

# Development of Hybrid Titanium Oxide-based Systems for the Surface Stabilization of Reactive Oxygen Radicals

Claudio Imparato\*, Jessica Passaro, Aurelio Bifulco, Francesco Branda, Domenico Pirozzi, Antonio Aronne

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale (DICMaPI), Università di Napoli Federico II, P.le Tecchio 80, 80125 Naples, Italy  
[claudio.imparato@unina.it](mailto:claudio.imparato@unina.it)

Hybrid materials based on amorphous titanium or zirconium oxide with specific organic ligands show oxidative activity toward organic pollutants in the dark, owing to the generation and unusual long-term adsorption of superoxide radical anions on their surfaces. Here an overview of perspectives for the development of these materials and their processing towards technological applications is presented, focusing on the TiO<sub>2</sub>-acetylacetonate system. First, the tuning and optimization of the sol-gel synthesis conditions is discussed, aimed at yielding the desired products, such as chemical gels or stable sols. Then the thermal stability of the hybrid dried gels is assessed, in relation to their ability to form superoxide radicals. Finally, electrospinning is introduced as an efficient and ecofriendly technique to support the xerogel powders embedding them in a porous nanofiber polymer network. The preliminary characterization of the electrospun composite polyvinylpyrrolidone-hybrid TiO<sub>2</sub> reveals potentialities for the realization of air filters or antimicrobial gauzes.

## 1. Introduction

Reactive oxygen species (ROS) can play a fundamental role in the contrast to environmental pollution and infectious diseases, since they trigger the degradation of contaminants in water or air (through Advanced Oxidation Processes) as well as the inactivation of bacteria and viruses (Iervolino et al., 2020). The production of ROS without the use of radical initiators and their stabilization are a complex challenge because of their high reactivity and short lifetime. Metal oxide semiconductors such as titanium dioxide (TiO<sub>2</sub>) are able to generate superoxide radical anions (O<sub>2</sub><sup>•-</sup>) and hydroxyl radicals (•OH) following proper activation, in particular light irradiation (photocatalytic mechanism), or thermal treatment in reducing conditions (Hayyan et al., 2016). Achieving this aim without the need for continuous irradiation or harsh pretreatments would give clear advantages for practical applications of ROS, for example in filtering membranes or self-cleaning coatings in any environment with low/absent illumination.

In the last years, TiO<sub>2</sub>-acetylacetonate (TiO<sub>2</sub>-acac, Sannino et al., 2015a) and ZrO<sub>2</sub>-acetylacetonate (ZrO<sub>2</sub>-acac, Sannino et al., 2014) hybrid materials synthesized by a sol-gel route by some of the authors, demonstrated the uncommon ability to spontaneously generate superoxide radicals on their surfaces in contact with air and stably adsorb them for exceptionally long times (i.e., years). These amorphous gels dried at low temperature have shown remarkable performance in the oxidative degradation of aqueous organic pollutants without any light irradiation: phenanthrene (Sannino et al., 2014; Sannino et al., 2015a), 2,4-dichlorophenol (Aronne et al., 2017) and chlorophenoxyalkanoic acid herbicides (Sannino et al., 2015b; Pirozzi et al., 2020). The formation and regeneration of O<sub>2</sub><sup>•-</sup> radicals by reduction of adsorbed O<sub>2</sub> is strictly related to the presence of metal-acac charge transfer complexes on the surface, however its precise mechanism is still under study. The oxidative catalytic activity, also due to •OH radicals subsequently produced in water, likely derived from O<sub>2</sub><sup>•-</sup> (Pirozzi et al., 2020), make these materials promising not only for water decontamination, but also for air purification and the elimination of microorganisms.

The design and fabrication of systems based on the hybrid oxides suitable for such applications involve both chemistry and engineering challenges that can be faced grounding in the sol-gel technique, which represents a versatile tool with a good scale-up potential (Iervolino et al., 2020). For example, the procedure leading to

homogeneous gelation can produce xerogels with adequate granulometry and mechanical resistance for a continuous flow process in a packed bed, but it is also adaptable for the preparation of monoliths or aerogels. On the other hand, it could be convenient to support the hybrid material on a suitable substrate. Stable  $\text{TiO}_2$ -acac sols, obtained by tuning the reaction parameters, can be deposited on different surfaces by means of techniques such as dip- or spin-coating, low-temperature spray coating or sol impregnation.

Another attractive strategy to support active particles is their embedding in a nanofiber network by electrospinning, a cost-effective and up-scalable technique. Composite nanofiber membranes of different polymers with  $\text{TiO}_2$  have been studied for sensing, photovoltaics, catalysis and photocatalysis, including air filtration, water purification and disinfection (Rodríguez-Tobias et al., 2019; Lee et al., 2018). Polyvinylpyrrolidone (PVP) is a particularly versatile and safe polymer, characterized by favorable interaction with various organic and inorganic compounds, solubility in water and many organic solvents, high biocompatibility and non-toxicity (Passaro et al., 2019). Thermal treated PVP-based electrospun mats were recently investigated by some of the authors for sound absorption (Del Sorbo et al., 2019), also showing water resistance and self-extinguishing capability when silica nanoparticles were used as filler and backbone in the polymer matrix (Passaro et al., 2019; Ciaburro et al., 2020; Giannella et al., 2020). PVP was often employed in the synthesis of titanium oxide as scaffold or template, then finally removed to obtain specific nanostructures, while the properties of PVP- $\text{TiO}_2$  composites were seldom explored (Lee et al., 2018; Shepa et al., 2020).

In this work the effect of some reaction conditions on the hydrolytic sol-gel synthesis of  $\text{TiO}_2$ -acac materials is discussed, evidencing how it can lead to gelation or sol stabilization. In environmental or catalytic applications, the hybrid materials might be exposed to relatively high temperatures, either during a process step (e.g. thermally activated reactions, regeneration treatments) or by some methods for the preparation of coatings and membranes (e.g. cold spray, reaching at least 200 °C, or the thermal treatment at 150-200 °C performed on PVP-based composites to provide water resistance). Therefore, the thermal stability of the hybrids is investigated here, with particular focus on the adsorbed superoxide radicals. Moreover, preliminary results about the electrospinning of PVP-based mats with a high content of hybrid  $\text{TiO}_2$  particles are presented.

## 2. Materials and methods

### 2.1 Sol-gel synthesis

The  $\text{TiO}_2$ -acac materials (HSGT, hybrid sol-gel titania) were prepared by a sol-gel route using Ti(IV) n-butoxide (97+ %), acetylacetone (2,4-pentanedione, Hacac, 99+ %), 1-propanol (99.8 %) and hydrochloric acid (all provided by Sigma-Aldrich) as previously described (Aronne et al., 2017). The procedure was carried out at room temperature. Briefly, a solution containing the Ti precursor, Hacac and 1-propanol was prepared under stirring, then a hydrolytic solution containing diluted HCl in deionized water and 1-propanol was added. A yellow colored sol or wet gel was obtained, according to the Ti concentration. The studied HSGT sample had molar ratios  $\text{Ti:Hacac:1-propanol:H}_2\text{O:HCl} = 1:0.4:5:10:0.02$ . After ageing, the gels were dried under airflow at 30–50 °C and the xerogel grains were ground in a mortar. A sample was further heated in air at 100, 150 or 200 °C for 1 h, then gradually cooled down to room temperature, to inspect the thermal behavior.

### 2.2 Preparation of electrospun composite PVP-HSGT

The electrospun solution was prepared by mixing an ethanol solution of polyvinylpyrrolidone (PVP, MW: 1,300,000 g/mol) with finely ground HSGT powder. The PVP and HSGT concentrations were respectively 10 and 20 wt%. After 1 h of stirring, the PVP-HSGT ethanol suspension was electrospun under a voltage of 40 kV at room temperature and humidity of  $45 \pm 10$  %. A flow rate of 0.010 mL/min was assured by the syringe pump; the fixed collection distance was 39 cm. To convey the electrospinning jet onto the collector, a copper foil was placed at the bottom of the chamber at the same potential of the needle nozzle. The as-prepared electrospun non-woven mats were dried out at 80 °C for 1 h and stored in a desiccator.

### 2.3 Characterization techniques

Fourier Transform infrared (FTIR) spectra were recorded using a Nicolet 5700 FTIR spectrometer (Thermo Fisher). The transmittance spectra of the HSGT powders were acquired mixing the sample in KBr pellets, those of electrospun mats by means of a single reflection Attenuated Total Reflectance (ATR) accessory, recording 32 scans with a resolution of  $2 \text{ cm}^{-1}$ . Electron Paramagnetic Resonance (EPR) spectra were acquired using a X-band (9 GHz) Bruker Elexys E-500 spectrometer. The xerogel powders and electrospun fibers were analyzed at room temperature, collecting 16 scans. The g values were evaluated by means of an internal standard,  $\text{Mn}^{2+}$ -doped MgO. Further experimental details were previously reported (Sannino et al., 2015a). Simultaneous Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) of the electrospun sample was performed on a TA Instruments SDT Q600, in nitrogen atmosphere, heating from 25 to 700 °C at a rate of 5 °C/min. Stereomicroscopy images were acquired by a Wild Heerbrugg microscope.

### 3. Results and discussion

#### 3.1 The sol-gel synthesis of TiO<sub>2</sub>-acac hybrid materials

The hydrolytic sol-gel route established for the synthesis of hybrid materials based on TiO<sub>2</sub> (Sannino et al., 2015a) or ZrO<sub>2</sub> (Sannino et al., 2014) with acetylacetonate as organic complexing ligand is a simple and reproducible one-pot procedure. Its conditions can be adapted to obtain specific products and optimized to further improve the cost-effectiveness and environmental sustainability. The preparation of the gels requires a limited amount of alcohol as solvent and is distinguished by high yields, as practically the total amount of metal precursor is converted into the oxide and there are no losses related to the recovery and washing of small particles. Moreover, the employed reagents are rather cheap. A cost analysis of the removal cycle of herbicides from water on ZrO<sub>2</sub>-acac was previously performed, estimating a specific cost of about 25 \$/kg for the large-scale production of the catalyst (Sannino et al., 2015b).

Homogeneous chemical gels are obtained at room temperature in a very short time (typically minutes). The drying step, performed at temperature not higher than 50 °C, removes the solvent from the gel structure and is crucial for the generation of the radicals on the surface by reduction of adsorbed O<sub>2</sub> (Pirozzi et al., 2020), so a full contact of the gel with air must be assured. As concerns the TiO<sub>2</sub>-acac system, it was verified that varying the initial acac/Ti molar ratio in the range from 0.5 to 0.25 does not produce significant changes in the properties of the amorphous xerogel (Imparato et al., 2017). From the TG analysis of samples prepared with different acac/Ti ratios the maximum effective amount of ligand retained in the structure is evaluated to be about 0.2 mol/mol Ti. Also a lower content (0.1 mol/mol Ti) results sufficient to yield a detectable amount of superoxide radical adsorbed on the surface, as revealed by the EPR spectrum (data not shown). However, a lower acac/Ti ratio implies higher condensation rate, and the process becomes so fast that the growth of the polymeric network (chemical gel) can be non-uniform. In this case the reaction rates have to be slowed down, which can be achieved by reducing the hydrolysis ratio (H<sub>2</sub>O/Ti molar ratio) from 10 to 4 or by lowering the Ti concentration (typically about 1 mol/L in the final solution). A small amount of HCl is usually added, acting as catalyst for the hydrolysis step and thus aiding a homogeneous condensation of the Ti-based clusters. Nonetheless, TiO<sub>2</sub>-acac hybrid gels can also be prepared at neutral pH, keeping the ROS generation ability. TiO<sub>2</sub>-acac sols stable for weeks or months are obtained in a range of conditions, as reported in a previous work dealing with their deposition on glass substrates and with the characterization of the resulting hybrid thin films (Addonizio et al., 2020). Owing to the excellent stabilizing effect of the acac ligand, hybrid sols can be prepared in ethanol or propanol, for example with [Ti] = 0.3 mol/L and Ti:acac:H<sub>2</sub>O molar ratio = 1:0.4:10, at pH 5-6, without the need for concentrated acids, usually required to prevent phase separation in TiO<sub>2</sub> colloids.

#### 3.2 Thermal stability of HSGT

Considering the possible exposure of the hybrid materials to relatively high temperatures during specific processing or functioning, it is important to know the effects of heating on their composition and properties. The FTIR spectra of HSGT samples heated at 100, 150 and 200 °C for 1 h are shown in Figure 1.

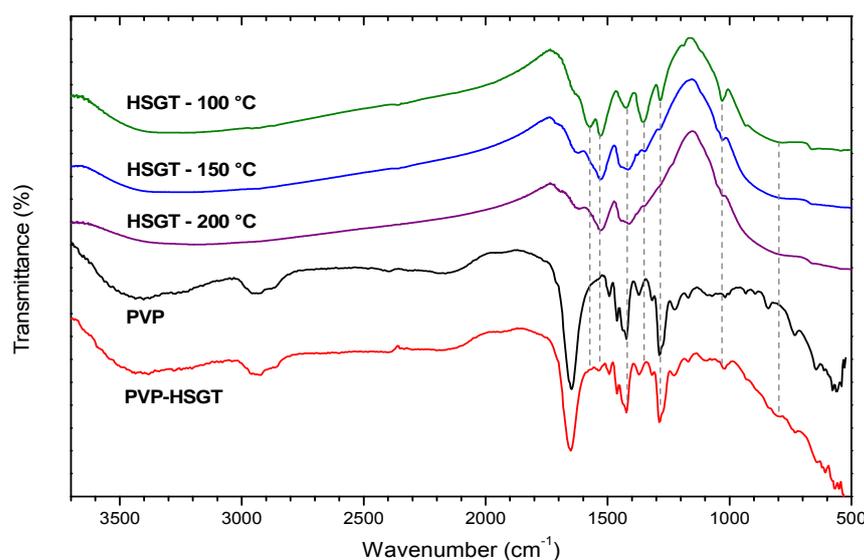


Figure 1: FTIR spectra of HSGT samples heated for 1 h at 100, 150 or 200 °C, electrospun PVP and composite PVP-HSGT mats (dotted lines indicate the main bands of TiO<sub>2</sub>-acac).

TiO<sub>2</sub>-acac materials are characterized by a series of IR bands in the 1000-1600 cm<sup>-1</sup> range, due to acac molecules coordinated to Ti ions, and by the broad lower frequency bands due to the Ti-O vibrations. The spectrum of the sample heated at 100 °C is coincident with that of the xerogel dried at 30 °C (Sannino et al., 2015a; Imparato et al., 2017), showing that its chemical structure is unaltered. After heating at 150 and 200 °C, although all the main bands associated with the organic component are preserved, some changes in their relative intensities can be spotted. In particular, the bands at 1575 and 1356 cm<sup>-1</sup>, attributed to stretching modes of the carbonyl groups of acac involved in bidentate Ti complexation, result weakened, which may indicate the breaking of some of the coordination bonds. Combined TGA and FTIR data showed that most of the acac is retained in the structure of the hybrid material even after heating up to 250 °C (Sannino et al., 2015a). This is in agreement with literature studies on the thermal decomposition of TiO<sub>2</sub>-acac xerogels (acac/Ti = 1), reporting that most of acac is volatilized over 200 °C as organic products (e.g. acetone and acetic acid) (Oja-Acik et al., 2007). The strong Ti-acac complexation stabilizes the ligand in the structure and reduces its thermal degradation rate, which is confirmed by the weight loss upon heating at 200 °C for 1 h, which is about 20 wt%, mainly due to adsorbed water and residual alcohol from the synthesis. However, the comparison of some degradation products is suggested by the color of the powders, turning from yellow to light brown after the treatments.

EPR spectroscopy provides information on the presence of radical species. The EPR spectrum of the HSGT xerogel heated at 100 °C (Figure 2) shows the two major components of the signal of superoxide radical adsorbed on TiO<sub>2</sub> surface (with g factor values 2.009 and 2.003), though its intensity is lower than on a dried sample (Pirozzi et al., 2020). Heating is expected to cause the desorption or conversion of O<sub>2</sub><sup>-•</sup>. Nonetheless, it was proved that the hybrid powders are able to regenerate the lost radicals by simple exposure to air (Pirozzi et al., 2020). Notably, even after the treatments at 150 and 200 °C the peak at g = 2.009 is still detectable, though overlapped with a single peak that grows with the temperature. This signal could be attributed to carbon-based radicals on some degradation product of the acac ligand. However, the partial modification of the organic component induced by heating does not seem to completely impede the formation of O<sub>2</sub><sup>-•</sup> on the hybrid surface.

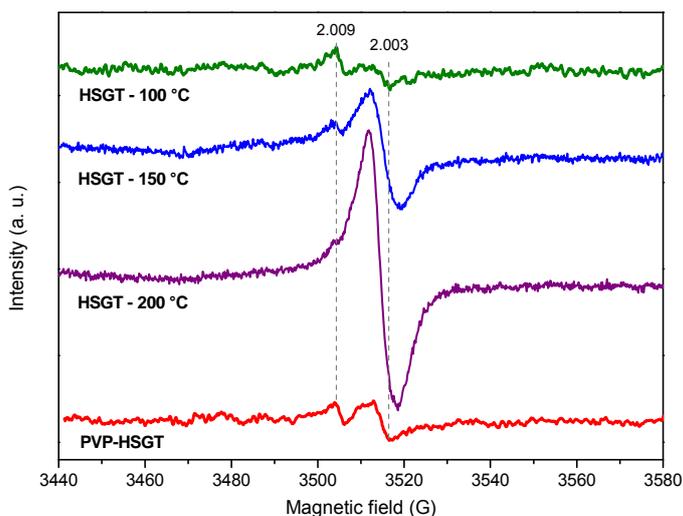


Figure 2: Room temperature EPR spectra of HSGT samples heated for 1 h at 100, 150 or 200 °C and electrospun PVP-HSGT mat (g values are indicated).

### 3.3 PVP-HSGT electrospun composite

Electrospinning of the suspension of TiO<sub>2</sub>-acac xerogel particles in PVP-ethanol solution produced a pale yellow composite mat, displayed in Figure 3a. In the stereomicroscope image (Figure 3b) it can be seen that HSGT particles (light dots) appear to be uniformly distributed throughout the polymer matrix. They are probably inserted between the fibers, being larger (tens of μm) than the average fiber diameter obtained for electrospun PVP in similar conditions (around 1 μm, Passaro et al., 2019). A strong interaction between surface hydroxyls of silica nanoparticles and the carbonyl groups of PVP was previously described (Passaro et al., 2019), suggesting the possibility of a similar interaction involving Ti-OH groups.

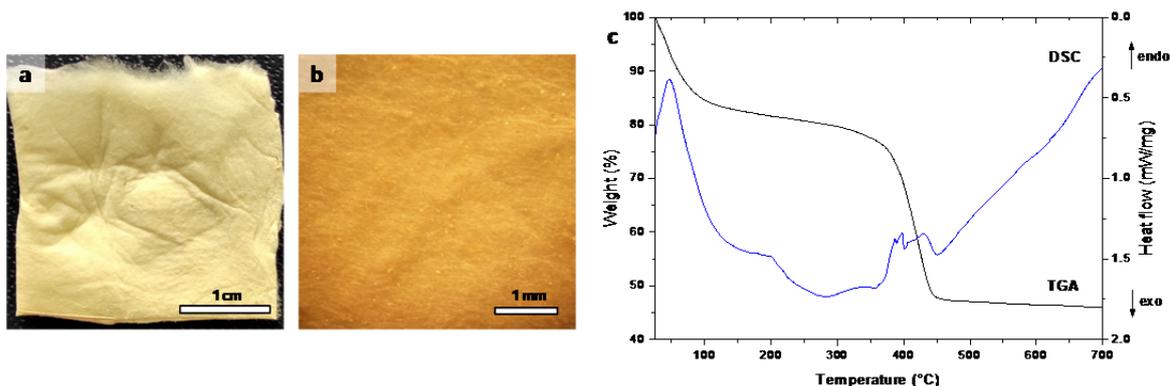


Figure 3: (a) Digital photograph and (b) stereomicroscope micrograph (40x) of a portion of the electrospun PVP-HSGT composite mat; (c) TGA and DSC curves of PVP-HSGT, recorded in nitrogen.

The ATR-IR spectrum of the composite mat (Figure 1) shows all the characteristic bands of PVP (Passaro et al., 2019). Unfortunately, most IR bands of the Ti-acac complex are overlapped with more intense PVP ones, thus they are hardly visible. Anyway, it is possible to observe the band at about  $1530\text{ cm}^{-1}$ , assigned to C=C stretching in the enolate form of acac, and an increased absorbance below  $800\text{ cm}^{-1}$ , confirming the presence of  $\text{TiO}_2$ -acac. The effective composition of the electrospun sample can be estimated by thermal analysis, which also provides information on the thermal stability and the interaction between the phases. The nominal  $\text{TiO}_2$ -acac content is 67 wt%, corresponding to about 44 wt%  $\text{TiO}_2$ , since the hybrid samples contain 30-40 wt% of organics and adsorbed water. The TG profile of as-prepared PVP-HSGT composite (Figure 3c) shows several stages of weight loss, although the degradation curve does not reveal significant differences with respect to the one of blank PVP fibers found in the literature (Passaro et al., 2019). Initial weight loss takes place at around  $80\text{ }^\circ\text{C}$  because of evolution of water and possibly residual ethanol from the electrospun PVP-based sample, hence confirming the hydrophilic character of the material and its swelling capability. This process is followed by a range of relatively constant weight. The thermal degradation of the electrospun fibers seems to start at around  $280\text{ }^\circ\text{C}$ , when also the removal of the majority of acac occurs (Sannino et al., 2015a), followed by a major weight loss ( $380\text{-}450\text{ }^\circ\text{C}$ ) when the main devolatilization arises. Above  $500\text{ }^\circ\text{C}$ , there is essentially no further weight loss, and the residual mass of 46 wt% is very close to the expected value. The DSC profile (Figure 3c) confirms a significant vaporization of water and residual solvent below  $100\text{ }^\circ\text{C}$ , observed as a broad endothermic peak. Besides, small endothermic effects appear at about  $180\text{ }^\circ\text{C}$ , likely due to the evaporation of bound water (i.e., adsorbed moisture) (Shepa et al., 2020), and at  $200\text{ }^\circ\text{C}$ , assigned to thermal cross-linking of the polymer chains (Hatch et al., 2019). Finally, the presence of endothermic peaks in the ranges  $300\text{-}350\text{ }^\circ\text{C}$  and  $370\text{-}450\text{ }^\circ\text{C}$  additionally confirms the occurrence of acac and PVP decomposition. The ROS production ability of the composite mat was verified by EPR. In the spectrum, shown in Figure 2, the two main components of the superoxide anion signal are still visible, despite the low intensity and a partially overlapped weak peak, attesting that after electrospinning and drying at  $80\text{ }^\circ\text{C}$  the embedded HSGT retains the capacity to form the radicals, which remain adsorbed on the exposed surfaces of the particles. This result hints at the likely oxidative activity of the PVP-HSGT mats. This activity could be enhanced using these composites in contact with air, that is, with large availability of  $\text{O}_2$  allowing the continuous generation of  $\text{O}_2^{\cdot-}$  with no need for light irradiation.

#### 4. Conclusions

The hydrolytic sol-gel procedure established for the synthesis of  $\text{TiO}_2$ -based hybrids is a straightforward and versatile process, which can be further improved towards a cost-effective larger scale production of granular solids and coatings. The paramount feature of these materials, i.e. the surface stabilization of superoxide radicals, is maintained even after heat treatments up to  $200\text{ }^\circ\text{C}$ , attesting the wide range of conditions in which their oxidative function can be exerted. Electrospinning was successfully applied to insert a high amount of  $\text{TiO}_2$ -acetylacetonate gel-derived particles (over 60 wt%) within a PVP nanofiber matrix. The radical stabilization ability was preserved on the so-obtained composite mats, foreshadowing potential applications based on ROS-mediated mechanisms. These promising results open the way to the design of electrospun membranes for the abatement of gaseous pollutants and antimicrobial bandages for wound dressing.

## Acknowledgments

The authors thank Prof. Gerardino D'Errico (University of Naples Federico II) for the access to EPR spectroscopy facilities.

## References

- Addonizio M. L., Aronne A., Imparato C., 2020, Amorphous hybrid TiO<sub>2</sub> thin films: The role of organic ligands and UV irradiation, *Applied Surface Science*, 502, 144095.
- Aronne A., Fantauzzi M., Imparato C., Atzei D., De Stefano L., D'Errico G., Sannino F., Rea I., Pirozzi D., Elsener B., Pernice P., Rossi, A., 2017, Electronic properties of TiO<sub>2</sub>-based materials characterized by high Ti<sup>3+</sup> self-doping and low recombination rate of electron–hole pairs, *RSC Advances*, 7, 2373–2381.
- Ciaburro G., Iannace G., Passaro J., Bifulco A., Marano D., Guida M., Marulo F., Branda F., 2020, Artificial neural network-based models for predicting the sound absorption coefficient of electrospun poly(vinyl pyrrolidone)/silica composite, *Applied Acoustics*, 169, 107472.
- Del Sorbo G.R., Truda G., Bifulco A., Passaro J., Petrone G., Vitolo B., Ausanio G., Vergara A., Marulo F., Branda F., 2019, Non Monotonous Effects of Noncovalently Functionalized Graphene Addition on the Structure and Sound Absorption Properties of Polyvinylpyrrolidone (1300 kDa) Electrospun Mats, *Materials*, 12, 108.
- Giannella V., Branda F., Passaro J., Petrone G., Barbarino M., Citarella R., 2020, Acoustic Improvements of Aircraft Headrests Based on Electrospun Mats Evaluated Through Boundary Element Method. *Applied Sciences*, 10, 5712.
- Hatch K.M., Hlavatá J., Paulett K., Liavitskaya T., Vyazovkin S., Stanishevsky A.V., 2019, Nanocrystalline Cellulose/Polyvinylpyrrolidone Fibrous Composites Prepared by Electrospinning and Thermal Crosslinking, *International Journal of Polymer Science*, 2019, 7103936.
- Hayyan M., Hashim M.A., AlNashef I.M., 2016, Superoxide Ion: Generation and Chemical Implications. *Chemical Reviews*, 116, 3029–3085.
- Iervolino G., Zammit I., Vaiano V., Rizzo L., 2020, Limitations and Prospects for Wastewater Treatment by UV and Visible-Light-Active Heterogeneous Photocatalysis: A Critical Review. *Topics in Current Chemistry*, 378, 7.
- Imparato C., Aronne A., Minieri L., D'Errico G., Pirozzi D., Sannino F., Pernice P., 2017, Sol–Gel Synthesis and Characterization of Hybrid TiO<sub>2</sub>-Acetylacetonate Materials, *Advanced Science Letters*, 23, 5912–5915.
- Lee C., Javed H., Zhang D., Kim J., Westerhoff P., Li Q., Alvarez P.J.J., 2018, Porous Electrospun Fibers Embedding TiO<sub>2</sub> for Adsorption and Photocatalytic Degradation of Water Pollutants, *Environmental Science & Technology*, 52 (7), 4285–4293.
- Oja Açıık I., Madarász J., Krunks M., Tonsuaadu K., Janke D., Pokol G., Niinistö L., 2007, Thermoanalytical studies of titanium(IV) acetylacetonate xerogels with emphasis on evolved gas analysis. *Journal of Thermal Analysis and Calorimetry*, 88, 557–563.
- Passaro J., Russo P., Bifulco A., De Martino M.T., Granata V., Vitolo B., Iannace G., Vecchione A., Marulo F., Branda, F., 2019, Water resistant self-extinguishing low frequency soundproofing polyvinylpyrrolidone based electrospun blankets, *Polymers*, 11, 1205.
- Pirozzi D., Imparato C., D'Errico G., Vitiello G., Aronne A., Sannino F., 2020, Three-year lifetime and regeneration of superoxide radicals on the surface of hybrid TiO<sub>2</sub> materials exposed to air, *Journal of Hazardous Materials*, 387, 121716.
- Rodríguez-Tobías H., Morales G., Grande D., 2019, Comprehensive review on electrospinning techniques as versatile approaches toward antimicrobial biopolymeric composite fibers, *Materials Science and Engineering: C*, 101, 306–322.
- Sannino F., Pirozzi D., Vitiello G., D'Errico G., Aronne A., Fanelli E., Pernice P., 2014. Oxidative degradation of phenanthrene in the absence of light irradiation by hybrid ZrO<sub>2</sub>-acetylacetonate gel-derived catalyst, *Applied Catalysis B: Environmental*, 156–157, 101–107.
- Sannino F., Pernice P., Imparato C., Aronne A., D'Errico G., Minieri L., Perfetti M., Pirozzi D., 2015a, Hybrid TiO<sub>2</sub>-acetylacetonate amorphous gel-derived material with stably adsorbed superoxide radical active in oxidative degradation of organic pollutants, *RSC Advances*, 5, 93831–93839.
- Sannino F., Pernice P., Minieri L., Camandona G.A., Aronne A., Pirozzi D., 2015b, Oxidative Degradation of Different Chlorinated Phenoxyalkanoic Acid Herbicides by a Hybrid ZrO<sub>2</sub> Gel-Derived Catalyst without Light Irradiation, *ACS Applied Materials & Interfaces* 7, 256–263.
- Shepa I., Mudra E., Pavlinak D., Antal V., Bednarcik J., Mikovic O., Kovalcikova A., Dusza J., 2020, Surface plasma treatment of the electrospun TiO<sub>2</sub>/PVP composite fibers in different atmospheres, *Applied Surface Science*, 523, 146381.