Chapter

Multifunctional ZnO Nanoparticle: Based Coatings for Cultural Heritage Preventive Conservation

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Abstract

Coatings based on nanoparticles embedded in various filmogenic materials are still a hot topic in nanomaterial research, due to the exceptional variety of applications. The chapter present recent progress in synthesis and characterization of hybrid material with ZnO nanoparticles and their use as functional coatings for various substrates. The antibacterial and UV protection efficiency of ZnO nanoparticle-based coatings on paper and stone are discussed, with particular emphasize on the specific requirements for application in cultural heritage preventing conservation. Functional materials based on ZnO are presented as possible treatment for protection of historic and **archaeological** textiles and metal artifacts. Trends in environmental friendly methods to fabricate the ZnO nanoparticles will be evaluated, compared to classic ones, in terms of material characteristics and efficiency.

Keywords: zinc oxide nanoparticles, multifunctional coatings, antimicrobial, superhydrophobic, cultural heritage

1. Introduction

Defined as "design, production and application of structures, devices and systems by controlling shape and size at nanometer scale", nanotechnology is the most emerging field designed to revolutionize material science. Due to their unique properties, nanomaterials become an important resource for the scientific community in solving many issues related to many domains, from medicine to aeronautics, optoelectronics, clean energy or waste treatment. Among the multitude of metals and metal oxides that can be used in the fabrication of nanoparticles, zinc oxide (ZnO) is of a great importance due to its specific physical and chemical properties, easiness in processing, low cost and abundance of precursors. Zinc oxide is a semiconductor type material, with the band gap of 3.36 eV and an exciton-binding energy of 60 meV, making it a suitable nanomaterial for the optoelectronic industry [1]. At nanometric size, ZnO exhibits antibacterial, antifungal, UV-blocking or photocatalytic properties [2, 3]. Due to these properties it is well suited for applications in various fields such as biomedicine, textile industry, pharmaceutical and cosmetic industry, sensors, electronics, rubber industry [4, 5]. The antimicrobial properties of ZnO nanoparticles gain interest in the last decades and recommend them as replacement to classic biocidal treatments for the surfaces. Their antifungal and antibiofilm activities were investigated in the last two decades as potential tools in preventive conservation of cultural heritage monuments [6].

Due to their unique physical and chemical properties Zinc oxide nanoparticles have become a key material in developing new nanotechnologies suitable for coating of different substrates. As seen from the plethora of synthesis routes and materials used as reagents, this kind of nanomaterials have a large variety of morphologies and sizes which lead to unique properties. Multifunctional ZnO nanomaterials could represent an interesting choice to be used in protecting the cultural heritage, besides their industrial applications, demonstrating their great versatility and offering multiple benefits in this field.

2. Synthesis of zinc oxide nanoparticles

Extensive use of ZnO nanoparticles (NPs) generate important attention to their synthesis route, in order to achieve better control of size and shape of the obtained material. There are many methods that can be used such as: sol–gel, chemical vapor deposition, thermal oxidation [7], etc. but the easiest and most frequently used are the hydrothermal and solvothermal ones. Briefly, the precursor (zinc salt solution and a base solution) are mixed at different molar ratios in suitable solvents (water or nonpolar organics). The as obtained precipitate is washed and dried. Sometimes polymers are added to stabilize the obtained nanoparticles. By varying the solvent, precursors, molar ration or other reaction parameters one can obtain different size and morphologies of the nanoparticles.

Among the various synthesis methods, the hydrothermal one brings the most advantages such as low temperatures, low aggregation levels or good control over particle morphology and size. Synthesis of ZnO NPs with different morphologies using a simple hydrothermal method was reported [8]. Flowerlike nanoparticles are synthesized using Zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$) and cetyltrimethyl ammonium bromide (CTABr,) dissolved in deionized water under magnetic stirring at room temperature. NaOH is then slowly added drop wise. The resultant solution is then added in a stainless-steel Teflon autoclave. The white precipitate obtained is centrifuged, and dried, obtaining flower-like structures. Same synthesis route in the absence of CTABr and NaOH is used to obtain nanoplates and nanoparticles. The XRD and SEM characterization showed wurtzite hexagonal structures, with the average diameter in the range of 40–80 nm for the nanoparticles, 30 nm thick nanoplates, and, nanoplates agglomeration forming flower-like structures of 2 μm diameter.

Complex three-dimensional nanoaggregates (**Figure 1**) with different flower-like morphologies, such as cauliflower-like, safflower-like microspheres and ixora-like nano-structures can be obtained by the hydrothermal method, at different concentrations of OH^- ions and Zn^{2+}-glutamic acid molar ratio [9].

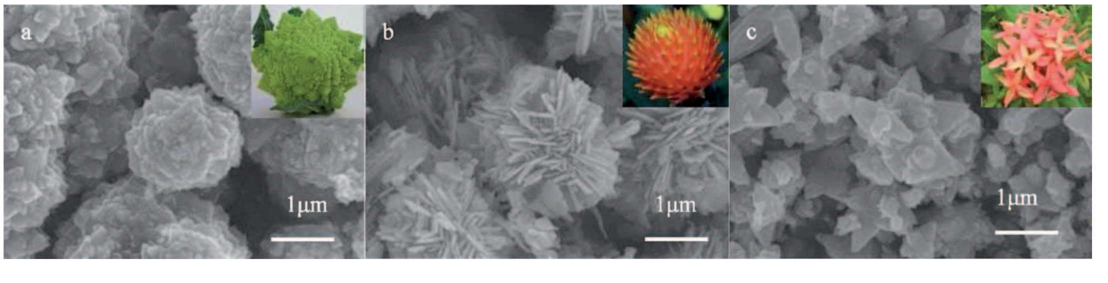

Figure 1.
SEM images of the ZnO 3D nanoaggregates (a, (cauliflower); b, (safflower); c, (ixora); [9].

By varying the base added to the precursor solution, Ekthammathat et al. [10] obtain rod-like, pencil-like and star-like particles. Zinc foils are used as solid reagent and substrates for the direct growth of ZnO films. NaOH, LiOH and NH_4OH solutions in deionized water are used as source of OH^- ions. The hydroxide are introduced in Teflon stainless-steel autoclaves, and the clean Zn foils were added to each solution. The as-synthesized films on Zn substrates were rinsed and dried. When using NaOH as precursor, 100 nm diameter and 500 nm length nanorods were obtained, pencil like nanostructures of 300 nm diameter and more than 800 nm length in the case when using LiOH and in the case of NH_4OH the authors obtained star-like nanostructures of 200 nm diameter and 1 μm length.

Stanković et al. [11] studied the influence of the stabilizing agents on the shape of ZnO NPs obtained from zinc acetate, $Zn(CH_3COO)_2{\cdot}2H_2O$ and NaOH as precursors. In the case when polyvinyl pyrrolidone (PVP) is used as stabilizing agent, a mixture of hexagonal prismatic rods and incompletely formed hexagonal pyramid-like structures is obtained, with length approximately 1 μm and diameter of about 100 nm. Different morphologies were obtained when using polyvinyl alcohol (PVA). The particles are spherical and well dispersed with average particle diameter around 30 nm, while ellipsoid shaped structures with the length of 500–600 nm and diameter of about 100 nm were obtained when using poly α,γ, l-glutamic acid (PGA). The morphology of ZnO nanopowders obtained in hydrothermal synthesis is also influenced by the variation of pH value. Kumaresan et al. [12] synthesized ZnO microparticles from $ZnCl_2$ and NH_4OH at different pH (7, 9, 11 and 13). When the pH is fixed at 7, the XRD and Field Emission Scanning Electron Microscope (FESEM) analysis reveal hexagonal shaped ZnO nanorods arranged in a flower like structure. The length and width of the nanorods which form nanorod-flower structure is about 4790 nm and 1000 nm respectively. When increasing the pH to 9, spheroidal and hexagonal disk shaped morphologies were obtained. Nanorods of various lengths and widths were observed when the pH value rise to 11, whereas in the case of pH = 13, nanoflower structures of 4.8 μm diameter can be observed.

The temperature, pressure and reaction time can be minimized using the microwave assisted hydrothermal synthesis [13]. Zinc oxide nanorods were produced from $ZnCl_2$ and hydrazine as reagent. The white precipitate initially formed is transferred in a Teflon container and the mixture was irradiated and then cooled at room temperature, centrifuged, rinsed and dried. The nanorods formed are polydispersed, with diameter between 65.14 and 170.93 and the length between 241.49 and 941.16 nm. Hasanpoor [14] reports both the effect of the precursors and of the radiation power over the size and shape of ZnO nanostructures. The ZnO powder prepared from the solution of $Zn(NO_3)_2{\cdot}6H_2O$ and ammonia to reach the pH 11.5, irradiated for 15 min at 510 W exhibit needle-shaped nanostructures. When the mixture was subjected to irradiation for 10 min at 680 W, the particles were flower like.

Zare et al. [15] proposed a solvothermal synthesis in the presence of surfactants to obtain ZnO nanoparticles of different morphologies. Methanol solutions of $Zn(NO_3)_2{\cdot}6H_2O$ and NaOH were mixed under constant stirring. Then surfactant solutions were added and the new mixture was transferred to a stainless-steel autoclave which was further heated and cooled at room temperature. The final product was washed and dried. When the surfactant was oleic acid, the obtained product has flower-like morphology (102 nm), when using gluconic acid the product was a snowflake structure (119 nm) and when using Tween 80 the morphology was granular, with quasi spherical nanoparticles (69 nm). A solvothermal and hydrothermal microwave assisted synthesis of ZnO nanoparticles are compared by Krishnapriya [16]. Two zinc precursors, $[Zn(NH_3)_4]^{2+}$and $[Zn(OH)_4]^{2-}$ were mixed with double distilled water, ethylene glycol and ethanol. The as obtained mixtures are added to a quartz vessel and heated in the microwave, thancooled to room temperature and the white precipitate obtained was filtered, washed, centrifuged and dried. The obtained nanoparticles have different flower-like morphologies, depending on the polarity of the solvent and on the precursor concentration. The diameter of the obtained nanoparticles is between 10 and 500 nm and their length between 300 nm and 3 μm.

Solvothermal methods can also be made in supercritical fluids. In a study done by our group [17], flowerlike ZnO nanoparticles were synthesized using an adapted method in supercritical CO_2. The reagent Zn $(NO_3)_2$, NaOH and cetyltrimethylammonium ammonium bromide (CTABr) were dissolved in a mixture of ethanol and water. The reaction is performed in high temperature and pressure conditions, in a stainless-steel autoclave with Teflon coating. In the modified synthesis in supercritical CO_2, the reaction cell was filled with carbon dioxide at certain temperature and pressure and remained at these conditions for the various period of time. After the system was cooled at −10°C was slowly depressurized. The white precipitates obtained in various conditions were collected, filtered and washed several time in water and alcohol. Both products obtained using the solvothermal synthesis performed in the autoclave and in the case of supercritical CO_2 variation were flower like aggregates of 700–900 nm, as seen in the SEM images presented in **Figure 2**.

In the last decade attention has been focused on using the green synthesis approach for nanoparticles in order to reduce the drawbacks of the classic methods

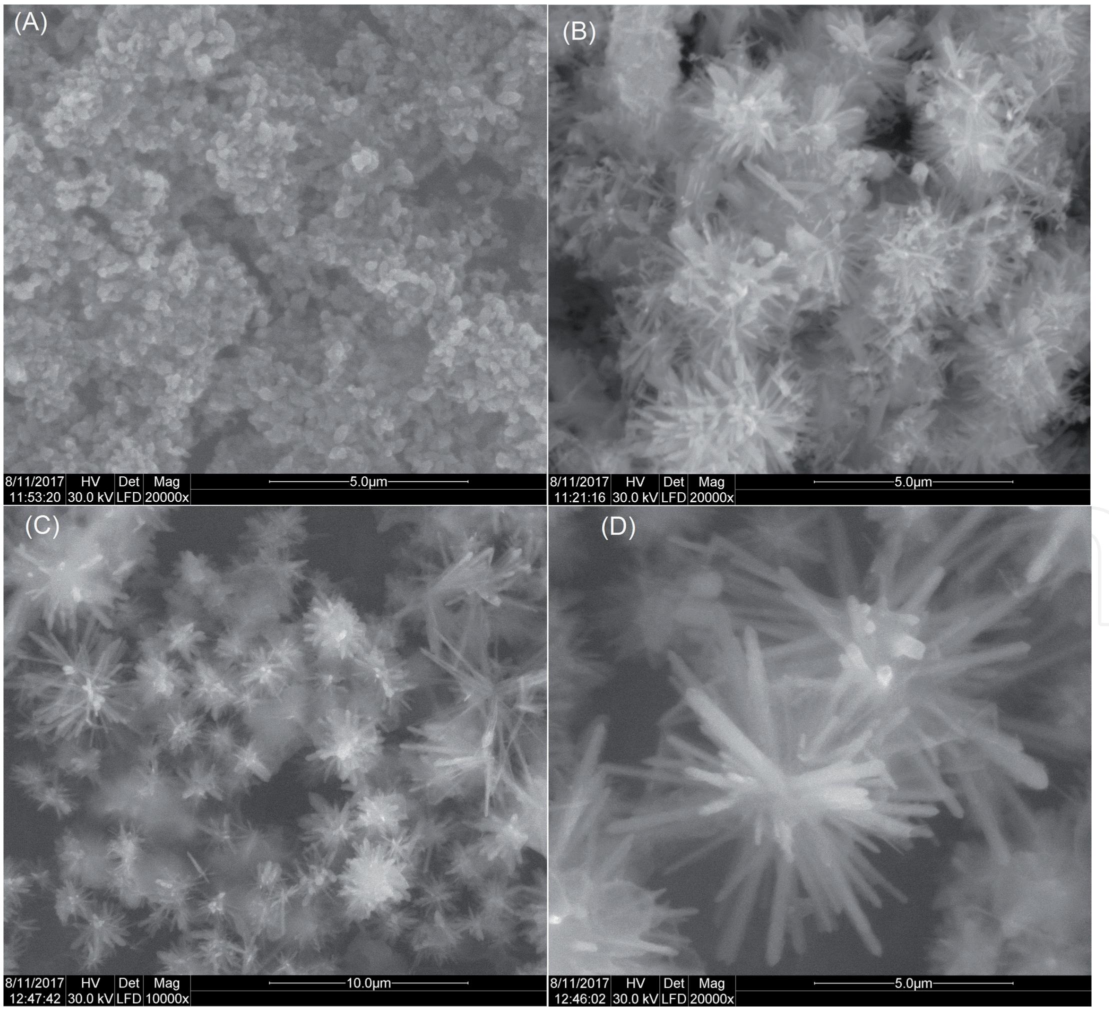

Figure 2.
SEM images of the ZnO nanopowders: (A) solvothermal synthesis in normal conditions, without surfactant; (B) solvothermal synthesis in autoclave, in the presence of surfactant CTABr; (C) supercritical CO2 assisted solvothermal synthesis, in the presence of surfactant CTABr (lowmagnification); (D) high magnification of sample C [17].

No.	Vegetal source	Precursor	Size(nm)	Morphology	Reference
1	Laurul Nobilis L.	Zn Nitrate Zn Acetate	25.26 21.49	Flowerlike Bullet like	[19]
2	Pineapple	Zn Nitrate	73–123	Flower rod	[20]
3	*Garcinia mangostana*	Zn Nitrate	21	Spherical and hexagonal	[21]
4	Deverra tortuosa	Zn Nitrate	9.26–31.18	Spherical	[22]
5	*Calotropis procera*	Zn Nitrate	15–25	Spherical	[23]
6	Protoparmeliopsis muralis	Zn Nitrate	178.06	Spherical	[24]
7	Costus pictus D. Don	Zn Nitrate	20–80	Hexagonal rod	[25]
8	*Prunus dulcis*	Zn Nitrate	25.2	Spherical	[26]
9	*Citrus sinensis*	Zn Nitrate	10–20	Spherical	[27]
10	*Phoenix dactylifera*	Zn Nitrate	31.6	Spherical	[28]
11	*Matricaria chamomilla* L	Zn Oxide	49.8–191	Hexagonal rods	[29]
12	*Citrus Limon*	Zn Oxide	60.8	Hexagonal prism	[30]
13	*Mentha spicata*	Zn Acetate	74.68	Spherical	[31]
14	Oak Tree	Zn Acetate	34	Spherical	[32]
15	*Tecoma castanifolia*	Zn Sulfate	70–75	Spherical	[33]

Table 1.
Green synthesis of ZnO nanoparticles.

discussed above (mainly the large use of toxic chemicals). The green approach implies the use of microorganisms (bacteria, fungus, algae) or plants in the synthesis of various nanoparticles [18]. Briefly, in this synthesis approach, a precursor molecule (zinc acetate more often) and the plant extract are mixed under stirring in order to form Zn^{2+} ions which are transformed into ZnO nanoparticles in a hydrolysis reaction. Some recent results on green synthesis of ZnO nanoparticles are summarized in **Table 1**.

The main advantage is that there is no need of any stabilizing agents, while phytochemicals (polysaccharides, polyphenolic compounds, vitamins, amino acids, etc) content from the plant act both as reducing agent and capping or stabilizing agent [18].

3. Properties of zinc oxide nanoparticles

As semiconducting materials, Zinc oxide nanoparticles were first used in the optoelectronic industry and for their catalytic properties. As it is shown in the previous sections, there are many ways of synthesizing ZnO nanopowders in a large variety of dimensions and morphologies. These two main characteristics dictate the properties and further uses of zinc oxide nanoparticles.

3.1 Antimicrobial activity

One of the most important properties of ZnO NPs is their ability to inhibit the growth of various bacterial and fungal strains, both in solution or on the surfaces. Although their mechanism of action is not fully understood, the researchers proposed two possible routes: the physical and chemical interactions. In terms of physical interactions, plasma membrane disruption, cellular internalization or mechanical damage are the most frequent mechanisms, while in the case of chemical interactions there are three possible ways: reactive oxygen species (ROS) production and Zn^{2+} release and the photoproduction of H_2O_2 [34].

Antifungal activity of ZnO NPs against Asperillus niger [35], a microorganism responsible for the deterioration of a large variety of common or historic objects was investigated. The material with antimicrobial effect was obtained by dissolving micrometric ZnO and urea in glycerol. The clusters obtained have a pseudo spherical morphology and possess hierarchical structures, with average size of 590 nm, while the pristine ZnO crystallites have 15–30 nm. The obtained product shows antifungal activity against fungus *A. niger* and also proved bactericidal activity against the bacteria *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). In both cases, the formation of bacterial colonies decreased at very low concetrations (3 ppm) of ZnO in the culture media.

Raghupathi et al. showed that the antibacterial activity of the ZnO nanopowders was inversely proportional to the size of the nanoparticles in the case of gram positive bacteria, *S. aureus* [36]. The tested ZnO NPs were spherical in shape, with size varying between 12 and 307 nm. To determine the antibacterial activity of the ZnO nanoparticles a wide range of microorganisms were studied: *S. aureus*, *S. epidermidis*, S. pyogenes, *E. faecalis*, *B. subtilis*, *B. cereus*, *E. coli*, S. typhimurium, P. alcaligenes, *E. aerogenes*, S. flexneri, etc. The patterns of growth inhibition of microorganisms were similar and 95% growth inhibition was achieved with a concentration of 6 mM colloidal suspension of zinc oxide nanoparticles.

Functional nanocoating [37] based on ZnO and carboxymethyl-chitosan, with antibacterial and UV protecting properties was reported. To obtain the bio nanocomposite a water-soluble solution of carboxymethyl-chitosan was prepared, and further used as reaction media to synthesized ZnO NPs, which were spherical with an average size of 100 nm. The antibacterial activity of the coating, applied in various concentrations on the cotton samples was measured against *S. aureus* and *E. coli*. The results show that all treated samples have inhibition zone larger than the untreated samples. As the concentration of the suspension increase, the zone of inhibition also increases. Also, the resistivity of *E. coli* is larger compared to *S. aureus*. The values of the UV Protection Factor (UPF) increased when increasing the temperature of curring of the nanocomposite treated fabrics. The same observations were made using UV transmittance tests. Unfortunately, the chitosan derivative was only used as stabilizing agent and polymer matrix, no study was performed to elucidate the role of biopolymer in the antibacterial activity of the nanocomposite.

The antimicrobial activity of ZnO NPs have been extensively investigated against many common bacterial and fungi, but systematic studies on the influence of size, shape, surface functionalization, specificity of strains are still missing. In particular, very few studies have been reported on the specific microorganism that colonize the historic monument or artistic artifacts.

3.2 Superhydrophobic functionalization of the surfaces

Another important property of zinc oxide nanoparticle is their ability to be used in superhydrophobic coating for different substrates. For a material to be considered superhydrophobic it must possess a certain roughness, with hierarchical structures in the micro and nano meter scale and the measured contact angle must be greater than 150°. Lee et al. [38] proposed a superhydrophobic nanocoating for various substrates, using a simple dispersion of ZnO nanoparticles in ethanol to ensure the suitable roughness. The colloidal suspension was spin-coated on a silicone substrate several times and immersed in an ethanolic solution of stearic acid. From SEM measurements, the as obtained ZnO nanopowders were spherical, with size ranging from less the 10 nm to hundreds of nm. The large distribution of particle size leads to a rough surface, the roughness increasing when the number of coating cycles increases. The wetting properties of the coated substrate were tested by measuring the water contact angle (WCA). The water CA of the untreated substrate was below 5°. After the chemical modification with the obtained nanocomposite the WCA increased beyond 150°, turning the material in superhydrophobic one. When the number of the coating cycles exceeded 20, the WCA dropped to 151°. All tested substrates (silicone, paper, cotton and polyethylene tereftalate) show similar behavior.

Zinc oxide based coatings with both superhydrophobic and antibacterial properties were synthesized by Shaban et al. [2]. The solvothermal method is used, with concentrations of zinc acetate dissolved in 2-methoxyethanol and mono ethanolamine as reagents. The pH of the solution was controlled using NaOH or acetic acid. Magnesium acetate tetrahydrate was added as dopant. Characterization methods showed that the morphology of the nanoparticles is cillindrical with the average diameter of 13.4 nm. The prepared ZnO doped dispersion was used for the treatment of cotton fabrics. The wettability of the coated textile was tested by water contact angle. Best results were obtained when the concentration of the zinc precursor was 0.5 M and the pH of the solution 7. The measured water contact angle was 154°, demonstrating the superhydrophobic character of the coating. The resistance of cotton samples against the attack of microorganisms *B. subtilis*, K. pneumonia, *E. coli*, and S. typhimurium was also investigated and all tested samples showed antibacterial properties.

The work of Ghasemi [39] present a facile one-step method for the preparation of a hybrid zinc oxide/octadecanethiol material with superhydrophobic and antibacterial properties that can be used as efficient coatings for cotton fibers. A fixed amount of octadecanethiol was mixed with zinc oxide NPs and chloroform. Fabric samples were immersed in this suspension for different amounts of time. Another approach was a two-step dip coating method: fabric samples were dipcoated in ZnO dispersion, removed and dried. The treated textile was then immersed in an octadecanethiol solution. As seen from SEM images one can observe some roughnesses on the surface of the fabrics, with the maximum cluster diameter of 2 μm. The wetting properties of the samples were determined by contact angle measurements. Pristine fabric and the samples coated with only ZnO or octadecanethiol showed hydrophilic behavior, while the textile samples coated with both ZnO dispersion and octadecanethiol exhibits superhydrophobic properties, with the measured WCA of 161°. Coated fabrics were tested for their antimicrobial properties by cultivating microorganisms *S. aureus* and *E. coli* on the surface of the textile materials. Results show that *S. aureus* severely colonized on the pristine fabric while the superhydrophobic sample was more resistant on the bacterial attack. The inhibition of the bacterial growth was more obvious in the case of *E. coli*, results corresponding to CFU measurements.

3.3 UV blocking and photocatalytic properties

Also it is worth mentioning the ability of zinc oxide to form UV absorbing and anticorrosion coatings. In a work developed by Becheri [40] ZnO NPs with UV-absorbing properties are synthesized using both hydrothermal and solvothermal method in order to obtain coating materials for cotton and wool fabrics. $ZnCl_2$ was dissolved in water or ethandiole and a solution of NaOH was added dropwise under stirring. The particles were separated from the supernatant, washed and peptized (to disrupt the micro aglomeration and release the nanounits of ZnO), washed again and calcinated. The as obtained nanoparticles had the average diameter of 21 nm (in the case of hydrothermal synthesis) and 9 nm (in the case of solvothermal synthesis). In both cases, the nanoparticles were spherical. Cotton and wool fabrics were conditioned and added to a 2-propanol dispersion of ZnO nanoparticles, dried and washed. The UV absorbing properties were tested by means of UV spectroscopy, UFP and UV transmittance. Untreated cotton does not absorb UV radiation, while the untreated wool absorbs in the 200–300 nm region. The application of ZnO nanoparticles on both cotton and wool increased the absorption of UV radiations over the entire investigated UV spectrum, with better results for the ZnO NPs obtained in the solvothermal synthesis, with smaller size.

ZnO based photocatalysts have been in the spotlight of research in the recent years because of their benefits such as low cost and high quantum efficiency. ZnO was found to decompose organic pollutants, for example dyes like Crystal Violet, Methylene Blue, Orange G or Methyl Orange at a faster rate compared to Degussa P25 (TiO_2 classic photocatalyst) under UV–visible light, indicating that the photosensitization of ZnO by dyes favored the visible light response with an enhanced charge carrier separation. Also, the discoloration of Methyl Orange was found to be greater for ZnO NP with smaller particle size [41].

3.4 Anticorrosion properties

ZnO was considered for many industrial applications due to its ability to act as anticorrosive protection for many metals. Superhydrophobic fluorinated polysiloxane-ZnO nanocomposite with corrosion resistance was developed [42] as multifunctional coating for metallic surfaces. The ZnO particles dissolved in butylacetate were vigorously stirred, followed by addition of stearic acid, washed and dried. Modified ZnO powder was added to an aqueous fluorinated α,ω-bis(hydrogen)-terminated poly (dimethylsiloxane) (FPDHS) dispersion and mixed in order to obtain the final nanocomposite (ZnO/FPDHS) which was deposited onto steel substrates. The water contact angle WCA of the nanocomposite was 166°. Polarization curves of the bare steel, FPDHS coating, modified ZnO coating and modified-ZnO/FPDHS coating were measured in % NaCl aqueous solution. It can be seen that the FPDHS coating shows better corrosion resistance than the bare steel, owing to its lower corrosion current density and corrosion rate. As expected, the modified-ZnO/FPDHS exhibits the lowest corrosion rate.

Despite the fact that ZnO NPs show spectacular properties, such as extended antibacterial activity on most species of microorganisms, ability to protect against corrosion, photocatalytic and UV blocking activities, they have been designed and tested in most cases for industrial uses. Exploitation of these properties of ZnO NPs in the protection of cultural heritage requires a deep knowledge of the rigors of this field and the adaptation of the novel nanomaterials to be compatible with the original materials of historical objects.

4. Application of ZnO nanoparticles in cultural heritage preservation

Cultural heritage monuments, although unanimously considered invaluable values of humanity, still in present days are exposed to various stress factors. Many of them cannot always be avoided and that inevitably result in the degradation and destruction of historic buildings or art objects. Thus, the development of novel techniques and materials with improved efficiency, that can be used in the cleaning and consolidation of art objects, is a very important issue in preventive conservation.

Due to their exceptional properties, ZnO nanoparticles are considered useful tools for development of multifunctional coatings with antibacterial, superhydorphobic, UV blocking, self-cleaning and anticorrosion properties. In the last decade, hybrid materials with ZnO nanoparticles embedded in various matrix have been used in conservation of historic buildings, paper artifact, textiles, etc.

4.1 ZnO nanoparticles - based composite materials in conservation of paper

Historic documents on paper are very sensitive, especially if they are kept in improper conditions, in spaces with high humidity, which favors the microbial attack. In addition, for documents with chromatic decorations or various types of ink, the pigments are subjected to a process of accentuated degradation under the conditions of lighting with strong UV radiation. The cellulose support itself can be damaged, with changes in strength and integrity due to prolonged exposure to sunlight, due to the action of UVA and UVB components. Jia et al. [43] propose a coating material for paper artifacts based on nanocellulose and ZnO nanoparticles. Hydroxypropyl cellulose (Klucel) was chosen because it is widely used in consolidating collections of documents, due to its very good compatibility with cellulose substrate. The ZnO nanoparticles were synthesized based on a facile hydrothermal reaction and obtained nanopowder was suspended in isopropanol together with pure nanocellulose to form a stabile dispersion. The treatment was applied on paper sample (Chinese newspaper from 1960) and proved to be efficient as antifungal agent against Aspergillus niger, Aspergillus versicolor and Rhizopus nigricans, common fungi that can be found in archives. Unexpectedly, the results obtained in this paper suggest similar antifungal activity regardless of the size of zinc oxide nanoparticles. The antibacterial and antifungal activity is dose dependent, the increase of ZnO concentration lead to an enhanced effect, but the composition should be adjust in order to not produce changes in visual appearance of the paper. In the study an optimal concentration of 0.55 g of ZnO nanoparticles in 100 mL Klucel solution is reported to inhibit the proliferation of fungi on treated samples without any visual effect on the paper.

The ability of ZnO nanopowders to absorb efficiently UV radiation has been exploited in recent decades for the production of industrial coatings for surfaces frequently exposed to sunlight or artificial light. Similar materials have been tested for the preventive conservation of historic paper artifacts, in order to protect them from the effect of prolonged lighting [44]. Functional coatings have been prepared from ZnO nanoparticles with average diameter 150 nm dispersed in ethanol (0.2 g% concentration) or ZnO NPs disperded in hydroxypropyl cellulose (Klucel) ethanolic solution, and deposited on the paper surface by a simple spraying procedure. Model paper artifacts, prepared by coloring samples with Alizarin using traditional techniques, were used to prove the protective effect of ZnO coating against dye degradation under UV exposure. Samples of untreated colored paper, paper coated with Klucel, paper coated with ZnO and paper treated with ZnO NPs in Klucel solution were subjected to irradiation with UV lamp (λ 270 nm, 30 W). Color fading (expressed as % of Alizarin absorbance reduction) after 120 minutes of exposure was 19% in the case of the paper treated with the nanocomposite ZnO NPs in Klucel, significantly lower compared to values obtained for untreated paper and paper treated with Klucel (34% and 31%, respectively). The coating with ZnO NPs in Hydroxipropyl cellulose (Klucel) deposited on sample of old paper possesses a high degree of transparency, thus produces no changes in color or gloss of the document (**Figure 3**).

The ability of nanoparticle –based coatings with ZnO and Ag to inhibit the growth of microorganism on the historic document was tested on strains isolated

Figure 3.
The visual aspect of old paper sample untreated (upper) and coated with nanocomposite ZnO NPs –Klucel (bottom) [44].

from a 1677 A.D. manuscript named "Serh Senk Adlky Geld Badr"("The biography of prophet Mohamed, Peace be upon him") deposited in Al-Azhar library, Cairo, Egypt [45]. Both Ag and ZnO NPs applied as treatment have been prepared using eco-friendly methods, biosynthesis mediated by endophytic fungal strain *Penicillium chrysogenum* and *Fusarium keratoplasticum*. The growth inhibition percentage of main strains identified on the studied documents (Bacillus subtilis and *Penicillium chrysogenum*) inoculated on model filter paper previously treated with Ag and ZnO NPs show very good performance. After 21 days, both Ag and ZnO NPs at low concentration of 1 M inhibit completely the development of *B. subtilis* colonies, while the *P. chrysogenum* were more resistant with an inhibition percentage of 59.9 produced by Ag and 51.9 by ZnO nanoparticles at the same concentration.

4.2 ZnO nanoparticles-based materials for the protection of stone heritage

Another interesting application of ZnO nanoparticles in development of functional coatings is devoted to consolidation and protective treatment of stone monuments or statues. An important number of heritage buildings are made from calcareous stone, very sensitive to the degradation by mineral transformation as a results of environmental stressors (temperature variation, humidity, rain, solar radiation, etc). Synergistic destruction effect occurs when the monument is exposed to microorganisms and their metabolic products. Many different microorganisms, such as algae, cyanobacteria, yeast, fungi, and lichens could colonize the surface or inner pores of stone, and their presence is a particular threat for monuments located in tropical climate, due to the high temperature and humidity conditions that favors microbial growth. The same antimicrobial and UV blocking properties of ZnO are used, in order to inhibit the colonization of stone surface with microorganism and to prevent the photo-oxidation of decoration due to the exposure to radiation. In addition, the ability of ZnO nanoparticles embedded in filmogenic matrices to produce suitable roughness leads to obtaining superhydrophobic coatings.

Fernandez et al. [46] reported the photocatalytic and antifungal properties of ZnO nanoparticles compared to MgO and Zn doped MgO NPs. Zinc doped nanoparticles exhibits the best performances both in photocatalytic destruction of methylene blue and in antimicrobial efficiency against many fungal species which produce stone deterioration, such *A. niger*, *P. oxalicum* and *P. maculans.*

Fungal infection is also responsible for biodeterioration of marble columns, thus ZnO antimicrobial properties recommend it for protective treatment of such monuments. Aldosari et al. [47] proposed a simple material obtained by dispersing commercial ZnO nanoparticles in acrylic polymer as a multifunctional biocidal and consolidating coating. The novel nanocomposite coating was applied to marble samples collected from various archeological sites in Egypt. The contact angle of water is enhanced from 112^0 on plain marble to 125^0 on marble treated with polymeric solution, and to a significantly higher value (140^0) in the case of treatment with ZnO-polymer nanocomposite. The color variation of marble sample subjected to various aging procedure prove the efficient protection of the treatment with ZnO NPs against UV exposure, together with minimal or no changes in optical properties following the coating.

Combination of ZnO nanorods and graphene nanoplatelets was proposed by Schifano et al. [48] as coating protective material for the prevention of biodeterioration produced by two bacteria (Arthrobacter aurescens and Achromobacter spanius) isolated from the Temple of Concordia (Agrigento's Valley of the Temples in Sicily, Italy). Three different materials Noto stone, Carrara marble and yellow bricks were tested as model lithic materials. The ZnO nanorods exhibit a high efficiency in reduction of bacterial growth for all strains (2% cell viability), at concentration ranging from 10 to 100 μg/mL. An unexpected result was obtain in antibiofilm properties tests. The biofilm formation on the samples treated with ZnO nanorods at concentration of 125 μg/mL was investigated. The ZnO nanomaterial is able to inhibit the adhesion of A. aurescens TC4 and A. spanius TC7 species on glass and plastic, while an effect of stimulation of biofilm formation was found for A. spanius TC1. Addition of graphene nanoplates to ZnO nanorods results in enhancement of the antibacterial activity and lead to biofilm inhibition also in the case of A. spanius TC1 strains.

One of the few cases of application of ZnO NPs coatings on real monuments is reported by van der Welf et al. [49]. Coating materials were prepared by mixing ZnO and Cu NPs with water-repellant or consolidant products commonly used in consolidation/restoration of historic stone monuments: Estel1000, Estel1100, and Silo111. This ready-to-use materials are based on siloxane oligomers (Silo111), tetraethoxysilane (Estel1000) and a combination of tetraethoxysilane and siloxane oligomers (Estel1100). Since the laboratory tests on similar calcareous stones from south Italy show that the treatment with 0.5w% ZnO NPs in commercial consolidant products Estel and Silo produced negligible changes in stone color and successfully inhibit the growth of *A. niger* fungal strains, in situ experiments were performed on an external area of the 12th-century church of San Leonardo di Siponto, Manfredonia, Italy (**Figure 4**).

As it is expected, the visual aspect after the application of ZnO –based nanocomposites is less modified compared to the use of Cu-NPs embedded in Estel1100 and Silo111. Chromatic variations produced by ZnO NPs were found to be below limit values after 6 months of application, and the biological colonization was reduced.

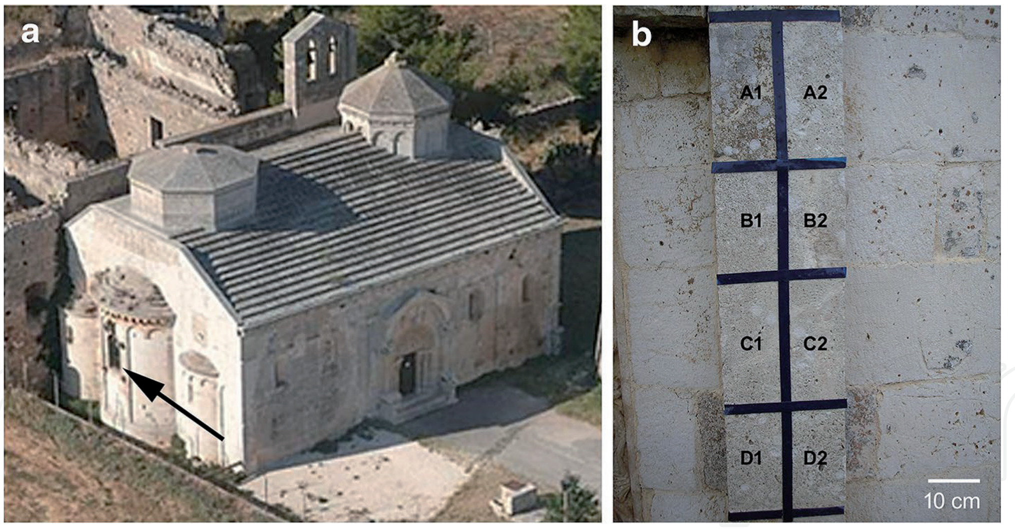

Figure 4.
Test area on the exterior of the san Leonardo di Siponto church (Manfredonia, Italy) (left). Effect of ZnO NPs treatment (right): A1 untreated area; A2 cleaned area; B1 cleaned area treated with Silo111; B2 cleaned area treated with Estel1100; C1 cleaned area treated with Silo111/ZnO-NPs; C2 cleaned area treated with Estel1100/ZnO-NPs; D1 cleaned area treated with Silo111/Cu-NPs; D2 cleaned area treated with Estel1100/Cu-NPs [49].

4.3 ZnO nanoparticles-based material for painting protection

Materials with ZnO NPs have also proven effective in protecting paper artifacts decorated with oil painting. El-Feky et al. [50] reported a simple transparent coating for protection of oil paintings on paper against dirt accumulation, UV aging and fungal attack.

ZnO NPs prepared by a simple hydrothermal method, with size ranging from 122 to 286 nm were dispersed at 2% concentration in a commercial varnish to obtain the coating material.

The effect on the protecting dyes against UV radiation exposure, microbial colonization and dirt was tested using Fabriano paper sheets painted with linseed oil-based colors.

The dyes tested were famous coloring materials used in different period: vermilion (mercuric sulfide) for red color, yellow ochre (iron oxide) for yellow color and ultramarine blue. The painted paper samples were varnished using a commercial acrylic varnish with or without ZnO nanoparticles. The presence of ZnO NPs in varnish coating drastically reduced the deposition of dirt during the 6 month period of exposure, compared to unprotected or simply varnished colored paper (**Figure 5**). The cleaning procedure using a soft brush very easy for the areas protected with the varnish containing ZnO nanoparticles. The ZnO-based varnish proved to be effective to reduce the UV aging of oil painted paper, in particular for ultramarine blue, which is the most sensitive color.

4.4 ZnO nanoparticles-based material for metal conservation

Corrosion is a process that severely affects all types of industrial construction, thus reducing its effects is still a major problem, even for advanced materials used in the aeronautical industry, in electrical components, ships used in maritime transport, oil pipelines, etc. Significant efforts have been made in nanomaterial research to develop nanoparticle-based coatings with increased efficiency in metal protection. Zinc oxide NPs have proven to be a low cost choice, easy to synthesize and process into film-forming materials, and highly effective as an anticorrosive treatment for many types of metals.

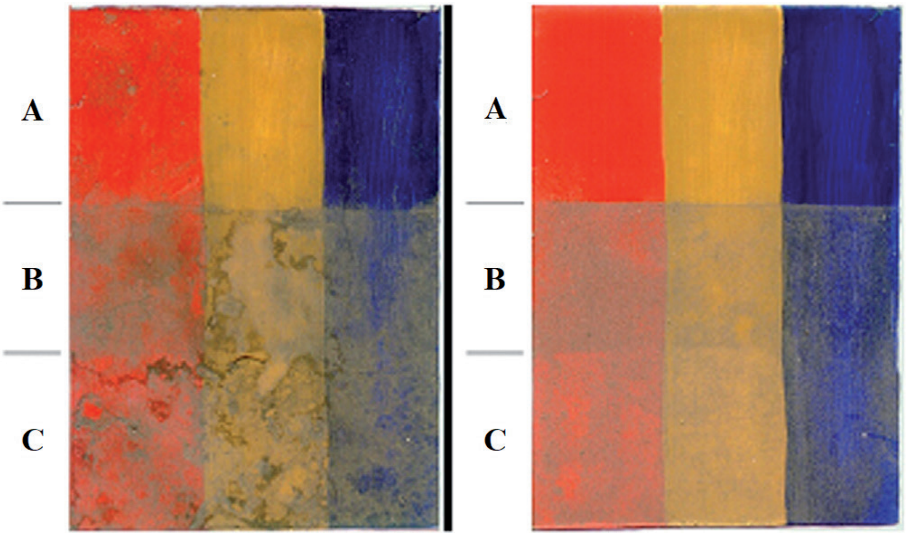

Figure 5.
Optical images of colored paintings after being left in open air for 6 months (left) and after cleaning with a brush and a dry piece of cotton (right). Area A: Painted with color + varnish + ZnO nanoparticles; area B: Painted with color + varnish; area C: Painted with color [50].

Composite materials consisting in ZnO NPs in various polymeric matrices exhibit superior performance from the point of view of corrosion resistance, since the presence of nanoparticles improve the properties of simple coatings in two aspects. The first effect is the enhancement of the barrier performance of the polymeric coating in the presence of ZnO nanopowder as filler, and the other one is the active anticorrosion action of ZnO material itself. Zinc oxide was extensively used in coating due to this active mechanism of corrosion inhibition, based to the possibility to slowly release Zn^{2+} cations through the solubility in water. Zinc ions react with hydroxyl groups on the metal surface (OH groups are present at cathodic corrosion sites on metals), with the formation of a protective layer preventing further reaction with the Fe^{2+} ions. Nanocoatings with various metal oxide nanoparticles (Al_2O_3, Fe_2O_3 and ZnO) at different concentrations in epoxy polymeric films were recently reported [51]. The performances in corrosion protection of carbon steel samples were tested, and the Bose plots show that even at low content of nanofiller in the polymeric matrix (i.e. 1 wt.%) the corrosion resistance of the film deposited on metal is significantly higher compared to plain epoxy treatment. At low concentrations of nanoparticles in the composite (1 wt.%) coating parameters expressed as coating resistance and non-ideal coating capacitance show similar values for all Al_2O_3, Fe_2O_3 and ZnO nanoparticles. Large differences are recorded at concentrations of 3 wt.%, where Al_2O nanoparticles prove to be more efficient than the others.

This type of coating, with low ZnO NPs content, could provide a solution as preventive anti-corrosion treatment for heritage buildings with steel elements, for example old skyscrapers in the historic New York City area or industrial heritage buildings in Manchester, England.

Purcar et al. [52] studied the influence of the silane derivative on the morphological, optical and wettability properties of hybrid nanomaterials based on ZnO nanoparticles. Organo-modified silane derivative (3-glycidyloxypropyl) trimethoxysilane (GPTMS), phenyl triethoxysilane (PhTES), octyltriethoxysilane (OTES), and octadecyltriethoxysilane (ODTES) have been used for the synthesis of coatings. The hybrid materials deposited on glass and metal leads to the formation of highly hydrophobic surfaces, with water contact angle up to 142^0. The hybrid coatings deposited on metallic coupons of Al, Cu and Fe exhibit good anticorrosion efficiency (unpublished data), in particular for the materials with octyltriethoxysilane (OTES), and octadecyltriethoxysilane (ODTES).

Despite the efforts made for the introduction of nanomaterials in the conservation of metallic heritage objects, nanoparticle – based treatments have failed to replace the classic solutions for anticorrosive protection [53]. Since the capability of nanocoatings, such as ZnO nanohybrids described above have been demonstrated in various cases on different metal alloy, with various organic or inorganic compatible matrices, further research is needed in order to develop and test materials designed for cultural heritage use.

4.5 ZnO nanoparticles-based material for textile conservation

The functionalization of textiles with coatings with various compositions, in order to ensure their antibacterial, anti-soiling and superhydrophobic properties is currently a trend in the modern textile industry. ZnO NP-based coatings are intensively studied and remarkable progress is reported for modification of various types of fabrics, from natural such as wool, cotton to synthetic ones [54].

As regarding the use of nanocoatings for the conservation of metal artifacts, case studies reporting the application of nanomaterials for the treatment of historic textiles are very rare.

In particular, the role of the prevention of the biological contamination of textile cultural heritage is to be taken into account. One of the very common causes of the damage of art and historical objects on textile support is the biodegradation produced by various microorganisms [55]. Although the antimicrobial and antifungal efficiency has been proven on a wide variety of microorganisms, in papers dealing with the application of functionalized fabrics for clothing or garments, no studies have been published on possibilities to use ZnO properties to inhibit the growth of specific fungi found on historic textiles under inadequate storage conditions.

The effect of ZnO nanoparticles on the fabrication of natural batik with antibacterial properties is reported by Eskany et al. [56]. Batik is a traditional Indonesian cloth, included since 2009 as part of Intangible Cultural Heritage of Humanity. The term batik refers to an artifact produced in a specific manner of coloring with natural dyes and wax the textile fabric, in order to obtain desired patterns. The most used support is cotton, which turns in a major disadvantage due to the overgrown with bacteria. ZnO NPs dispersions (1–2% concentration) have been applied on cotton textile samples before or after batik process, by using a common pad-dry-cure method. The antibacterial effect was tested on Gram-positive bacteria *S. aureus* and Gram-negative bacteria *E. coli*, with better results when ZnO was applied after the batik process. The ZnO treated batik cloth show good resistance to the microbial attack, together with an improvement of the quality of coloring.

5. Conclusions

Nanotechnology offers numerous solutions with increased efficiency both in cleaning and consolidation of artistic and historic artifacts, from microemulsion and gels to nanoparticles and nanocomposites. While other nanoparticles, such as silica or $Ca(OH)_2$ ones are already used in the protection of cultural heritage monuments, even they are not routine treatments, ZnO NPs still not gain their place in the practice of restoration of art works.

The fabrication of ZnO nanopowders for various industrial applications leads to the development of many methods, as they are summarized in this chapter. A large variety of size and morphology of the ZnO material could be obtained, resulting in variation of optical, electrical, photocatalytic and antimicrobial properties. In particular, UV blocking and antibacterial and antifungal activity of ZnO nanoparticles were discussed, since such properties could be employed in protection of the cultural objects against the main stress factors that induce degradation processes. The antimicrobial and antibiofilm activity of ZnO NPs against fungal and bacterial strains isolated from various archeological and historical sites have been proved, in addition to minor changes produced on visual aspect of the treated samples. The inhibition of microorganism growth was effective on various substrates (stones, marble, paper, textiles), thus the protective coatings containing ZnO NPs could be produced in a customable manner to fit many cultural heritage objectives.

One of the major barrier in extend the acceptability of ZnO-based treatments is the public concern on the environmental impact due to the release of the nanoparticles from the nanomaterials used in conservation/restoration procedure at large scale applied on monuments. Further research are needed to tailor the ZnO NPs to increase the efficiency and compatibility with the historic material, but also to assess their ecotoxicological long-term effect.

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Conflict of interest

The author(s) declared no potential conflicts of interest.

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