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*Editorial*

# Nanomaterials for Environmental Purification and Energy Conversion

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Nanomaterials, engineered structures of which a single unit is sized (in at least one dimension) between 1 to 100 nm, are probably the fastest growing market in the world. Although, nanotechnology is still a new discipline (proposed by Richard Feynman's talk "There's Plenty of Room at the Bottom" in 1959; and named by Norio Taniguchi in 1974), nanomaterials have already been commercialized for various purposes, including medicine, food, cosmetics, technology, and industry, as well as human and environmental health. A lot of studies on the preparation of more efficient, stable, and safe nanomaterials have been performed each year, as clearly shown by the growing number of published papers (Figure 1). Although, nanomaterials are extremely important for industrial and household purposes, it should be pointed out that properties of nanomaterials differ substantially from those of bulk materials of the same composition, resulting in high reactivity. Accordingly, possible undesirable effects might cause harmful interactions with the environment, living organisms, and humans and their parts (e.g., influence on structural integrity and functions of essential proteins, enzymes, and DNA), and thus have the potential to generate toxicity [1,2]. Therefore, possible negative impacts of novel materials (toxicity) must be also considered in the design of efficient, but also safe products. It is believed that most importantly, for future human development, nanomaterials/nanotechnology could be used to solve three of the top ten of humanity's problems (proposed by Prof. Smalley [3]), i.e., environment, water, and energy (which is critical for the rest of the problems). It is known that nanomaterials might be used for purification of water and air [4–6], wastewater treatment [7–10], microorganisms' inactivation [11–13], and energy conversion to the electricity and fuels [14–16].

Therefore, the special issue of *Catalysts* has been announced to discuss the progress of recent research on synthesis, properties, and applications of nanomaterials for environmental purification and energy conversion. This Special Issue was mainly dedicated as a platform for the contributions from The Symposium on Nanomaterials for Environmental Purification and Energy Conversion (SNEPEC), which was held in Sapporo, Japan in February 2018 (http://www.cat.hokudai.ac.jp/icat-nepec/). The contributions from those who could not attend SNEPEC were also welcomed. The Symposium covered a broad range of topics focusing on the exceptional role of catalytic nanomaterials in solving environmental and energy problems of modern societies. Accordingly, the Special Issue "Nanomaterials for Environmental Purification and Energy Conversion" is a collection of 17 papers, including 16 research papers and one review. Eleven papers present heterogeneous photocatalysis for efficient degradation of organic pollutants (phenol [17,18], 2-propanol [19], dyes [20–22], humic acid [23]), inactivation of microorganisms (*Escherichia coli*, *Staphylococcus epidermidis* [24], *Bacillus subtilis,* and *Clostridium* sp. [18]), $H_2$ evolution [25], and $CO_2$ reduction [26,27]. Six other papers focus on conventional catalysis ("dark" reactions), reporting efficient $H_2$ production [28,29], synthesis of ethanol and butanol [30],

direct conversion of $CO_2$ and methanol to dimethyl carbonate [31], water purification [32], and advanced characterization of catalysts by X-ray absorption fine structure (EXAFS) spectroscopy [33]. The majority of studies have been performed with particulate catalysts (nanoparticles (NPs)), but organized nanostructures, such as nanotubes ($TiO_2$/$Cu_xO_y$ [18], carbon nanotubes (CNTs) [30,32]) and nanowires ($CeO_2$ [31]) have also been used.

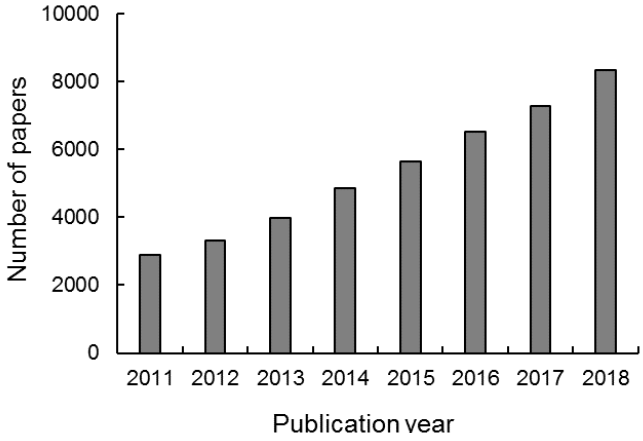


**Figure 1.** Number of papers published annually on nanomaterials (searched in Web of Science using "nanomaterials", 9 October 2019).

Fu et al. prepared $CeO_2$ nanowires by the advanced solvothermal method for direct catalytic synthesis of dimethyl carbonate from $CO_2$ and methanol [31]. They found that the surface reduction under $H_2$ atmosphere formed acidic/alkaline sites on the catalyst surface, and thus significantly improved catalytic activity, reducing the activation energy barrier from 74.7 to 41.9 kJ/mol. Complex catalytic studies were performed by Hafizi and Rahimpour for catalytic $H_2$ production [28]. The effect of alumina and Mg-Al spinel as the support for the formation of $Fe_2O_3$ catalyst was investigated. The $Fe_2O_3$–$MgAl_2O_4$ with narrowed mesopore-sized (2.3 nm) was successfully synthesized as an ultra-pure lattice oxygen transport medium. Furthermore, Daneshmand-Jahromi et al. analyzed the role of yttrium promoted Ni/SBA-16 as an oxygen carrier in steam methane reforming [29]. The reaction temperature, Y and Ni loading, steam/carbon molar ration, and lifetime of the oxygen carrier were investigated. The best catalytic activity was obtained for mesoporous silica (SBA-16) modified with 25 wt% Ni and 2.5 wt% Y, resulting in 99.83% $CH_4$ conversion and 85.34% $H_2$ production.

The synthesis of ethanol and butanol from synthesis gas on multiwalled carbon nanotubes (MWCNTs) functionalized with salicylic acid and impregnated with copper–cobalt catalyst was proposed by Zou et al. [30]. It was found that salicylic acid did not only functionalize carbon nanotubes, but also promoted the synthesis of ethanol and butanol, instead of methanol. Moreover, the surface properties of MWCNTs were crucial for efficient alcohol synthesis, i.e., the best activity was obtained with MWCNTs of 30 nm diameter. Carbon nanotubes (CNTs) were also used for efficient water purification by Li et al. [32]. The conductive cotton filter anodes were fabricated by a facile dying method to incorporate CNTs as filters. The developed filtration device achieved physical adsorption of organic compounds (ferrocyanide, methyl orange dye, and antibiotic tetracycline), and additionally, an application of external potential resulted in chemical oxidation of pollutants. The CNTs amount, total cell potential, and surfactant were key parameters affecting the electrochemical oxidation. It was proposed that the conductive cotton filter might be efficiently used for low-cost and energy-saving water purification. This very important research was reported by Wakisaka et al. who demonstrated the extended X-ray absorption fine structure (EXAFS) spectroscopy as an efficient technique to characterize Pt–Au fuel cell catalysts [33]. Previously, range-extended EXAFS was only achieved in high-energy resolution fluorescence detected XAFS (HERFD-XAFS). The presented results confirmed the feasibility of the range-extended EXAFS using the bent crystal Laue analyzer (BCLA) for fuel cells models containing Pt and Au.

Most papers discussed photocatalytic reactions on nanomaterials (heterogeneous photocatalysis). Titania (titanium(IV) oxide, $TiO_2$) is one of the most well-known and widely studied photocatalysts, due to its advantages, such as high activity, stability, low-cost, and nontoxicity (excluding toxicity of nanomaterials), as also confirmed in this issue (seven papers [17–19,21,24,26,27]). However, titania has two main shortcomings, i.e., recombination of charge carriers (typical for all semiconductors) and inactivity under visible light irradiation (due to wide bandgap). Therefore, various studies have been performed to improve photocatalytic performance of titania. The comprehensive review by Giovannetti et al. on recent advances in graphene-based $TiO_2$ nanocomposites for synthetic dye degradation shows the increasing potential of titania photocatalysts based on graphene matrix, in the field of extending the light absorption of $TiO_2$ from UV into the visible light range of radiation [21]. In this regard, the idea of titania modification is strongly present in the papers collected in the issue, e.g., titania surface modification with copper oxides ($Cu_2O$ [19] and $Cu_xO_y$ [18]), organic compounds (glucose [24] and urea [19]), polymers (polydopamine [27]), graphene [21], carbon/nitrogen [17], and titania doping (self-doped or hydrogenated) [34]. All kinds of modifications resulted in enhanced activity under either UV, visible light or solar radiation. Guan et al. prepared and characterized the colored core-shell structure of $TiO_2$@$TiO_{2-x}$ [26]. They reported visible light activity of this material towards $CO_2$ reduction under a simulated flue gas system. Visible light-induced photoreduction of $CO_2$ was also conducted with polydopamine-sensitized $TiO_2$ by Wang et al. [27]. The successful titania modifications with D-glucose was achieved by Markowska-Szczupak et al. [24], where the photocatalytic activities of suspended and immobilized photocatalysts were compared. In this study, it was shown for the first time that titania modification with monosaccharides could be efficient for water disinfection, and the immobilization of the photocatalyst on the concrete discs might be a prospective method for public water supplies and water storage tanks (as exemplified for a home aquarium in Figure 2a). The synergistic effect was observed by Janczarek et al. for titania bi-modification with urea (formed poly(amino-s-triazine) [35]) and $Cu_2O$ [19]. Two types of possible mechanisms of visible light activity were proposed, i.e., the type II heterojunction and Z-scheme. An important issue was the morphological form of the photocatalytic material based on titania. Golabiewska et al. prepared highly active microspheres in the presence of ionic liquid and Kozak et al. designed $TiO_2/Cu_xO_y$ nanotubes with visible light activity in the degradation of organic pollutants and bacteria inactivation. It was proposed that these nanotubes could be efficiently used for environmental purification under natural solar radiation, as shown on the journal cover (Figure 2b).


**(a)** **(b)**

**Figure 2.** Journal covers of *Catalysts* showing possible applications of (**a**) modified titania with D-glucose for water tanks; volume 8, issue 8 (https://res.mdpi.com/data/covers/catalysts/big_cover-catalysts-v8-i8.png) [24] and (**b**) $TiO_2/Cu_xO_y$ nanotube arrays for environmental purification; volume 8, issue 6 (https://res.mdpi.com/data/covers/catalysts/big_cover-catalysts-v8-i6.png) [18].

It should be pointed that also other semiconductors have been used successfully for environmental applications, such as ZnO [36], graphitic carbon nitride (g-C3N4) [37], $WO_3$ [10], $BiVO_4$ [38], and $SrTiO_3$ [39], and some of them exhibited higher activity than that of titania even under UV irradiation [40–42]. Accordingly, the photocatalytic activity of other semiconductors has also been discussed in this special issue, such as $ZnCr_2O_4$ [23], $TiOF_2$ (modified with NaOH) [20], $SnO_2$ (fluorine-doped $SnO_2$ (FTO), surface modified with Cu NPs) [25], and rectorite/$Fe_3O_4$/ZnO [22]. Wang et al. prepared rectorite/$Fe_3O_4$/ZnO composities with photocatalytic and magnetic properties enabling efficient photocatalyst separation after reaction [22]. Liu et al. obtained Cu/fluorine-doped tin oxide nanocomposites (Cu/FTO) dedicated to visible light-induced hydrogen production and photocurrent generation [25]. The high stability during recycling (24-h irradiation) should be considered as high advantage of this material. The nanosized $ZnCr_2O_4$ was synthesized by Dumitru et al. by thermolysis of a new Zn(II)–Cr(III) oxalate coordination compound [23]. The photocatalyst was much more efficient for humic acid degradation than simple photolysis (7%), reaching 60% degradation after 3 h of UV irradiation. Finally, $TiOF_2$ modified with NaOH of network structure was prepared via a modified low-temperature solvothermal method by Hou et al., and efficiently used for Rhodamine B degradation [20].

In conclusion, the significant role of catalytic nanomaterials in environmental remediation, energy production, and chemical synthesis systems has been discussed in the collected papers. We do believe that the SNEPEC symposium and this associated Special Issue have provided further insights to this area. We are looking forward to seeing how things will be progressed at the next SNEPEC symposium (July 2020).

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