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Editorial

10th Anniversary of *Inorganics*: Inorganic Materials

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1. Introduction

To celebrate the 10th anniversary of the journal *Inorganics*, the "Inorganic Materials" section launched this Special Issue entitled "10th Anniversary of *Inorganics*: Inorganic Materials", which collected 25 interesting papers (i.e., 20 articles, 1 communication, and 4 reviews), thus becoming the second most valued Special Issue in terms of the number of published contributions to the journal *Inorganics* (the first Special Issue in the "Inorganic Materials" section,). Moreover, despite the fact that the "Inorganic Materials" section in *Inorganics* is very recent (i.e., the beginning of 2022), it has rapidly grown, becoming an important cornerstone of the journal. The reason for this positive result is the continuously growing demand for advanced functional inorganic materials in a large variety of technological fields and applications.

Furthermore, the recent and numerous public demonstrations in support of climate and ecological justice, and the energy crisis have revealed the actual importance of technological sustainability. The "Inorganic Materials" section in *Inorganics* strongly supports a transition towards a 'green' and sustainable future based on renewable energy and with closed life-cycles for all used materials. The aim of the "Inorganic Materials" section is to serve as a medium for ground-breaking research that forms the fundamentals for new technologies still unknown today.

Therefore, this Special Issue is composed of a collection of several contributions mainly focused on the sustainable production of inorganic materials following alternative eco-friendly methods, new protocols and strategies for the reuse of materials (saving minerals and raw materials), the reduction in waste production, and environmental clean-up approaches.

The final aims of this Special Issue are to increase the knowledge of the latest advances, highlight challenges, address unresolved issues, and present newly emerging areas of interest involving the sustainable use of inorganic materials.

Prior to proceeding with the overview of the contributions, the Guest Editors would like to thank all the reviewers who spent their valuable time thoroughly reviewing and improving the articles published in this volume. We also sincerely thank all the authors for choosing "Inorganics Materials" as the section in which to publish their excellent science.

2. An Overview of Published Articles

As expressed above, the scope of this collection covers the entire focus area where inorganic materials can play a key role in order to reach a sustainable future, and this

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is exemplified by the various topics covered by the 25 articles published in this Special Issue. This section provides a brief overview of the contributions, organizing them into discreet subsections that include: sustainable synthesis, surface modifications, structural properties and reactivity, environmental remediation and catalysis, energy, composites, and nanomaterials against COVID-19 (Table 1).

Table 1. Correlation between subsections and contributions collected in the present Special Issue.

Subsections	Contribution No.	Title
Sustainable synthesis	1	Preparation of environmentally friendly BiVO4@SiO_2 encapsulated yellow pigment with remarkable thermal and chemical stability
	2	Microwave-mediated synthesis and characterization of $Ca(OH)_2$ nanoparticles destined for geraniol encapsulation
	3	Alternative synthesis of MCM-41 using inexpensive precursors for CO_2 capture
	4	Continuous and intermittent planetary ball milling effects on the alloying of a bismuth antimony telluride powder mixture
	5	Tetragonal nanosized zirconia: hydrothermal synthesis and its performance as a promising ceramic reinforcement
Surface modifications	6	Modification of graphite/SiO_2 film electrodes with hybrid organic–inorganic perovskites for the detection of vasoconstrictor Bisartan 4-butyl-N,N-bis{[2-(2H-tetrazol-5-yl)biphenyl-4-yl]methyl}imidazolium bromide
	7	Enhanced thermal stability of sputtered TiN thin films for their applications as diffusion barriers against copper interconnect
Structural properties and reactivity	8	Combination of multiple operando and in-situ characterization techniques in a single cluster system for atomic layer deposition: unraveling the early stages of growth of ultrathin Al_2O_3 films on metallic Ti substrates
	9	Gd_2O_3 doped UO_2(s) corrosion in the presence of silicate and calcium under alkaline conditions
	10	Incorporation of antimony ions in heptaisobutyl polyhedral oligomeric silsesquioxanes
	11	Hydrazine oxidation in aqueous solutions I: N_4H_6 decomposition
Environmental remediation and catalysis	12	Photocatalytic degradation of emerging contaminants with N-doped TiO_2 using simulated sunlight in real water matrices
	13	Synthesis of polystyrene@TiO_2 core–shell particles and their photocatalytic activity for the decomposition of methylene blue
	14	Method for decontamination of toxic aluminochrome catalyst sludge by reduction of hexavalent chromium
	15	Hydrogen incorporation in $Ru_xTi_{1-x}O_2$ mixed oxides promotes total oxidation of propane
	16	Superoxide radical formed on the TiO_2 surface produced from $Ti(OiPr)_4$ exposed to H_2O_2/KOH
Energy	17	Binder-free $CoMn_2O_4$ nanoflower particles/graphene/carbon nanotube composite film for a high-performance lithium-ion battery
	18	Hydrogen storage properties of economical graphene materials modified by non-precious metal nickel and low-content palladium
	19	Integration of CO_2 capture and conversion by employing metal oxides as dual function materials: recent development and future outlook
	20	ZnO-doped CaO binary core-shell catalysts for biodiesel production via Mexican palm oil transesterification

Table 1. *Cont.*

Subsections	Contribution No.	Title
Composites	21	Basalt-fiber-reinforced phosphorus building gypsum composite materials (BRPGCs): an analysis on their working performance and mechanical properties
	22	The mechanical properties of geopolymers from different raw materials and the effect of recycled gypsum
	23	How to address flame-retardant technology on cotton fabrics by using functional inorganic sol–gel precursors and nanofillers: flammability insights, research advances, and sustainability challenges
Nanomaterials against COVID-19	24	Nanomaterials used in the preparation of personal protective equipment (PPE) in the fight against SARS-CoV-2
	25	Emerging nanomaterials biosensors in breathalyzers for detection of COVID-19: future prospects

2.1. Sustainable Synthesis

The encapsulation of chemicals is an area of research undergoing rapid growth, as it can be used for improving the efficiency, stability, compatibility, safety, and the delivery of end products, thus, allowing their use into a multitude of applications [1,2]. Chen et al. (Contribution 1) reported the encapsulation of $BiVO_4$, a brilliant yellow pigment characterised by having a poor thermo-chemical stability, in a SiO_2 matrix with the formation of a core-shell structure following a sol–gel process, evaluating the effects due to both pre-treatment conditions of the $BiVO_4$ dispersion, and the calcination temperature (350–800 °C) on the phase composition, morphology, and colour-rendering properties. The resulting encapsulated pigment showed comparable chromatic parameters to pure $BiVO_4$, coupled with an enhanced thermal stability (up to 700 °C), resistance against acid corrosion, and good compatibility in PP matrix. Tryfon et al. (Contribution 2) evaluated the possibility of encapsulating geraniol in hydrophobic $Ca(OH)_2$ nanoparticles coated with oleylamine following a one-step microwave-assisted synthesis. The results indicated an efficient encapsulation and loading of geraniol, a release rate of geraniol which can be modulated by varying the pH and temperature, and an antifungal inhibition activity against *B. cinerea*.

Another interesting field of research related to inorganic materials is the development of substrates for the capture and storage of CO_2 [3]. In this context, the use of porous materials as CO_2 sorbents is gaining substantial attraction due to many advantages, such as the low energy requirements for the adsorbent regeneration, high adsorption capacity, and selectivity for CO_2. Among the different systems proposed for this purpose, mesoporous SiO_2 has emerged as particularly noteworthy candidate, due to its well-defined pore structures, high surface area, and chemical surface composition suitable for functionalisation with reactive species selective for the CO_2 chemisorption. Aquino et al. (Contribution 3) reported the synthesis of an MCM-41 SiO_2 starting from low-cost industrial sources of silicon and surfactants. Templates were removed by either oxidant thermal treatments or simple washing steps. Finally, the surface of porous SiO_2 particles was modified by grafting with 3-aminopropyltrimethoxysilane to enhance the CO_2 adsorption capability. The results indicated that: (i) silanol groups are retained under mild conditions, (ii) all amino-functionalised materials showed performances as CO_2 adsorbents comparable to those reported in the literature, with better performance for materials with higher concentration of silanol groups, and (iii) chemisorbed gas is retained, thus suggesting the potential of these inorganic materials for the CO_2 storage.

Samourgkanidis et al. (Contribution 4) investigated the effects of continuous and in-steps mechanical alloying of a bismuth antimony telluride ($Bi_{0.4}Sb_{1.6}Te_{3.0}$) powder mixture via the mechanical planetary ball milling process as a function of milling time and powder mixture amount, and the thermoelectric properties of the alloys obtained at optimised conditions. Because of the mixture's high agglomeration tendency, the results revealed a significant difference in the alloying process in terms of milling time and powder mixture quantity, varying the ball milling process. Regarding the thermoelectric properties of the produced powders, the results revealed a very good thermoelectric profile, consistent with the literature.

ZrO_2 is one of the most studied and industrially applied metal oxides extensively exploited mostly in gas sensing and in biomedicine. Most of the properties of ZrO_2 are strongly influenced by its crystalline organization and the consequent interphase transformation [4]. In this context, Liu et al. (Contribution 5) reported the synthesis of a pure tetragonal phase ZrO_2 using a hydrothermal route in the presence of propanetriol as additive, finding that an appropriate amount of propanetriol was favourable for the generation of the pure tetragonal-phase, whereas the increment of the hydrothermal temperature gradually transformed the monoclinic phase into the tetragonal phase. Interestingly, ultrasonication and mechanical stirring influenced the particle size and distribution, whereas the addition of dispersant effectively alleviated the occurrence of agglomeration phenomena. The resulting nanoparticles were introduced into a 3Y-ZrO_2 (3:1) matrix to produce high-performance ZrO_2 nanopowders with improved flexural strength.

2.2. Surface Modifications

The majority of the electrochemical methods for the modification of electrodes needs the growth of nanostructured porous materials to enhance and increase the electroactive surface area and to improve their mechanical strength and chemical stability [5]. In fact, by using a modifier, it is possible to dramatically improve both the sensitivity and selectivity of an electrode. Papathanidis et al. (Contribution 6) reported the surface functionalisation of a graphite paste/SiO_2 film electrode with a hybrid organic–inorganic perovskite semiconductor to fabricate a promising, sensitive sensor for the vasoconstrictor, bisartan BV6 (an angiotensin II receptor blocker). The perovskite-modified film electrode exhibits an enhanced electrocatalytic activity towards the oxidation of BV6 with a relatively low LOD, high reproducibility, and stability towards BV6 determination.

Interconnect materials (e.g., Cu) are favourable substrates for integration circuits, owing to their high resistance to electro-migration and low electrical resistivity. However, the electrical performance of these circuits is severely damaged/degraded since Cu diffuses into the Si/SiO_2 substrates, thus refractory metal nitrides have been used as diffusion barriers in Cu metallization [6]. Aljaafari et al. (Contribution 7) investigated the deposition of TiN thin film on Si/SiO_2 substrates using a direct current sputtering technique and its application as a diffusion barrier film against Cu interconnect material. The results showed that TiN film can be successfully used as the diffusion barrier for metallization in Cu up to a temperature of 700 °C, whereas at higher temperatures, the diffusion of Cu through the TiN film barrier occurred, with formation of various copper silicide phases.

2.3. Structural Properties and Reactivity

Fundamental research focused on the structure–reactivity relationship in inorganic materials is a very important activity for favouring the integration of this class of materials into different technological fields of emerging interest. For instance, Morales et al. (Contribution 8) reported a new ultra-high vacuum cluster tool to perform systematic studies of the early growth stages of atomic layer-deposited ultrathin Al_2O_3 films on metallic Ti substrates following a surface science approach combining both operando and in situ characterisation techniques. The role of the metallic substrate at both low- and high-temperature conditions has been discussed, considering the hetero- and homo-deposition growth regimes, thus favouring the optimisation of the deposition process, and decreasing the amount of wasted precursor and associated costs. Interestingly, Garcia-Gomez et al. (Contribution 9) investigated the anodic reactivity of UO_2 (i.e., radionuclides are usually located within a UO_2 matrix) and Gd_2O_3-doped UO_2 by electrochemical methods in slightly alkaline conditions in the presence of both silicate and calcium ions. The results showed that both Gd_2O_3 doping and the presence of silicate and calcium in solution are factors that decrease the reactivity of UO_2, which is beneficial for the assessment of repository safety of the spent nuclear fuel, as an important fraction of the radionuclide release would be inhibited. Lastly, Marchesi et al. (Contribution 10) reported the direct incorporation of Sb(V) ions into a polycondensed silsesquioxane (POSS) network based on heptaisobutyl POSS units through a corner-capping reaction carried out under mild experimental conditions, potentially exploitable as novel flame-retardant for polymeric composites.

Regarding the reactivity of inorganic compounds, Breza et al. (Contribution 11) investigated the oxidation mechanism involving a mixture of non-labelled and ^{15}N-labelled hydrazine in an aqueous solution to N_2 molecules, identifying the formation of N_4H_6 intermediate molecules, which decompose following a complex pathway involving different energetically favoured reactions.

2.4. Environmental Remediation and Catalysis

One of the strategies largely studied and adopted to effectively degrade organic pollutants in contaminated water is the employment of photocatalysts [7]. Gaggero et al. (Contribution 12) investigated the photodegradation performances of N-doped TiO_2 photocatalysts synthesized through both the sol–gel and hydrothermal methods with enhanced absorption of visible light for the abatement of some representative emerging contaminants (i.e., benzotriazole, bisphenol A, diclofenac, and sulfamethoxazole). Experiments conducted solely with the visible portion of sunlight exhibited a noticeable advantage in the use of N-doped materials and a sensitive efficiency of the photocatalysts produced through the sol–gel method, both in ultrapure and real water matrices.

Another important parameter which can dramatically affect the photocatalytic efficiency of TiO_2 is the tendency of nanoparticles to agglomerate. To solve this issue, TiO_2 particles have been immobilized on polymer substrates, finding a further difficulty in obtaining uniformly sized particles due to rapid sol–gel reaction rates of TiO_2 precursors. In their study, Toyama et al. (Contribution 13) explored the growth of homogeneous PS@TiO_2 core-shell particles following a sol–gel synthesis. The results showed that the PS@TiO_2 core–shell particles exhibited superior photo-activity against methylene blue than that of a comparable commercial reference sample.

Interestingly, Pyagay et al. (Contribution 14) investigated the neutralization of the harmful effects of aluminochrome catalyst sludge (for the presence of hexavalent chromium), a waste product from the petrochemical process of dehydrogenation of lower paraffins to C3–C5 olefins. In the present study, the reduction of hexavalent chromium was carried out with different reagents: Na_2SO_3, $FeSO_4$, $Na_2S_2O_3$, and $Na_2S_2O_5$, finding that sodium metabisulfite ($Na_2S_2O_5$) is the most preferred reagent working at a neutral pH, precipitating chromium in the form of hydroxide, thus saving the use of concentrated sulfuric acid and the additional precipitant reagents more commonly adopted.

Furthermore, Wang et al. (Contribution 15) reported a synthetic approach for the hydrogenation of mixed RuO_2/TiO_2 metal oxides, varying the oxide compositions. The effectiveness of the hydrogen insertion in the mixed oxide lattice has been evaluated by measuring the catalytic activity against the total oxidation of propane, reporting that after treating metal oxides with hydrogen the highest activity is encountered for compositions where both Ru and Ti have similar concentrations, whereas in the absence of the hydrogen treatment, the higher the Ru concentration the higher the activity. These results demonstrated that hydrogen insertion affects the electronic structure of the mixed RuO_2/TiO_2 metal oxides that is expected to be responsible for the improved catalytic activity. Samoilova et al. (Contribution 16) contributed a study dealing with the formation of superoxide radicals by treating $Ti(OR)_4$ alkoxides with H_2O_2 in the presence of KOH. The use of EPR spectroscopic techniques revealed the stabilization of superoxide radicals near the potassium ion and its involvement in the formation of a strong hydrogen bond with the surface.

2.5. Energy

The considerable progress of human societies since the late part of the 19th century has strongly depended on fossil fuels, with consequently serious environmental pollution problems and the persistent risk of energy depletion. To overcome this issue, novel energy sources and devices for efficient energy storage and conversion are under investigation [8,9]. In their contribution, Tong et al. (Contribution 17) reported on the design of flexible films made with $CoMn_2O_4$ nanoflowers supported on graphene/carbon nanotube 3D networks by means of a filtration strategy followed by a thermal treatment process. These films were deposited onto Ni foams without using binders and were successfully tested as electrodes in Li-batteries. Instead, Chen et al. (Contribution 18) investigated the hydrogen storage capacities of a Ni/Pd co-modified graphene material obtained via the solvothermal route, showing an excellent hydrogen storage performance due to the synergistic hydrogen spill-over effect of the Pd–Ni bimetal.

Tan et al. (Contribution 19) analysed the scientific literature describing the use of mixed metal oxides as dual function materials able to perform both CO_2 capture and CO_2 conversion. The authors recognised that the effectiveness of CO_2 capture and conversion depends on different factors, such as the basicity of the materials, surface area and porosity, crystallite size and dispersion of active sites, reducibility of the active metals, and availability of oxygen vacancies.

Arenas-Quevedo et al. (Contribution 20) investigated the catalytic production of biodiesel (i.e., a sustainable fuel) from Mexican palm oil in the presence of methanol using binary core-shell catalysts made by CaO and ZnO. During the optimisation process, the authors found that several factors (e.g., surface basicity, ZnO content, phase compositions, thermal treatment conditions) might influence the quality of the biodiesel produced.

2.6. Composites

Even in the field of composites, inorganic materials can play a crucial role, enhancing the mechanical properties of the composites or introducing specific properties and abilities [10,11]. For example, Wu et al. (Contribution 21) reported the preparation of a phosphorus-building gypsum composite reinforced with basalt fibres, registering a mechanical improvement in the composite due to the addition of the basalt fibres. However, even if the addition of fibres in the matrix promotes the mechanical properties, there is an adverse effect in terms of working performance (i.e., decrease in fluidity and setting time), thus, the authors evidenced that there is a trade-off between these two important aspects that should be considered for choosing the amount and length of the basalt fibres. Korhonen et al. (Contribution 22) investigated the mechanical response of geopolymers obtained from different raw materials (thus, with a different composition), evaluating the effect of the addition of recycled gypsum on these. The results indicated that the chemical composition of the raw materials had a significant impact on the properties of geopolymers. Furthermore, recycled gypsum affected the setting time of the geopolymers, depending on the calcium content, whereas it had no effect on the total shrinkage of the geopolymers.

Trovato et al. (Contribution 23) analysed the scientific literature describing the latest advances in the use of inorganic fillers and sol–gel-based flame-retardant technologies for textile treatments, with a clear focus on the cotton matrix. In this review, the enhanced safety of inorganic functional fillers with respect to their organic counterpart was evidenced, also providing some perspectives on the use of inorganic flame-retardant solutions coupled with environmentally suitable molecules, in line with the 'green chemistry' principles.

2.7. Nanomaterials against COVID-19

The coronavirus (COVID-19) pandemic arrived like a storm in our society, becoming one of the greatest global crises in recent history, touching many different aspects of our daily living. Apart from the health risks due to COVID-19 disease, what was really shocking was the lack of comprehensive strategies, plans, and toolboxes to manage COVID-19 by the governments of the entire world [12]. To hopefully avoid further serious situations like the ones that happened during the last pandemic, everyone has to try to contribute to this issue. Hence, even the field of inorganic chemistry can positively contribute against the COVID-19 disease, proposing interesting technological solutions involving inorganic materials. This is, for instance, the case of the review paper written by De Luca et al. (Contribution 24), where the key role played by nanomaterials to support the fight against COVID-19 was analysed. In particular, in this work, the authors reported the more representative examples of available personal protective equipment (e.g., masks and fabrics, sensors) involving the use of nanomaterials, explaining their mechanisms of action. Additionally, Rajendrasozhan et al. (Contribution 25), in their review paper, analysed the scientific literature describing the recent advancements in the potential use of integrating nanomaterial-based biosensors within breathalysers to favour the rapid detection of COVID-19, highlighting their principles, applications, and implications.

3. Conclusions

With this Special Issue "10th Anniversary of *Inorganics*" published in "Inorganics Materials" section, and also published as a book, the Editors hope that the high quality of the contributions collected here will receive the visibility and attention they deserve. These would help readers to increase their knowledge in the field of inorganic materials, and be a new source of inspiration for novel, focused investigations.

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List of Contributions

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