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ScienceDirect
Current Opinion in
Green and Sustainable Chemistry

Benign-by-design advanced nanomaterials for environmental and energy-related applications

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This contribution aims to disclose recent advances and key benign-by-design systems for a number of environmental and energy-related applications.

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Current Opinion in Green and Sustainable Chemistry 2019, **15**:98–102

This review comes from a themed issue on **Selected papers from the 3rd Green and Sustainable Chemistry Conference 2018**

Edited by **Klaus Kümmerer** and **Zhimin Liu**

https://doi.org/10.1016/j.cogsc.2018.12.007

Society is facing significant daunting challenges in the 21st century, mostly related to the availability of resources, climate change, energy demands, water supply, and efficiency of processes for a more sustainable development. The future generations will have to address those issues through a multidisciplinary approach encompassing disciplines including (bio) chemistry, materials science, and engineering in an unprecedented coordinated monitoring and modeling of many factors, from social to economic, and environmental standpoints [1,2]. This major task will be possible only by a multistakeholder global strategy involving not only natural and social scientists and engineers but also the industrial world, the civil society, and governments.

Advances in (nano)materials' design and engineering will pave the way to innovative systems that will combine improved efficiencies to maximize the use of resources and performance (as compared to current productions) with biocompatibility and environmentally soundness. This is essentially the benign-by-design concept applied to the design of novel functional materials as a paradigm for a more sustainable supply and production of chemicals and energy (Figure 1).

A number of recent advances in the field of heterogeneous photocatalysis, biocatalysis, electrocatalysis, and environmental catalysis have significantly contributed to set the key milestones for the future. These include applications in catalysis, energy conversion and storage, and environmental remediation. In this respect, extensive research efforts have been addressed to cope with issues to secure clean and sustainable water supply [4], and a remarkably simple solution for electrocatalytic mineralization of pollutants (e.g. microcystins) from wastewater has been recently achieved using sustainable electrode materials based on cheap commercial graphite cylindric bar–supported titania anodes [5].

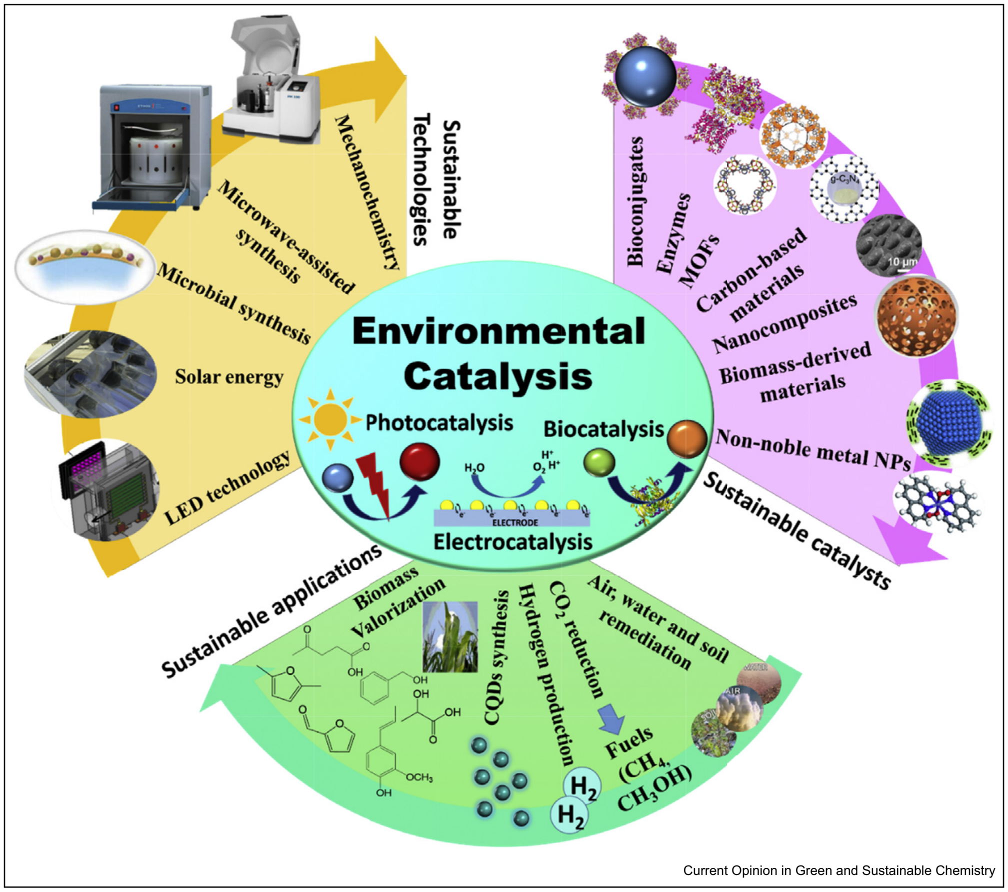
Most current strategies to fabricate potential electrocatalysts usually require hazardous and expensive precursors, external heteroatom-containing compounds, and additional templates and chemicals, which clearly give rises to costs and limit their economic applications [6]. To overcome these drawbacks, the conversion of natural resources into carbon-based materials or the modification of cheap commercial graphite is opening new horizons as effective strategies to engineer more sustainable materials with advanced electrocatalytic properties.

In a recent work, graphite carbon cylinders (3 cm × ∅ 2 mm; c.a. 1.2 g) from cheap commercial pencils were used as based anode upon convenient and effective modification with nanosized titanium oxide nanoparticles (TiO_2@Carbon) via microwave-assisted deposition at moderate temperatures (ca. 120 °C). The synthesized anode was used in the remediation of nodularin cyanotoxin, both under defined media conditions (NaCl 10 mmol L^{-1}) as well as most importantly tap water, for which a quantitative degradation of the cyanotoxin was achieved within 20–60 min (Figure 2).

Several advantages of the proposed electrocatalytic method include (1) the control of processes by the potential at electrode/electrolyte interfaces for complete mineralization; (2) versatility and applicability to a wide range of wastewaters containing varying pollutants in different concentrations; and (3) cost-effectiveness, simplicity, compactness, and robustness with potential for scale-up applications.

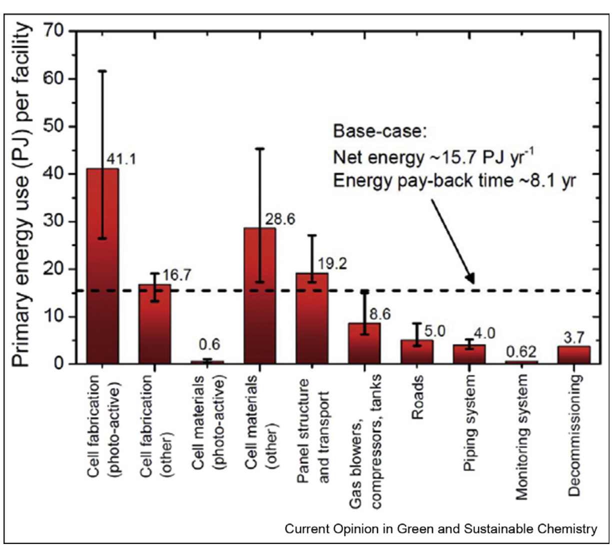
Dedicated to Dr. Rajender S. Varma, colleague and dear friend, for his inspiration and leadership in the field over the past decades.

Figure 1



Benign-by-design technologies for the design of sustainable materials for relevant future applications. Light emitting devices (LED), Carbon Quantum Dots (CQD), nanoparticles (NP) and Metal Organic Franeworks (MOF).

Figure 2



Life-cycle net energy assessment of large-scale hydrogen production via photoelectrochemical water splitting. Reproduced by permission of the Royal Society of Chemistry from reference 14.

Photoelectrocatalysis, commonly defined as a type of catalysis that results in the modification of electrochemical reaction rates at the electrode/electrolyte interfaces via light irradiation, has also recently emerged as a useful tool toward energy production [7–9]. Importantly, the development of environmentally friendly strategies toward the synthesis of benign-by-design (photo)electrocatalysts has captured the attention of the scientific community in the last few years because of the ever-increasing demand for sustainable conversion and storage of renewable energy.

In this regard, photoelectrochemical (PEC) reactions have to date been reported to efficiently afford both the generation of hydrogen from water and the (photo) electroreduction of CO_2 to produce carbon-based fuels from renewable resources. Following seminal reports in literature [10] and several important overviews in the field [11,12], an elegant recent approach on scalable water-splitting photocatalysts has described a solar-to-hydrogen energy conversion efficiency exceeding 1.1% using La- and Rh-codoped $SrTiO_3$ ($SrTiO_3$:La, Rh) and

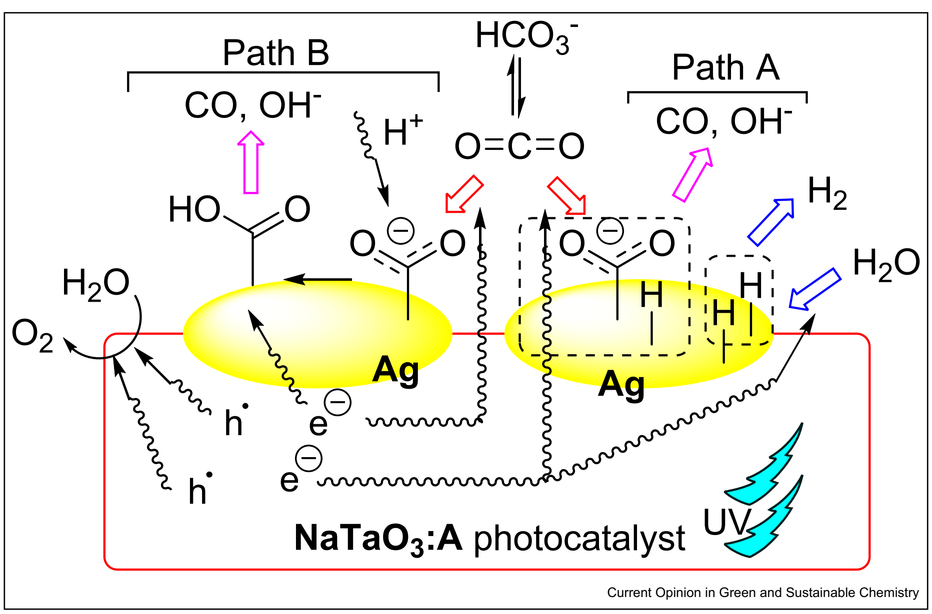
Mo-doped $BiVO_4$ ($BiVO_4$:Mo) powders embedded into a gold (Au) layer [13]. A remarkable enhancement of the electron relay could be achieved by annealing and suppression of undesirable reactions through surface modification to allow pure water (pH 6.8) splitting to hydrogen with an apparent quantum yield of more than 30% at 419 nm. The proposed system allowed the fabrication of scalable water-splitting devices using particulate semiconductors, certainly most useful to pave the way to future hydrogen production designs.

The most interesting information toward the assessment of large-scale production of such PEC systems was also present [14] to back up the recent reported work by Domen et al. [13]. In these studies, a life-cycle net energy assessment of a hypothetical large-scale PEC hydrogen production facility with energy output equivalent to 1 GW continuous annual average (1 GW HHV = 610 metric tons of H_2 per day) was provided. Based on a number of premises, the energy payback time was 8.1 years, the energy return on energy invested was 1.7, and the life-cycle primary energy balance over the 40 years projected service life of the facility is +500 PJ under base-case conditions. The most important model parameters affecting the net energy metrics were the solar-to-hydrogen conversion efficiency and the life span of the PEC cells. Other parameters associated with the balance of systems, including construction and operation of the liquid- and gas-handling infrastructure, were found to play a minor role, providing guidelines for the application of the model system to PEC and photochemical devices in the future.

The (photo)electrochemical reduction of CO_2 to valuable chemicals including CO, CH_4, and alcohols has also attracted a great deal of interest, covered by a couple of recent contributions in the field [15,16]. An inventive approach to investigate the products distribution during the electrochemical reduction of carbon dioxide has been recently proposed by an advanced analytical method, making use of differential electrochemical mass spectrometry [17]. The coating of the electrocatalyst (Ag and Cu) on a pervaporation membrane enabled the sampling and characterization of species released close to electrode–electrolyte interface, thereby allowing to measure not only the intrinsic kinetic of the CO_2 reduction but also the relative abundance of aldehyde and alcohol products near the cathode surface. Hypothesis on the mechanism and reaction intermediates was so formulated.

Another remarkable procedure described the photoreduction CO_2 in a dual-chamber reactor equipped with a multicomponent catalyst comprised of Cu_2O, graphene and an array of TiO_2 nanotubes [18]. Graphene played multiple roles by protecting Cu_2O against photocorrosion, promoting charge separation and electronic transfer across the heterojunction interfaces, and preventing backward reactions. Moreover, the high electron density of graphene enhanced the selectivity for the multielectron reduction of CO_2 to methanol which was generated at a rate of 45 µmol cm^{-2} h^{-1}. At 420 nm, the corresponding quantum efficiency was 5.71% [18].

Figure 3



Photoreduction of CO_2 catalyzed by mixed oxides in the presence of water using a Ag-based cocatalyst. Copyright Wiley-Verlag VCH. Reproduced with permission.

Last, but not least, CO_2 photoreduction was also reported using a catalyst based on a A-doped $NaTaO_3$ (A = Mg, Ca, Sr, Ba, or La) in the presence of water as electron donor and an Ag cocatalyst (Figure 3) [19].

The conduction band level of A-doped $NaTaO_3$ allowed photogenerated electrons on the surface of Ag cocatalyst, potential of which was high enough for the reduction of both CO_2 to CO and H_2O to H_2, according to paths a) and b). Notably, the selectivity for the formation of CO has been around 90%, with an activity in the range of 88–176 μmol CO h^{-1} [19].

Conclusions and prospects

Promising methodologies and novel technologies for the environmentally friendly design of catalytic systems, as well as emerging materials with low toxicity and costs and performances for environmental catalysis, will be part of the future in the field. Special attention should be paid to protocols including mechanochemistry, microwave-assisted and photo (electro)chemical processes for catalyst design, and derived sustainable uses.

Photocatalysis and electrocatalysis have been considered because of their applicability in crucial processes to solve environment-related problems. Methods for artificial photosynthesis and photo (electrochemical) conversion including water splitting and CO_2 reduction have an enormous potential, most of it remaining to be disclosed yet. From the economic standpoint, a challenge in the coming decades for the future of photo (electro)reduction methods must also focus on point sources of CO_2 because the current capturing from air (where the average concentration is of only 400 ppm) still shows uncompetitive high costs of approximately 500 € per tonne of captured CO_2 [20].

Additional emerging trends and topics will relate to the combination of photocatalytic and thermocatalytic effects to enhance catalytic performance combined with the use of sunlight as already demonstrated in the literature [21,22] including, for example, H_2 photoproduction [23], and fuels production from CO_2 [22,24]. Future strategies in electrocatalysis also include the use of renewable sources such as wind and solar to obtain renewably generated electricity.

Besides advances in environmental catalysis achieved so far at the laboratory scale, ways must be sought to integrate such results to the needs of industry through scale-up analysis of sustainable catalytic materials and processes. We hope that the key emerging topics and contributions summarized in this work may inspire the scientific community to move toward benign-by-design materials and processes for a more sustainable future.

Acknowledgements

R.L. gratefully acknowledges funding from MINECO under Project CTQ2016-78289-P, co-financed with FEDER funds. M.S. gratefully acknowledges support from Universita Ca' Foscari for a sabbatical stay at group FQM-383 from Universidad de Cordoba. The publication has been prepared with support from RUDN University Program 5–100.

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