

Editorial

New Advances into Nanostructured Oxides

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Inorganic nanostructured (metal) oxides are a large class of inorganic materials extensively investigated for their unique and outstanding properties that allow for their use within a multitude of technological fields of emerging interest, such as (photo)catalysis, environmental remediation processes, energy storage, controlled transport and/or release of drugs and chemicals, biomedicine, sensing, development of smart materials, stimuli-responsive materials, and nanocomposites [1–6]. The large applicability of nanostructured (metal) oxides is primarily due to the possibility of easily exerting a high level of control in the design of their morphology, in particular in terms of particle dimensions, shapes, and surface porosities, by means of proper synthetic routes and innovative templating processes [7–9]. However, exerting morphological control might be not always enough. In fact, even surface residual functionalities and surface reactivity play key roles in the determination of a nanomaterial's final properties [10]. Hence, for this reason, nanostructured (metal) oxides often require surface functionalization with specific chemical moieties (thus, eventually forming inorganic–organic hybrid systems) to further extend their field of application.

Nowadays, the research on this class of inorganic materials is still very dynamic, as documented by the recent achievements in the field, and it is expected to further increase in the coming years, with particular attention on the continuous search for more ecofriendly synthesis and templating approaches alternative to the traditional inorganic chemistry routes [11]. This Special Issue, entitled “New Advances into Nanostructured Oxides”, is specifically dedicated to the recent advancements in the design of the most promising nanostructured (metal) oxides and their technological application. Altogether, this Special Issue collects nine original research articles and three review papers, covering diverse nanostructured (metal) oxides and different technological applications.

Palma et al. [12] reported the effects of the experimental parameters over the solution combustion synthesis of Ce-doped Sr ferrates with the perovskite structure. The authors demonstrated that the full gelification of the *sol* is crucial to obtain single-phase perovskite materials, avoiding secondary phase formation and cerium oxide segregation, whereas the presence of secondary phases might induce the formation of Sr carbonate at the perovskite's surface that negatively affects the material's catalytic activity. Interestingly, the authors also evaluated that the presence of segregated cerium oxide has a positive effect on the availability of oxygen vacancies in low temperature conditions, thus favoring the interaction with polar substrates and bettering the material's catalytic activity. Concerning the thermocatalytic activity of these nanostructured materials, tests were performed against two different target substrates, namely: Orange II dye and Bisphenol A at alkaline pH (to avoid metal leaching from perovskites). Experimental results indicated that the best performances are obtained for samples containing the highest amount of segregated cerium oxide, probably due to the formation of a higher number of oxygen vacancies, which are available during the catalytic process.

The formation of heterojunctions between C_3N_4 and nanostructured (metal) oxides is a very promising technological solution to exploit sunlight (i.e., visible frequencies) in a multitude of photocatalytic processes, such as fuel production (i.e., CO_2 photo-reduction, water photo-splitting), and photo-degradation of contaminants in wastewater. In this



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context, Actis et al. [13] systematically investigated different synthesis techniques used to prepare bare C_3N_4 and combined C_3N_4/ZnO mixed systems. In particular, the authors compared different synthetic protocols, namely: (i) the formation of combined C_3N_4/ZnO mixed systems from supramolecular precursors, (ii) the direct growth of C_3N_4 on pre-formed ZnO nanoparticles, and (iii) the ultrasonic/mechanical solid-state mixing of both pre-formed C_3N_4 and ZnO nanopowders. Experimental data pointed out a trend existing between these three different synthetic processes. In detail, in the case of the synthesis from supramolecular precursors, a tighter association between the two phases forming the heterojunction has been recognized (with the appearance of adsorption bands in the visible region) coupled with low crystallinity. An opposite trend was registered in the case of ultrasonic/mechanical solid-state mixing. Crystalline materials with a modified morphology are obtained this way, with the consequent formation of a high-crystalline heterojunction characterized by lower visible light harvesting, deriving from the minor cooperation between the two components at the interface. Lastly, the approach based on C_3N_4 growth on pre-formed ZnO shows an intermediate condition in terms of both crystallinity and optical activity under visible frequencies. Chebanenko et al. [14] reported the production of ZnO-decorated graphitic carbon nitride ($g-C_3N_4$) nanocomposites synthesized following a three-step process, namely: (i) heat treatment of urea, (ii) ultrasonic exfoliation of the colloidal solution by introducing different ratios of ZnO precursor, and (iii) final thermal treatment. The authors reported a very interesting photocatalytic system by placing $g-C_3N_4$ in close contact with ZnO nanoparticles, since the formation of a heterojunction between these two components allows for the achievement of both excitation by visible light and a better charge separation with the formation of O-containing radicals. Nanocomposites were tested in the photocatalytic abatement of Methylene Blue dye as a target molecule under visible light. Experimental results indicated that the best performances were obtained for the nanocomposite containing 7.5 wt.% of ZnO. Moreover, Said et al. [15] reported the synthesis of a mesoporous $g-C_3N_4/CaO$ nanocomposite using a step-by-step ultrasonication technique. Furthermore, such a composite was successfully tested in the capture of Basic Fuchsin dye by means of a sorption mechanism. After the optimization of the sorption conditions, it was demonstrated that: (i) dye sorption is pH-independent, (ii) interaction between nanocomposite and dye follows the Freundlich model, (iii) sorption capacity increases with contact time (reaching an equilibrium after ca. 30 min), and (iv) maximum sorption capacity at the optimized condition is quantified as 813 mg/g. Furthermore, the authors experimentally demonstrated that the adsorption mechanism involves both hydrogen bonds and π - π stacking interactions.

Pereira et al. [16] reported the preparation of V-doped titania/ WO_3 (1:1 molar ratio) nanocomposites with different dopant concentrations and dispersed them in high-surface-area fibrous polymeric membranes obtained by means of electrospinning deposition. Evidence demonstrated that: (i) V^{5+} ions doped the atomic structure of titania (anatase phase), (ii) the titania crystallite sizes slightly increased by increasing the dopant concentration, and (iii) both W^{6+} and V^{5+} occupies Ti^{4+} vacancies in the anatase crystal lattice, allowing for a greater degree of local vibrations, which favors the occurrence of photocatalytic processes. Furthermore, the introduction of V into the TiO_2/WO_3 system caused a significant decrease in the titania bandgap as it generates an n-type extrinsic semiconductor. Electrospun fibrous membranes containing the nanocomposites were successfully tested in the photocatalytic abatement of Rhodamine B dye from the water environment under visible light. Experimental results indicated that the best performances (92% dye degradation after 2 h of visible light irradiation) are reached by the nanocomposite containing 5 wt.% of vanadium oxide, as it shows an improved photoresponse and charge separation efficiency, coupled with the presence of high active site density.

Peralta et al. [17] reported novel ecofriendly routes for the synthesis of nanostructured core-shell magnetic particles based on the polyol method and using biowaste-derived bio-based substances (BBSs) as both stabilizers and structure-directing agents. Subsequently, the covering of such BBS-stabilized magnetite nanoparticles with either mesoporous silica shell

or titanium dioxide was performed by means of a sol–gel method carried out in alkaline environment. Experimental results evidenced that the size/shape and the aggregation of the magnetite nanoparticles strongly depend on the starting BBS concentration (the higher the concentration of BBS, the smaller the sizes of the magnetite nanoparticles). Additionally, the presence of BBS is also crucial concerning the growth of both the mesoporous silica shell and the homogeneous titania shell, probably due to interactions involving the carboxylic groups of BBS. Such core–shell systems were successfully tested as nanocarriers of ibuprofen and adsorbing agents against Methylene Blue dye from aqueous solution, and as photocatalysts in the degradation of Methylene Blue dye. In particular, the mesoporous silica core–shell systems show an ibuprofen loading capacity of 13% and a very fast adsorption capacity of Methylene Blue dye, achieving 76% of dye removal within the first 15 min, whereas the titania core–shell systems show a photocatalytic degradation efficiency against Methylene Blue dye, analogous to bare titania. This last result is very surprising (and potentially a breakthrough), as the direct contact between magnetite and titania typically brings an unfavorable heterojunction, which accelerates the recombination of the electron–hole pairs and weakens the photocatalytic activity of the catalyst.

Dekyvere et al. [18] reported a novel strategy for the fabrication of nano zero-valent-iron (nZVI) carbon-based mesoporous materials derived from iron-containing metal-organic frameworks (MOFs) using zinc oxide nanorods as sacrificial nuclei. Here, the breakthrough idea is the utilization of the nanostructured zinc oxide under the shape of nanorods (i.e., aspect ratio 10) as sacrificial consumable nuclei for shaping the final highly porous materials (with specific surface area in the 185–270 m²/g range). The mesoporous materials thus obtained were tested as adsorbing agents against Methylene Blue dye, reaching an impressive sorption of 78% after only 2 min and close to total sorption (99%) after 6 min. The best-performing system also showed excellent recyclability, with 99% of abatement after 60 min of contact time for 10 consecutive cycles. As highlighted by the authors, the high number of mesopores produced by the sacrificial zinc oxide rods significantly enhanced the adsorption capability of the nanomaterial by increasing the contact area with the adsorbate. Furthermore, this innovative strategy opens the possibility of exerting further control over the pore size when forming the final porous material by changing the morphology of the starting nanostructured sacrificial nuclei.

Newar et al. [19], instead, tested the use of different commercial (metal) oxide nanoparticles as sorbing systems against low specific activity ⁹⁹Mo radiotracer solution. The commercial (metal) oxides investigated were: silica, titania, zirconium oxide, cerium oxide, tin oxide, and mixed systems, such as an aluminosilicate, cerium aluminum oxide, aluminum titanium oxide, and cerium zirconium oxide. The authors evaluated the adsorption behavior under different experimental conditions (pH, initial concentration of Mo, contact time, and temperature). Experimental results showed that: (i) the optimum adsorption pH for all systems is pH 2–4, (ii) the Freundlich isotherm model fitted the experimental data (mainly physisorption), (iii) the maximum adsorption capacity at optimized conditions was registered by zirconium oxide (73 mg/g), followed by cerium oxide and titania. This study clearly demonstrates that the investigated nanostructured (metal) oxides showed higher static sorption capacities than conventionally used alumina (2–20 mg/g) and potentially opens up the possibility of further improving the sorption capacity of these systems by varying both morphologies and porosities of these nanostructured (metal) oxides.

Chang et al. [20] evaluated the possibility of using a metal matrix nanocomposite reinforced with titania nanoparticles towards a potential endodontic instrument using a co-deposition approach with pulse electroplating for dental applications. In this study, the authors registered that the electrodeposition of the nanocomposite produced a smooth sidewall and surface, thus maintaining structural integrity and revealing a promoted formability, whereas cytotoxicity tests revealed high cell viability, high cell proliferation behavior and excellent biocompatibility.

Sfamini et al. [21] contributed to this Special Issue with an interesting overview dealing with the surface modification of textile fabrics to confer specific implemented and new

properties by means of inorganic sol–gel approaches. In this review, different examples and methodologies based on sol–gel inorganic coatings for textile finishing are evaluated, considering a wide range of inorganic precursors and functional additives to fabricate textiles showing different/implemented properties. Moreover, with respect to conventional textile finishing processes, synthetic routes based on functional nanoparticles and nanosols represent a more ecofriendly and safe approach than the most commonly employed formulations containing harmful substances. In the present review, sol modification techniques and functional applications for textile materials are classified into three sections, properly discussed with examples taken from the literature. Inorganic protocols are organized into methods for improving wear resistance of textile fabrics, for UV protection textile finishing, and for antimicrobial textile finishing, with a further classification based on the active nanoparticles involved.

Scarpelli et al. [22] reviewed the recent advancements in the synthesis of nanostructured iridium oxide. Iridium oxide is a very peculiar (metal) oxide as it is characterized by showing metallic-type conductivity and also displaying a low surface work function (which is the energy required for moving an electron from the Fermi level to the local vacuum level), high chemical stability, and good stability under the influence of high electric fields. Iridium oxide can be synthesized as various nanostructures, which significantly affect its surface work function. In this regard, the authors provided a very interesting overview of the nanostructuring of iridium oxide, with a special emphasis on the different strategies to drive the synthesis toward specific nanostructures. In this context, the authors organized the text into four sections, dedicated to the description of the different synthesis methods to obtain spherical nanoparticles, one-dimensional nanostructures (e.g., nanotubes, nanorods, nanowires, and nanofibers), unusual shapes (e.g., urchin-like, and nanoneedles), and thin films.

Nisticò [23] reviewed the recent advances in the exploitation of naturally occurring clays (phyllosilicates), including more non-conventional applications. Within the entire review, the author analyzed clays' peculiar properties, such as their ability to exchange (capture) ions, their layered structure, surface area and reactivity, and their biocompatibility, pointing out the deep correlation existing between the field of application and the structure–property relationships involved. After providing an introduction mainly focused on the economic analysis of the global trade in clays, the review was organized into two main sections. Section I is dedicated to the classification of clays based on their structural and chemical composition, together with a schematic summary of the main relevant structure-induced properties, which are strongly correlated to the nature and quantity of chemical species at the interlayer, exchange capacity, interlayer thickness, surface area, and hydration/gel-forming capacity. Section II, instead, is dedicated to the analysis of the unconventional advanced uses of clays in technological fields of emerging interest, providing a further organization into biomedical applications (ranging from the development of scaffolds and drug delivery systems to cancer diagnosis and therapy), environmental applications (wastewater treatments and membrane technology), additive manufacturing, and sol–gel processes.

Personally, the hope is that readers will enjoy this Special Issue, now edited as a book. Many examples of interesting and challenging research are collected in this “scientific compilation”. In some cases, the focus was on the nanostructuring of (metal) oxides, in others, their exploitation towards target advanced applications, but the common thread remains the continuous progress of this important class of inorganic materials.

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