, P.C., Sreekanth, T.V.M., Tettey, C.O., Jun, Y.I, Mook, S.H. 2014. Characterization, antibacterial, antioxidant, and cytotoxic activities of ZnO nanoparticles using Coptidis Rhizoma. – *Bioorganic and Medicinal Chemistry Letters,* 24, 4298–4303.

Nezamzadeh-Ejhieh, A., Khorsandi, S. 2014. Photocatalytic degradation of 4-nitrophenol with ZnO supported nano-clinoptilolite zeolite. – *Journal of Industrial and Engineering Chemistry*, 20(3), 937-946.

Nouri, H., Habibi-Yangjeh, A. 2014. Microwave-assisted method for preparation of Zn1−xMgxO nanostructures and their activities for photodegradation of methylene blue. – *Advanced Powder Technology*, 25, 1016-1025.

Ong, C.B., Ng, L.Y., Mohammad, A.W. 2018. A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications – *Renewable and Sustainable Energy Reviews*, 81(1), 536-551.

Oskoei, V., Dehghani, M.H, Nazmara, S., Heibati, B., Asif, M., Tyagi, I., Agarwal, S., Gupta, V.K. 2016. Removal of humic acid from aqueous solution using UV/ZnO nano-photocatalysis and adsorption. – *Journal of Molecular Liquids*, 213, 374–380.

Páez, R., Ochoa-Muñoz, Y, Rodriguez-Páez, J.E. 2019. Efficient removal of a glyphosate-based herbicide from water using ZnO nanoparticles (ZnO-NPs) – Biocatalysis and Agricultural Biotechnology, 22, 101434.

Shukla, P., Shukla, J.K. 2018. Facile sol-gel synthesis and enhanced photocatalytic activity of the V_2O_5-ZnO nanoflakes – *Journal of Science: Advanced Materials and Devices*, 3(4), 452-455.

Sitthichai, S., Phuruangrat, A., Thongtem, T., Thongtem, S. 2017. Influence of Mg dopant on photocatalytic properties of Mg-doped ZnO nanoparticles prepared by sol–gel method – *Journal of the Ceramic Society of Japan*, 125, 122-124.

Steffy, K., Shanthi, G., Markyb, A.S., Selvakumar, S. 2018. Enhanced antibacterial effects of green synthesized ZnO NPs using Aristolochia indica against Multi-drug resistant bacterial pathogens from Diabetic Foot Ulcer – *Journal of Infection and Public Health*,11 (4), 463-471.

Sun, X., Chen, X., Deng, Z., Li, Y. 2003. A CTAB-assisted hydrothermal orientation growth of ZnO nanorods – *Materials Chemistry and Physics*, 78, 99-104.

Tachikawa, S., Noguchi, A., Tsuge T., Hara, M., Odawara, O., Wada, H. 2011. Optical properties of ZnO nanoparticles capped with polymers – *Materials (Basel*), 4, 1132-1143.

Vidhya, K., Saravanan, M., Bhoopathi, G., Devarajan, V.P., Subanya, S. 2015. Structural and optical characterization of pure and starch-capped ZnO quantum dots and their photocatalytic activity – *Applied Nanoscience*, 5, 235-243.

Vidyasagar, C.C., Arthoba Naik, Y. 2016. Surfactant (PEG 400) effects on crystallinity of ZnO nanoparticles – *Arabian Journal of Chemistry*, 9, 507-510.

Vijayakumar, S., Saravanakumar, K., Malaikozhundan, B., Divya, M., Vaseeharan, B., Durán-Lara, S.F., Wang M.H. 2020. Biopolymer K-carrageenan wrapped ZnO nanoparticles as drug delivery vehicles for anti MRSA therapy – *International Journal of Biological Macromolecules*, 144, 9-18.

Wang, Z., Ye, X., Chen, L., Huang, P., Wang, Q., Ma, L., Hua, N., Liu, X., Xiao, X., Chen, S. 2021. Silver nanoparticles decorated grassy ZnO coating for photocatalytic activity enhancement – *Materials Science in Semiconductor Processing,* 121, 105354.

Wu, Q., Chen, X., Zhang, P., Han, Y., Chen, X., Yan, Y., Li, S. 2008. Amino acid-assisted synthesis of ZnO hierarchical architectures and their novel photocatalytic activities – *Crystal Growth and Design*, 8, 3010-3018.

Zhang, L., Mohamed, H.H., Dillert, R., Bahnemann, D. 2012. Kinetics and mechanisms of charge transfer processes in photocatalytic systems: a review – *Journal of Photochemistry and Photobiology C*, 13, 263–276.

Zhu, S., Xu, L., Yang, S., Zhou, X., Chen, X., Dong, B., Bai, X., Lu, G., Song, H. 2020. Cobalt-doped ZnO nanoparticles derived from zeolite imidazole frameworks: Synthesis, characterization, and application for the detection of an exhaled diabetes biomarker – *Journal of Colloid and Interface Science*, 569, 358-365.