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Editorial

Metallic or Metallic Oxide (Photo)catalysts for Environmental Applications

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During the last century, industrialization intensified in a growing number of countries around the world, and in various industries, particularly in the chemical, pharmaceutical, cosmetics, horticulture, food, and petroleum sectors. This intense industrialization has resulted in the emergence of a large variety of organic pollutants, such as dyes, aromatics, pesticides, solvents, EDCs (Endocrine Disrupting Chemicals), and PPCPs (Pharmaceuticals and Personal Care Products). Additionally, various litter is produced as wood or forest residues, waste from food crops (wheat straw, bagasse), horticulture (yard waste), or human waste from sewage plants. All this pollution and waste need to be treated and valorised in order to maintain a safe and clean environment. Numerous innovative catalytic and photocatalytic processes are being developed to eliminate these by-products of our industries. In this Special Issue, we are dealing with innovative (photo)catalytic processes for environmental applications based on metallic or metallic oxide materials. The papers concern either the (photo)catalytic transformation of various waste to produce high-value chemicals, or the (photo)catalytic degradation of pollutants. Advances highlighted in the issue are summarized in the following paragraphs focusing on these two main topics: photocatalysis for pollutant removal and catalytic valorisation of biomass.

1. Photocatalysis for pollutant removal

In this collection of articles, four different photocatalyst materials were explored for pollutant degradation: TiO_2, ZnO, SnO_2, and BiOX (X = Cl, Br, I).

In Kang et al. [1], titania nanopowders were produced with many defects (such as vacancies, Ti^{3+}, N lattice heteroatoms) to increase their photocatalytic performance in the visible region for the degradation of malachite green (MG) and the disinfection of *Geobacillus stearothermophilus*. These defects were produced thanks to sensitization by (a) high temperature nitridation in NH_3 atmosphere and (b) reduction in H_2 atmosphere. It results in two types of materials: N-doped TiO_2, showing absorption in visible range, and C-doped TiO_2, with no visible absorption. As expected, the N-TiO_2 sample showed the best performance under visible light illumination. The MG solution was completely decolorized after 3 h of illumination, while the endospore suspension was inactivated by 70% after 5 h. It should be underlined that by contrast both commercial TiO_2 P25 and C-TiO_2 showed no activity towards the inactivation of the endospore suspension in the presence of visible light.

N-doping of TiO_2 was also performed by hydrothermal synthesis and using urea as the N source [2]. The research results confirmed that N doping had been successfully performed, which shifted TiO_2 absorption into the visible region, allowing it to be active under visible irradiation. This photocatalyst was used for Pb(II) removal thanks to photo-oxidation under visible light to form PbO_2. The highest photocatalytic oxidation of 15 mg/L Pb(II) in 25 mL of the solution could be reached by employing 15 mg TiO_2 doped with

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10 wt.% of N, in 30 min and at pH 8. The stability of the removal activity was shown for three consecutive experiments. The highly effective process of Pb(II) photo-oxidation under benign conditions, producing less toxic and handleable PbO_2 with a recyclable photocatalyst, suggests an applicable method for Pb(II) remediation on an industrial scale.

A co-doping of titania with N and Fe has also given an increased pollutant removal rate under visible light. Indeed, Douven et al. [3] developed an ecofriendly synthesis of N,Fe-co-doped TiO_2 thanks to a sol-gel process in water. Crystalline materials were obtained without any calcination step and all samples displayed a higher visible absorption and specific surface area than P25. The photoactivity was assessed with the powder samples on p-nitrophenol showing 65% degradation after 24 h of visible illumination. Coatings of these materials were performed on steel substrates and their activity was assessed also on p-nitrophenol under UV-A and on Rhodamine-B under LED light. Degradation activity was maintained on both molecules. The possibility of producing photocatalytic films without any calcination step that are active under low-energy LED light constitutes, also, a great step forward for an industrial depollution development.

The development of methods to produce different shapes of photocatalysts is also of interest for industrial applications. In particular, the shaping of titania coating on the inner surface of quartz tubes was successfully performed by Svetlov et al. [4]. In this case, the introduction of two-phase (gas–liquid) flow with the gas flowing in the middle of the tube and a thin liquid film of synthesis sol flowing near the hot tube walls allows a TiO_2 coating deposition. The liquid flow rate in the annular flow regime allows to control the coating thickness between 3 and 10 micron and the coating porosity between 10% and 20%. By increasing the liquid flow rate, the coating porosity can be substantially reduced. The coatings obtained were active in the reactions of photocatalytic decomposition of methylene blue and rhodamine B under UV light with no observed catalyst deactivation.

ZnO is also a semiconductor material which presents good photocatalytic property for pollutant removal. In Mahy et al. [5], a green sol-gel process was used to produce ZnO with many different morphologies. Crystalline ZnO materials were obtained without any calcination. The most important parameter controlling the shape and size was found to be pH, thanks to a DoE plan and statistical analysis of the results. The photoactivity study on a model pollutant (p-nitrophenol) degradation shows that the resulting activity is mainly governed by the specific surface area of the material. A comparison with a commercial TiO_2 photocatalyst (Evonik P25) showed that the best ZnO nanoparticles obtained can reach similar photoactivity.

Composite materials with two semiconductors are also developed to enhance the photoactivity. In Rogé et al. [6], ZnO/SnO_2 heterostructures were directly synthesized in macroporous glass fibres membranes for water treatment. Hydrothermal ZnO nanorods have been functionalized with SnO_2 using an atomic layer deposition (ALD) process. The covering of ZnO by SnO_2 controlled the resulting photoactivity. Indeed, the highest degradation of methylene blue was obtained with a 40% coverage rate of SnO_2 over ZnO. This covering led also to a passivation of the surface and a better stability of the catalyst resulting in a more efficient photocatalyst in reuse.

Specific assemblies could also be produced to improve photocatalytic properties. Indeed, Baranowska–Korczyc et al. [7] produced core/shell Ag/SnO_2 nanowires for the degradation of organic compounds under visible light. In this study, Ag nanoparticles were coated with SnO_2 leading to visible absorption. Rhodamine B and malachite green were selected as model pollutants. Their degradation was investigated under 450 nm light and both pollutants were completely degraded after 90 and 40 min, respectively. The efficient photocatalytic process is attributed to two phenomena: surface plasmon resonance effects of AgNWs, which allowed light absorption in the visible range, and charge separations on the Ag core and SnO_2 shell interface of the nanowires which prevents recombination of photogenerated electron-hole pairs.

The last semiconductor photocatalyst explored in this Special Issue was Bismuth oxyhalides, BiOX (X = Cl, Br, I). These materials were synthesized via a mannitol-assisted

solvothermal method [8]. The resulting materials had dominant (110) facets, first time reported with this type of synthesis using mannitol which acted simultaneously as a solvent, capping agent, and/or soft template. At the lowest mannitol concentration, it acted as a structure-directing agent, causing unification of nanoparticles, while at higher concentrations, it functioned as a solvent and soft template. The photoactivity of BiOX was evaluated on the oxidation of Rhodamine B and 5-fluorouracil, and on the reduction of Cr(VI). BiOCl and BiOBr photocatalysts presented the best photocatalytic activities leading to a total degradation or reduction in the model pollutants. This study demonstrated that BiOX prepared in mannitol solution could be useful for efficiently removing a wide range of micropollutants.

2. Biomass valorisation

In this second topic, different catalysts were developed for the transformation of biomass in high added-value molecules. Noble metals supported on various supports in particular were prepared, characterized, and tested.

In Drault et al. [9], various metals (Co, Ni, Zn, Ag, Cd, Cs, and Au) supported on silica were used as heterogeneous catalysts for the direct CO_2 carboxylation of furoic acid salts (FA, produced from furfural, derivative of inedible lignocellulosic biomass) to 2,5-furandicarboxylic acid (2,5-FDCA, a building block in the synthesis of green polymers). An experimental setup was firstly validated, and then several operation conditions were optimized, using heterogeneous catalysts instead of the semi-heterogeneous counterparts (molten salts). The preliminary results confirmed the possibility to decrease the reaction temperature to 230 °C, obtaining an acceptable conversion (74%) with the best catalyst, namely Ag/SiO_2.

Ru-based catalysts were also developed for cellulose valorisation. Haynes et al. [10] focused on the protection of active Ru nanoparticles supported on carbon black (CB) by various mesoporous silica coatings. The influence of key parameters, such as the protective layer pore size and the solvent nature of the catalytic reaction were investigated. The results showed that the hydrothermal stability was highly improved in ethanolic solution with low water content (silica loss: 99% in water and 32% in ethanolic solution); and that the silica layer pore sizes greatly influenced the selectivity of the reaction (shifting from 4% to 68% by increasing the pores sizes from 3.4 to 5 nm). The addition of an acidic co-catalyst ($CB–SO_3H$) led to sorbitol production through the hydrolytic hydrogenation of cellobiose (used as a model molecule of cellulose), demonstrating the high potential of the presented methodology to produce active catalysts in biomass transformations.

Finally, catalytic furfural valorisation was also investigated by Al Rawa et al. [11] with Au_x-Pty and Au_x-Pdy bimetallic nanoparticles supported on TiO_2. In this work, furfural (FF) was converted into furoic acid (FA) and maleic acid (MA) by a base-free aerobic oxidation in water. By comparing the monometallic Au-, Pt-, and Pd-based catalysts to the bimetallic counterparts, the synergetic effect of alloying was evidenced. The monometallic catalysts were by far less active than the bimetallic catalysts in terms of FF conversion, and in the formation of FA, MA, and FAO intermediates. The highest selectivity (100%) to FA was obtained using a Au_3-Pd_1 catalyst, with 88% FA selectivity using 0.5% Au_3-Pt_1 with about 30% of FF conversion at 80 °C. Using Au-Pd-based catalysts, the maximum yield of MA (14%) and 5% of 2(5H)-furanone (FAO) were obtained by using a $2\%Au_1$-Pd_1/TiO_2 catalyst at 110 °C.

In conclusion, this Special Issue entitled "Metallic or metallic oxide (photo)catalysts for Environmental Applications" gives an overview of the latest advances in the development of metallic or metallic oxide (photo)catalytic materials, with environmental applications for the elimination of organic pollutants or the valorisation of biomass. These studies open the way for the development of new and green processes and present materials for a better environment.

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