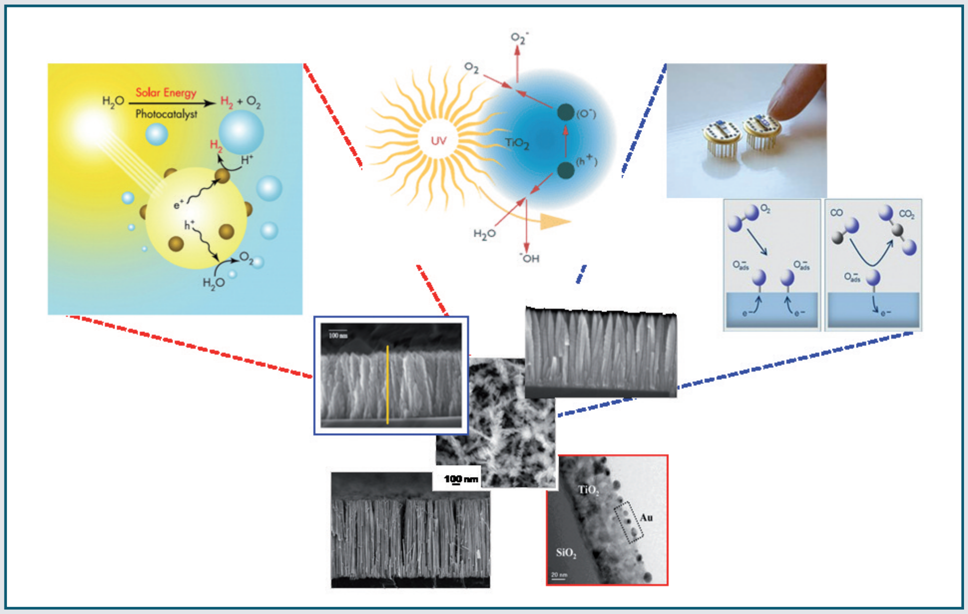
CRITICAL REVIEWS



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MULTI-FUNCTIONAL OXIDE NANOMATERIALS: SUSTAINABLE APPLICATIONS IN GAS SENSING AND PHOTOCATALYSIS

This contribution reports on the tailored synthesis of metal oxide nanosystems for sustainable technological applications. In particular, the attention is devoted to the detection of pollutants by gas sensing devices, to their photocatalytic conversion into non-toxic products, and, finally, to H_2 production by photo-splitting of aqueous solutions.

Introduction

Over the last decades, the increasing concern on environment and human health and the limited fossil fuels availability have significantly stimulated research activities on sustainable technological applications [1]. In this context, air quality has been the subject of many studies aimed at establishing the risks of exposure to high pollution levels [2-5] especially in the developing world, where living conditions have not greatly improved since the Great Smog of London of 1952 (Fig. 1). In particular, considerable attention has been paid to the development of efficient and reliable gas sensors for the most important pollutants, such as NO_x, CO, Volatile Organic Compounds (VOCs), SO_2 [6-8]. Nevertheless, many of these efforts have not reached commercial viability, since the main sensor requirements (***3S***, *i.e.* sensitivity, selectivity, stability) are still far from being simultaneously available [3, 6, 8, 9].

In addition, a great interest has been devoted to pollutant conversion into non-toxic products. In this regard, oxide semiconductor PhotoCatalytic Oxidation (PCO), based on the activation of redox

Fig. 1 - (a, b) The Great Smog of London (1952);
(c, d) the sky over Bejing (2006-07)

reactions through light absorption, has gained a remarkable interest for its green character and the ultimate possibility of being activated by direct solar radiation [10, 11]. Yet, most of the works have been addressed at the liquid-phase decomposition of organics for wastewater purification, whereas less studies on gas-phase pollutant photodegradation, that possesses a strategic interest, are indeed available [4, 12-14].

Beside being an environmentally friendly alternative for air and water decontamination [15, 16], photocatalysis represents a strategic pathway for energy-related issues. In this framework, the vision of an energy infrastructure with H_2 as a clean energy vector in combination with efficient fuel cells is extremely attractive [17-20]. Yet, one of the main open problems is the availability of synthetic routes for H_2 green and cost-effective production, even on small- and medium-scales. Among the various methods, such as natural gas reforming, electrolysis and thermal cracking, solar photocatalytic splitting of water is the ultimate challenging dream to provide clean and recyclable H_2 energy and possesses a great strategic interest, since the discovery of the first H_2O splitting system (Pt-TiO_2) in 1972 [21-25].

A valuable solution for the open problems in the above mentioned fields is the development of tailored 0D, 1D, 2D and 3D nanosystems [8]. Their common feature is the presence of at least one dimension in the 1-100 nm range, resulting both in a high surface-to-volume ratio and in the presence of various surface defects. These properties, along with size effects arising from charge carrier confinement [26, 27], induce a peculiar chemical reactivity with respect to that of the corresponding bulk counterparts, widely diversified as a function of the material characteristics [9, 28]. In sensing applications, beside providing an enhanced response, organized oxide nanomaterials can reduce both the working temperature and the consumed power [29-31]. In particular, 1D-like metal oxide (MO_X) nanostructures enable higher conductance modulations upon interaction with target gases, since their lateral dimensions are comparable to the extension of the surface charge region [3, 8, 32].

In addition, modern frontiers of air purification techniques rely on the use of nano-semiconductor PhotoCatalysts (PCs) to efficiently degrade organic compounds, providing higher selectivity for the desired products, along with a lower energy consumption [4, 28]. The development of supported nanostructured photocatalytic systems can also enhance performances for H_2 preparation and eliminate the necessity of filtration processes for the recovery of powdered catalysts, thus enlarging the actual horizons of H_2O photocatalytic splitting [18, 19, 33].

An ambitious goal in these fields is the development of multi-functional materials capable of actuating pollutant detection and degradation as sequential processes (Fig. 2). To this regard, a challenging concern is the design and bottom-up preparation of MO_X

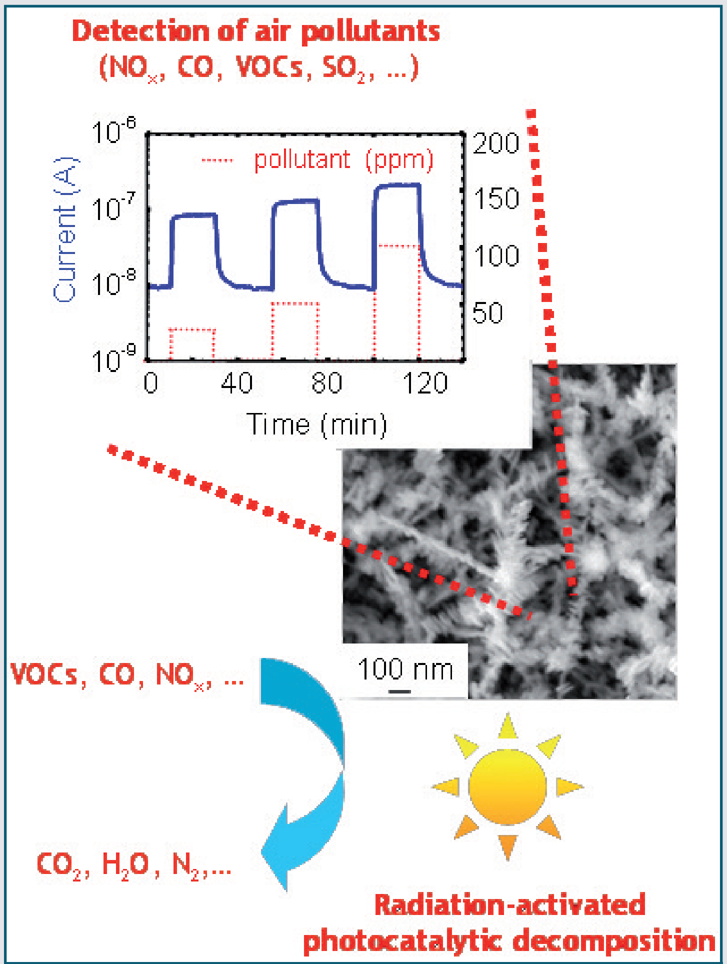


Fig. 2 - Multi-functional oxide nanomaterials can enable pollutant detection from the gas phase and subsequently, whether activated by suitable radiation, can induce their conversion into non-toxic products with negligible environmental impact

nanosystems with controlled morphology [8, 24]. Yet, despite the recent progresses in synthetic routes have enabled an appreciable improvement of functional properties [3, 27, 31] as recently evidenced, "*Room at the bottom, plenty of tyranny at the top*" [34]. This means that, despite MO_X nanosystems are endowed with a plethora of attractive applicative features, their tailored low-cost synthesis, assembly, manipulation and characterization are still open questions, due to the intrinsic problems of working at the nanoscale [17, 35].

This critical review aims at highlighting the scientific progresses and most relevant open issues of MO_X nanomaterials in the fields of pollutant gas sensing/photocatalytic degradation, and in H_2 production by H_2O photo-splitting. Despite several publications on these topics have appeared in the literature, reports bridging these applications as a function of the active MO_X nanomaterials are quite scarce. This review will present a brief survey on these topics, outlining in particular the importance of controlling the system morphology and assembly for the above mentioned applications.

Sustainable applications of tailored oxide nanomaterials: three representative examples

Gas sensing devices for the monitoring of air quality

The working principles of nano-sensors are similar to those of conventional MO_X sensors [29, 31]. It is commonly accepted that species such as O^-/O_2^-, chemisorbed on the MO_X surface, undergo charge-transfer reactions with gas analytes. In the case of *n*-type semiconductors exposed to reducing species R (*e.g*. CO, VOCs, H_2S, ...), electron release results in a conductivity increase, whereas adsorbed electron-withdrawing species (*e.g*. NO_2) determine a decrease of the system conductivity [8] [Equations (1)-(2)]. In the case of *p*-type semiconductors, the opposite effect is observed.

$$R + O^- \rightarrow RO + e^- \qquad (1)$$

$$NO_2 + e^- \rightarrow NO_2^- \qquad (2)$$

Since these mechanisms involve adsorption processes, higher surface-to-volume ratios and an increased surface defect density favor gas-solid interactions, resulting in a lower response time and a higher sensitivity. Hence, several techniques have been adopted to deposit nano-oxides for toxic gases (CO, NO_x,...) detection, with special attention to quasi-1D materials [3, 8, 29, 31].

A large number of MO_X nano-sensors with different morphologies, such as TiO_2, Cu_xO (x=1,2), ZnO, In_2O_3, SnO_2, can be found in the literature [9, 36, 37]. In this section, the sensing behavior of some of the most representative systems will be briefly discussed.

Studies on TiO_2 nanofibers prepared by electrospinning [3] demonstrated a resistance increase higher than 800% upon exposure to 500 ppb of NO_2. As regards Cu_xO, we have recently reported on 1D-like CuO sensors with an outstanding response in the detection of VOCs, and detection limits as low as 0.1 ppm [39]. This behavior could be traced back to the co-presence of a high surface active area and reduced lateral dimensions, providing a preferential pathway for charge carriers.

Great attention has been devoted to ZnO nanosystems with different morphologies, such as nanotetrapods [26] and nanorods [9]. Concerning the former, obtained by the combination of vapor transport and controlled oxidation, good responses to 50 ppm of CO and 100 ppb of H_2S were reported, with performances increasing at lower grain sizes. In particular, nanorod sensors, deposited on Al_2O_3 starting from a polyvinyl alcohol solution, could detect down to 0.05 ppm of H_2S at room temperature [8].

The preparation of mixed nano-MO_Xs has been often reported as a promising approach to obtain an enhanced sensitivity, thanks to the combination of the single oxide properties. For instance, ZnO nanocrystals doped with Cu_2O, resulting in the formation of *n-p* heterojunctions, enabled an increased CO detection, down to 20 ppm [29]. In a similar way, porous ZnO-TiO_2 nanocomposites, obtained by Chemical Vapor Deposition (CVD) [36, 37] provided sensing performances increasing proportionally to the TiO_2 content (Fig. 3). Their responses towards VOCs and NO_2 were appreciably higher than those previously reported, due to the concomi-

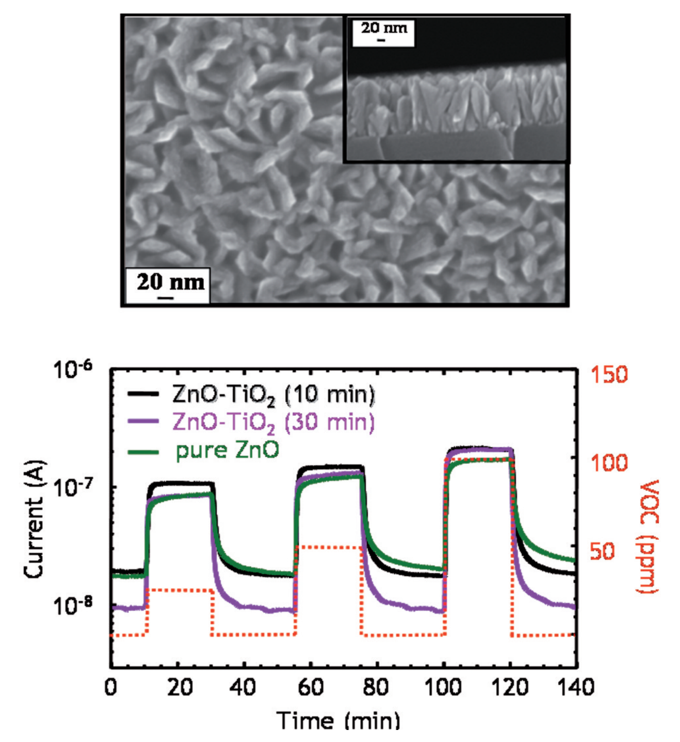


Fig. 3 - Typical SEM image of a ZnO/TiO_2 nanocomposite system synthesized by CVD and dynamical responses upon espoure to VOCs. TiO_2 content increases with the corresponding deposition time [36, 37]

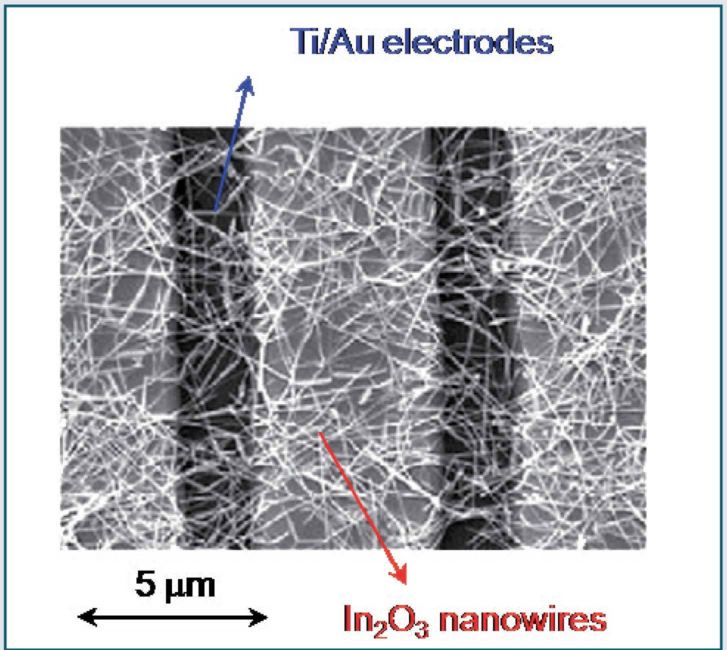


Fig. 4 - SEM image of the In_2O_3 multi-wire device, where In_2O_3 nanowires are contacted by metal electrodes (adapted from [9])

tance of the TiO_2 catalytic action and the peculiar system morphology, resulting in a higher defect content and an improved reactivity.

Vomiero *et al.* [8] synthesized In_2O_3 nanowires (NWs) by thermal evaporation, obtaining a broad distribution of the wire diameters. Lower dimensions enabled to achieve higher sensitivities to VOCs and CO, mainly for the higher active areas. Other workers demonstrated detection of NO_2 down to ppb levels using an In_2O_3 NW network [3, 9], synthesized by a laser ablation route. This is actually the lowest room temperature detection limit achieved so far, thanks to the formation of peculiar NW-NW junctions between the metal electrodes, a feature available in multiple-NW devices, but missing in the single NW ones (Fig. 4). Upon NO_2 exposure, such junctions should form a depleted layer around the intersections, thus blocking the electron flow more effectively than in the case of single In_2O_3 NWs.

Great attention has also been devoted to SnO_2 nanobelts/wires obtained by Evaporation-Condensation (E-C), resulting in systems with high crystallinity and small lateral dimensions [27]. The detection limit for CO and NO_2 reached a few ppb for single SnO_2 nanobelts, thanks to the intrinsically small grain size and the high surface-to-volume ratio [8, 9]. In addition, decoration of the sensor surface with metal nanoparticles (NPs; *e.g.* Ni, Pd, Ag, Au) has been demonstrated as an effective mean to improve the sensitivity towards CO and shorten the recovery time. This effect has been ascribed to the metal NP capability of acting as catalysts for O_2 dissociation, facilitating its subsequent reaction with chemisorbed CO molecules and consequent electron release [3, 29]. Yet, poisoning and coalescence by surface migration of metal NPs at high operating temperature should be carefully taken into account, since it may result in detrimental performance losses.

Very recently, Comini *et al.* [30] have reported on the growth of longitudinal and radial heterostructured SnO_2-In_2O_3 NWs by a sequential E-C process, respectively with and without the use of Au catalytic particles. The effect of gold NPs is in fact to promote either local nucleation of SnO_2 at the In_2O_3 1D structure apex, or a complete backbone coverage. Electrical characterization indicated the presence of an *n/n* MO_Xs heterojunction, forecasting the technological exploitation of the interface properties.

Even hierarchical and hollow MO_X nanostructures have been adopted to improve the sensor characteristics. For instance, SnO_2-based hollow spheres exhibited an appreciable response improvement with respect to homologous nanoparticle films. Hollow Cu_2O/CuO and In_2O_3 spheres displayed response times even lower than 10 s in CO detection, thanks to the rapid gas diffusion to the sensing surface, that can be tailored by controlling the nanoporous shell structure [31].

In the last years, research has also been extended to less conventional MO_Xs, such as columnar CeO_2 nanostructures obtained by CVD [32, 36, 38]. These systems displayed a response appreciably higher than continuous films in the sensing of both VOCs and NO_2, with a ppb detection limit for the latter. Apart from the higher surface-to-volume ratio, these performances could be also ascribed to the enhanced conductance modulation in the interaction with the target gases, as a consequence of the small nanoarchitectures lateral size.

Photocatalytic systems for pollutant degradation

PCO processes have several appealing technological advantages: 1) GRAS (Generally Recognized As Safe): the most commonly used catalyst is by far TiO_2, which is also a component of toothpastes and pharmaceutical suspensions; 2) Mild Oxidant: it has been demonstrated that the principal oxidation source is molecular O_2, a milder reactant than H_2O_2 or O_3; 3) PCs are active at room temperature; 4) the dominant view of various mechanisms proposes $^{\cdot}OH$ radicals as the main active species for TiO_2 activity towards various contaminants (aromatics, alkanes, olefins, halogenated hydrocarbons,...) [4, 5, 11, 13, 14]. Hitherto, over 3,000 kinds of organic pollutants have been reported to be degraded by nano-sized TiO_2 under UV irradiation [10, 28].

As anticipated, PCO air purification commonly uses nano-semiconductor catalysts, usually based on TiO_2, and UV light (Fig. 5). The process is initiated by electron photo-excitation from the valence to the conduction band, leaving a positive hole in the former. The generated electrons and holes, in turn, trigger reduction and oxidation processes, respectively, of compounds adsorbed on the semiconductor surface [4].

To date, TiO_2 P-25 from Degussa® is indeed the benchmark for

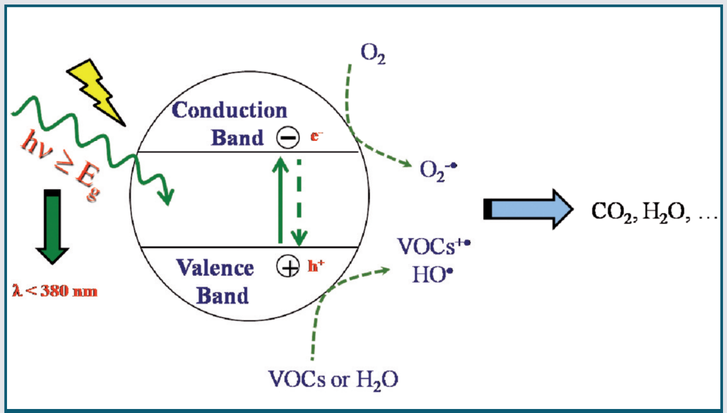


Fig. 5 - Schematic representation of TiO_2 UV photocatalytic oxidation of VOCs (adapted from [4, 10])

powder PCO [14-16, 19] and various chlorinated and aromatic VOCs could be completely degraded by modified P-25 powders within a few minutes [5]. Yet, in spite of the relevant number of publications on TiO_2 PCs, its low quantum yield and the lack of Vis light activation still hinder its large-scale utilization [10, 15, 40]. Whereas the former is due to the high electron/hole recombination rate, the second issue is related to the high band gap energy (≥3.0 eV) of the various titania polymorphs, allowing to exploit only a small part (≈4%) of the incoming solar energy [1, 4, 17, 20, 21]. To solve this problem, TiO_2 doped with suitable metals (*e.g.* Co(III), Cr(III), Fe(III), Mn(II), Pb(II), lanthanides,…) and M-TiO_2 nanocomposites (M=Ag, Pt, Au,..) have been investigated [5, 11, 15, 40]. In particular, the main role of M nanoaggregates consists in: i) improving the separation of photo-generated charge carriers, electrons being transferred to M and holes being simultaneously accumulated at the M-TiO_2 interface; ii) promoting the subsequent transfer of trapped electrons to oxygen adsorbed on TiO_2 surface; iii) inducing the pollutant adsorption (*e.g.*, CO on Pt) and catalyzing its degradation; iv) extending the absorption towards the Vis region; v) changing the selectivity or yield of a particular product.

Another viable method consists in the preparation of nanostructured MO_X composites, such as ZnO-TiO_2, WO_3-TiO_2 and SnO_2-TiO_2, since the heterojunction formation between two semiconductors with suitable redox energy levels results in a better separation of photo-generated carriers [5]. The obtainment of Vis and/or solar-light efficient PCs is further ensured by the high surface area and the peculiar morphological features of the resulting nanostructures [21, 37]. Differently, composites of TiO_2 particles encapsulated in nanoporous silica shells have been obtained in view of possible incorporation in fibres or paints. These systems, endowed in particular with voids between the TiO_2 core and the silica shell, have shown an efficient photocatalytic decomposition of light VOCs and a higher TiO_2 resistance to deactivation [13, 14, 41]. Other works have proposed the use of anionic dopants (*e.g.* C, N, B,...) to extend TiO_2 photocatalytic activity into the Vis region [1]. To this aim, beside minimizing recombination processes, co-doping of high area TiO_2 nanopowders, for instance with N and B, resulted in the simultaneous generation of intra-gap empty electronic states and filled Ti 3*d* levels as a consequence of N and B introduction, respectively [11].

A comprehensive overview of various TiO_2-doped PCs, both as powders and supported thin films, for the degradation of various air pollutants (VOCs, NO, NO_2, SO_2,…) has been recently reported, along with an examination of the PCO kinetic aspects [1, 4]. In particular, the preparation of supported films, for instance by sol-gel or CVD, resulted in improved performances, beside being practically advantageous [15, 28, 41]. To this regard, sol-gel routes with organic templating agents have been applied to the synthesis of TiO_2-coupled nanomaterials, containing WO_3 and eventually Pt nanoparticles, for CO oxidation [21]. A high on-site stability and a conversion efficiency close to 100% were reported even for high CO levels (>3000 ppm), thanks to the high system active area. Similarly, Liu *et al.* [40] recently proposed a template-assisted route to hollow Ag-TiO_2 nanostructures, whose porosity, in conjunction with the dispersion of silver nanoaggregates, was responsible for an improved PCO efficiency. Indeed, nano-sized

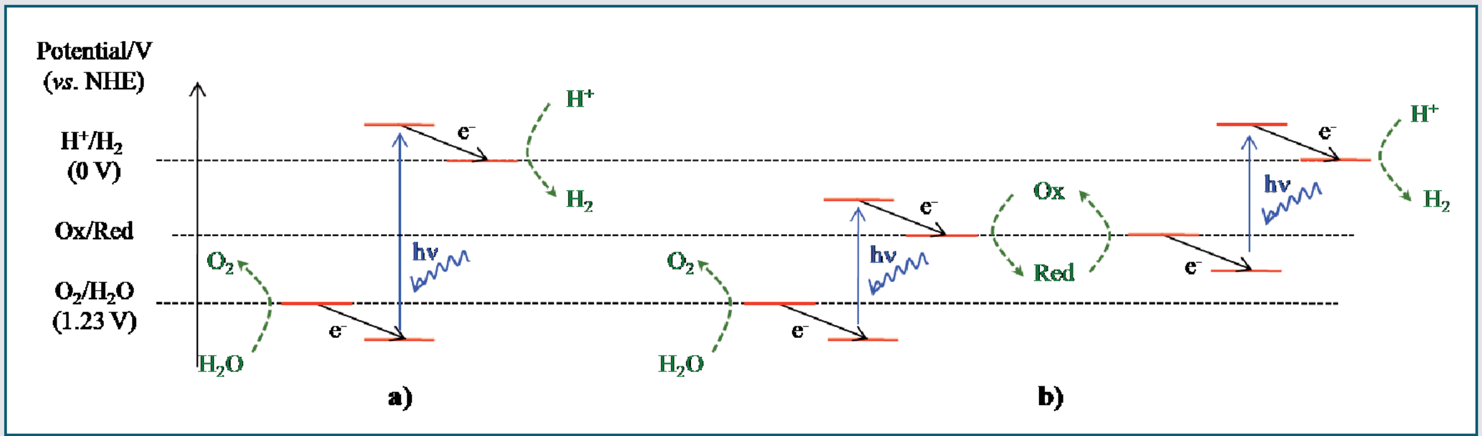


Fig. 6 - Schematic representation of energy diagrams for photocatalytic H_2O splitting in the case of: a) a one-step excitation system; b) a two-step excitation system (adapted from [22, 23])

Ag-TiO_2 powders were successfully used for the degradation of various VOCs [28]. In addition, mesoporous TiO_2-systems have been shown to be highly selective (>80%) in the gas-phase oxidation of benzene to phenol [10].

Beside TiO_2 systems, various nano-MO_Xs with different morphologies have been proposed for PCO, such as Fe_2O_3, ZnO, SnO_2, WO_3 [4, 13, 28]. Among them, ZnO appears an attractive candidate, since it possesses chemico-physical properties and photodegradation mechanisms similar to those of TiO_2 [12, 16].

To this regard, ZnO and TiO_2 NP activities have been recently compared in the PCO of SO_2 and aliphatic hydrocarbons [42]. Nonetheless, catalyst deactivation in gas-phase PCO might occur either for the decrease of active sites under illumination, or due to fouling effects (*i.e.* the formation of particle material from intermediate products), that might reduce the active nanosystem surface [4, 14, 42]. Indeed, at variance with sensing applications, detailed studies on the interrelations between the system efficiency and the peculiar 1D, 2D, 3D morphological organization are not available up to date.

Getting to the H_2 highway via the nanoroad

The immediate lure of the H_2 highway - vehicles powered by hydrogen-fuelled batteries - is that the only exhaust product is water vapor. Hydrogen also becomes a renewable source of energy if it is produced by solar water splitting through equation (3), wherein photon energy provides the required energy input to compensate the large positive change in the Gibbs free energy [19, 22, 25, 33]:

$$H_2O \rightarrow H_2 + 1/2O_2 \qquad \Delta G° = 237\ kJ\cdot mol^{-1} \qquad (3)$$

Fig. 6 provides a sketch of the energy diagram for photocatalytic H_2O splitting in one- and two-steps excitation systems. Similarly to the case of Fig. 5, the process is initiated by the photo-generation of charge carriers - electrons and holes in the conduction and valence band - that can induce reduction and oxidation reactions, respectively, when thermodynamic requirements are satisfied. In the simpler one-step excitation system, based on a single semiconducting material (Fig. 6a), holes oxidize H_2O to O_2 and electrons reduce protons, leading to H_2 formation. In a different way, in the two-step oxidation system (Fig. 6b), two semiconductors with small band gap values can be connected through reversible redox reagents (Ox/Red couple), and O_2 and H_2 are evolved over the two different materials. In both systems, as already discussed in the previous paragraph, the introduction of metal nanoparticles, such as Au, is extremely beneficial for an improved separation of the photogenerated charge carriers [19-22].

As can be observed, H_2 evolution is feasible only provided that the lower edge of the PC MO_X conduction band is more negative than H^+ reduction potential, and this is often satisfied for energy gap values over 3 eV, implying an inherent difficulty in exploiting Vis/solar radiation for hydrogen production.

In this scenario, similarly to the case of pollutant degradation, TiO_2 in various forms is undoubtedly the most investigated material [17, 23]. As a matter of fact, the low conversion rates and quantum conversion efficiencies obtained for the direct photocatalytic H_2O splitting over titania [19] forced to: (i) the addition of sacrificial molecules in the aqueous system; (ii) the tailoring of new nanocomposite catalysts, where the morphological organization is a key point in determining the system performances.

Concerning (i), it has been reported that the efficient H_2 photo-assisted production from aqueous solutions can be achieved at expenses of suitable "sacrificial" electron donors, such as methanol and ethanol, able to suppress undesired electron-hole recombination phenomena [18, 24]. As regards point (ii), the use of proper nanostructures can enhance surface adsorption and photocatalytic reactions, and also the ability to utilize Vis light even on unexpected systems due to the occurrence of quantum size effects.

In this context, both nanoarchitectures based on TiO_2 and on other MO_Xs, such as Fe_2O_3, ZnO, SnO_2, WO_3, have been proposed [17]. A recent detailed review [23] presents a wide survey of the used PCs and their pertaining features. In the following, the attention will be focused only on some of the most representative systems.

Rayalu *et al.* [33] reported on nanocomposite TiO_2 systems supported on various zeolites obtained by solution routes. In this case, the peculiar dispersion of the active phase, along with the introduction of Co(II) centers to expand the absorption into the Vis range, led to higher performances than P-25 and to a maximum H_2 yield over 2300 $\mu mol\cdot g^{-1}\cdot h^{-1}$, appreciably higher than other reported values for supported TiO_2-based PCs.

In particular, Pt-loaded TiO_2 films obtained by sputtering have enabled photocatalytic H_2O splitting with an efficiency up to 34% already under Vis illumination, opening intriguing perspectives for on-site use in fuel cells [1, 25]. Under analogous conditions, porous TiO_2 nanomaterials prepared by sol-gel, containing WO_3 and Pt nanoparticles, enabled an H_2 photo-production rate up to 25 $\mu mol\cdot min^{-1}$ [21], thanks to the high nanostructure active area and the presence of narrow band-gap WO_3. Yet, the high Pt cost, toxicity and scarcity has fuelled the search for alternative dopants. For instance, the dispersion of Au particles has been reported to be beneficial in terms of H_2 production, due to their electron scavenger action, as already observed for PCO processes. In particular, Au-TiO_2 nanocomposites prepared by spray pyrolysis have enabled an appreciably more efficient hydrogen production than that observed by bare Degussa P-25 powders under the same conditions [19].

Other studies have focused on nanostructured Zn-Ga oxynitrides *via* calcination, that are active for the overall H_2O splitting reaction under suitable conditions [22], leading to H_2 evolution rates higher than 200 $mmol\cdot h^{-1}$.

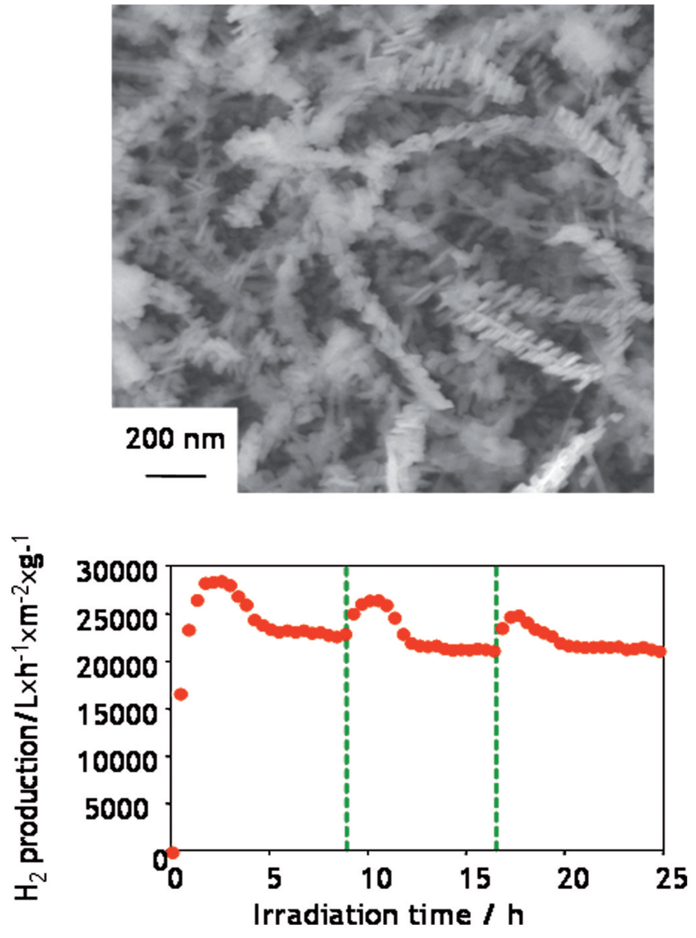


Fig. 7 - (Upper) Plane-view SEM micrograph of quasi-1D CuO nanostructures deposited by CVD on Si(100); (Lower) H_2 evolution rate *vs.* UV irradiation time on the above CVD CuO nanosystem. Vertical bars mark the switching-off of the illumination for 12 h (adapted from [18])

Among the published papers, three works outline the peculiar role of the MO_X morphology in determining the PC activity for H_2 production, with particular regard to quasi-1D systems. Yang *et al.* [20] reported on the use of heterojunctions between Si and TiO_2 in high density core-shell nanowire arrays obtained by an aqueous etching method. These systems were characterized by a higher photoactivity than the homologous planar structures, being very promising for solar H_2O splitting applications.

Arrays of well-aligned, cone-shaped VO_2 nanorods, obtained by heating V sheets [24], have been utilized for H_2 synthesis, an unprecedented use of V(IV) oxides. The authors reported evolution rates up to 800 mmol·m^{-2}·h^{-1} from water-ethanol solutions by using UV light incident along the rod axis, corresponding to the maximum amount of absorbed radiation, with a conversion efficiency of 38%.

In addition, hyper-branched quasi-1D CuO nanostructures prepared by CVD have been used in H_2 photo-production, presenting evolution rates of 2000 and 26000 L·h^{-1}·m^{-2}·g^{-1} under Vis and UV activation from H_2O-CH_3OH solutions, respectively (Fig. 7) [18]. This unexpected reactivity, accompanied also by a negligible deactivation under prolonged cycling, could be ascribed to the peculiar morphology of the obtained nanosystems, and, in particular, to the more extensive light absorption and reduced recombination phenomena related to the 1D structuring.

Conclusions and perspectives

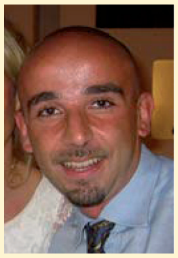
This critical review was focused on a synoptical overview of the most recent advances in the synthesis of tailored MO_X nanosystems for the sensing and photocatalytic degradation of pollutants and photocatalytic H_2 production. Rather than offering a comprehensive survey, this paper highlighted some cutting-edge results and trends bridging these different applications.

The synthetic progresses achieved in the last decades have enabled significant functional improvements in all the above fields. Yet, as regards gas sensing, despite the enhanced stability and sensitivity of quasi-1D systems, there are still various open issues, among which the applications of nano-sensors to security, *i.e.* detection of poisons, explosives, drugs [9], the improvement of their selectivity and the need of a more detailed insight into the nano-MO_X sensing mechanisms as a function of their peculiar morphology [8, 26, 30]. The most attractive future perspectives regard individual NW-based sensors, whose first prototypes stand out by the low energy consumption and fast dynamic response [35]. Yet, the large-scale production and integration of these devices with low-cost industrial processes is still an open challenge.

A similar consideration holds even for photocatalytic applications (pollutant degradation/H_2 production), for which more stable and reliable nano-PCs are still needed and a systematic approach regarding morphology-performance interrelations is missing. In addition, PCO reaction mechanisms for various VOCs are not fully understood up to date, and attention should be devoted to the possible generation of harmful intermediates in certain processes [4].

Photocatalytic H_2O splitting for H_2 production is a rapidly expanding field, facing an exponentially growing research interest for the expected environmental benefits. Recent works have evidenced the high potential of morphology control in determining such performances [18, 20, 24], and further advantages can be predicted by exploiting semiconductor heterojunctions, producing hierarchical nanoarchitectures with improved long-term stability. Yet, major problems related to the large-scale availability of cost-effective production routes, as well as obstacles related to H_2 distribution on a large scale, are still far from being solved, thus enabling to forecast only the possible medium-scale H_2 use in the near future.

Finally, it is worth recalling that, despite the high nanosystem potential for the above applications, any technology can be a double-edged sword. In fact, the short- and long-term hazards related to MO_X nanomaterials manipulation and large-scale use have not been elucidated in detail and undoubtedly deserve further investigations [28].



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RIASSUNTO

Nanomateriali multifunzionali a base di ossidi: applicazioni sostenibili in sensoristica e fotocatalisi

Questo articolo illustra alcuni aspetti innovativi nella sintesi mirata di nanosistemi funzionali a base di ossidi metallici per applicazioni tecnologiche sostenibili. In particolare, l'attenzione è rivolta alla rivelazione di inquinanti mediante sensori di gas, alla loro conversione in prodotti non tossici ed, infine, alla produzione di idrogeno mediante fotodecomposizione di soluzioni acquose.