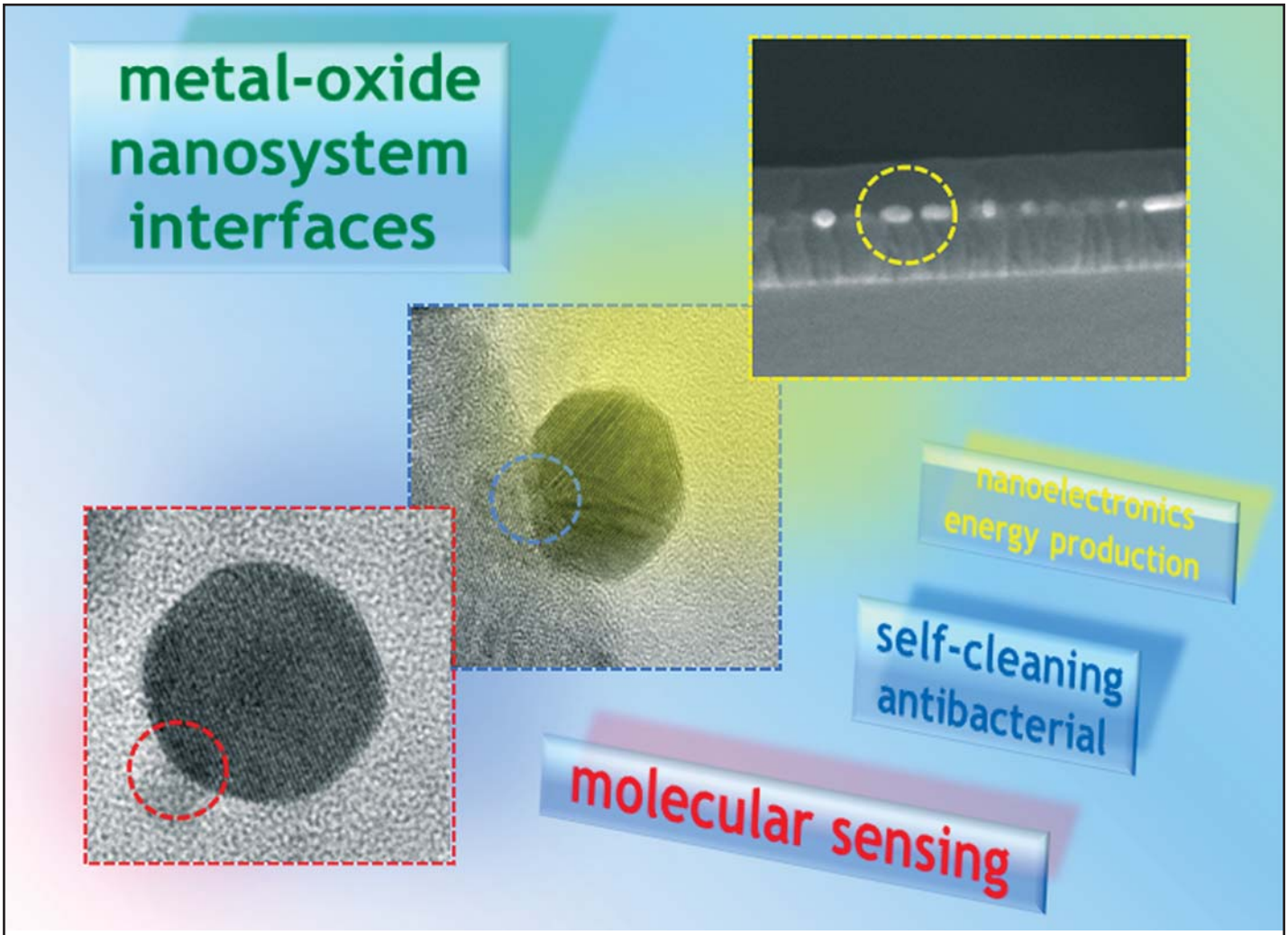

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Title: Metal/oxide interfaces in inorganic nanosystems: what's going on and what's next?

An attempt to address the most challenging issues regarding metal/oxide interfacialinteractions in inorganic nanostructures is performed. Particular emphasis is given to the system assembly and functional properties, highlighting the current trends and future directions in the science and technology of the target materials.

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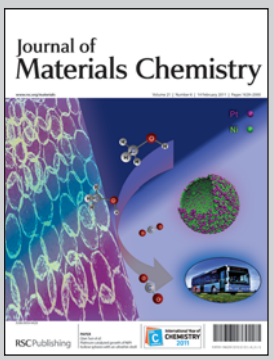

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Metal/oxide interfaces in inorganic nanosystems: what's going on and what's next?

Davide Barreca,*[a] Alberto Gasparotto[b] and Eugenio Tondello[b]

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Metal/oxide nanosystems with different spatial organizations have attracted a remarkable interest for their unique features and multi-functional properties, which can be finely tuned by controlling the interplay between their structure, morphology and composition. Their assembly and ultimate utilization depend indeed on the nature of metal/oxide interfaces, the birthplaces of a multitude of fascinating phenomena. A detailed insight into interfacial chemical/physical properties by advanced experimental techniques would thus deliver significant advantages from both a fundamental and an applicative point of view.

Introduction

The controlled assembly of metal/oxide (M/O) nanosystems with peculiar architectures has been the focus of intense research activities, in view of their fascinating and often unexpected characteristics.[1–5] The latter, ranging from size-dependent optical properties to novel chemical reactivity, have stimulated considerable attention for various applications, from heterogeneous catalysis/photocatalysis to gas sensing and energetics, from microelectronics to photonics and magnetic data storage.[2,6–14] Remarkable advancements to attain specifically targeted functions have been enabled by the *bottom-up* chemical design of M/O nanomaterials.[5,15] In this context, the degrees of freedom introduced by the tailoring of surface, size, shape and defects are globally interconnected[13,16,17] and their control has fuelled the preparation of various kinds of M/O nanomaterials, from 0D- to 1D-, 2D- and 3D-structures (Fig. 1).[4–7,9,18] Despite these considerable progresses, there is still a black box hindering further developments in the science and engineering of such systems, *i.e.* the thorough understanding of M/O interfacial interactions role, that, in spite of its importance, has so far been underestimated or neglected.[3,19,20] To this aim, as pointed out by H. Kroemer in his Nobel lecture, "…it may be said that the interface is the device".[21] In particular, interfaces between complex oxides have emerged for their potential in future electronics.[22]

Even M/O interfacial interactions, that might appreciably depend on the presence of defects, compositional gradients and roughness, play a pivotal role in directing the system functional performances.[6,23] For instance, the formation of Schottky barriers at the interface between metal nanoparticles (NPs) and semiconducting oxides[24] leads to improved charge carriers separation and transfer, with significant benefits on luminescence, sensing and photocatalytic properties.[12,25] Hence, a full exploitation of M/O heterojunction functionalities in advanced device structures relies on a thorough insight into interfacial phenomena,[6,7] although their detailed characterization still remains an open issue.[26]

On this basis, this highlight is mainly focused on the question: what is going on at metal NP/oxide interfaces? Far from being exhaustive, this paper provides some representative examples regarding

[a]*CNR-ISTM and INSTM, Department of Chemistry, Padova University, Via Marzolo, 1, 35131, Padova, Italy. E-mail: davide.barreca@unipd.it; Fax: +39 049 8275161; Tel: + 39 049 8275170*

[b]*Department of Chemistry, Padova University and INSTM, Via Marzolo, 1, 35131, Padova, Italy*

Davide Barreca

Davide Barreca is a Senior Research Scientist at the ISTM-CNR Institute in Padova, Italy. He is the European Editor of Nanoscience and Nanotechnology Letters and Associate Editor of Journal of Nanoscience and Nanotechnology. During his career, he published more than 160 papers on the synthesis and characterization of inorganic nanosystems based on metals, oxides and sulfides.

Alberto Gasparotto

Alberto Gasparotto is a Research Scientist at Padova University, Department of Chemistry, since 2007. His main research activity is devoted to the preparation and functional investigation of inorganic nanosystems synthesised by CVD, both thermal- and plasma-assisted, RF-sputtering and sol–gel. Up to date, he has published more than 100 papers on international journals.

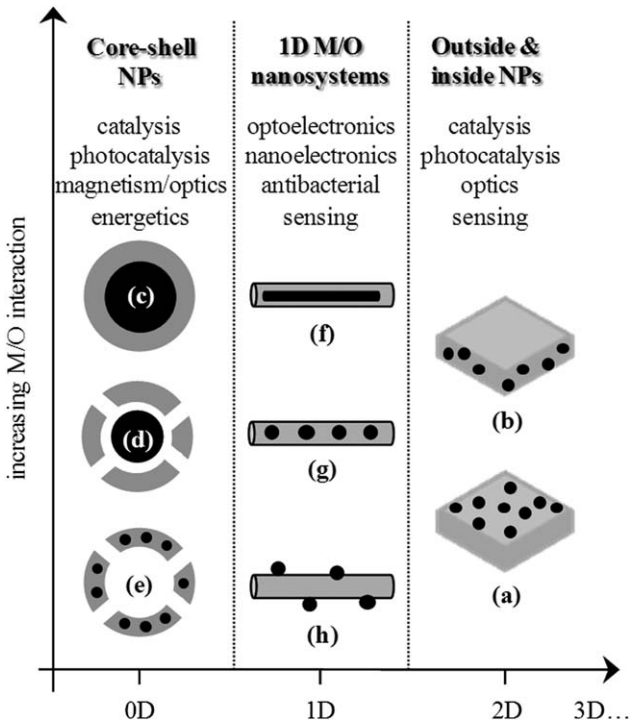

Fig. 1 Schematic illustration of the various types of M/O nanosystems considered in this highlight. M and O are marked in black and grey, respectively. For each category, the most relevant functional applications are also reported.

the influence of interfacial phenomena on: (i) the assembly of M/O nanosystems,[27] with particular attention on metal NPs spatial organization; (ii) the functional properties of the target materials and their interrelations with size- and shape-dependent features. Indeed, the processes involved in assembly phenomena span from physical interactions up to chemical bond formation, directly influencing the system performances.[13] These challenging issues will be briefly discussed in relation to the case studies displayed in Fig. 1.

Outside and inside NPs

These categories of M/O nanosystems (outside NPs, Fig. 1a) and, in particular, gold and silver NPs on metal oxides, have drawn a great attention for their optical, catalytic and sensing properties.[7,28–33] The use of physical techniques, such as sputtering[34,35] and pulsed laser ablation followed by laser irradiation,[36] has been reported for the tailored formation of Au and Ag NPs on SiO_2. In this regard, a major role in metal nucleation is believed to be played by surface –OH groups, despite no specific evidence of the exact M/O interaction is available. Modeling studies of M-on-O laser nanostructuring have considered M/O heat transfer and the metal propensity for oxide formation as the main parameters controlling the process evolution,[36] but the role of chemical interactions has not yet been considered in detail.

A great interest has also been focused on the introduction of metal NPs inside oxide matrices (Fig. 1b).[37,38] Armelao *et al.*[39] found that the growth of Ag nanoaggregates into SiO_2 *via* sol–gel is mediated by M/O interfacial interactions involving the formation of Ag–O–Si species around silver NPs. On the other hand, M/O interactions have a direct impact on functional properties. A recent report on Au-doped TiO_2 films[3] has evidenced a direct involvement of metallic NPs in the kinetics of gases detection thanks to M–O peripheral sites, promoting the analyte activation through charge transfer with the hosting matrix.

As concerns inside NPs, recent trends are focused on the precise control of metal aggregates spatial organization and integration into ordered arrays.[27] In fact, the possibility of tailoring the properties through coupling interactions not only with other NPs, but also with the surrounding medium, discloses intriguing perspectives for applications in lasers and surface-enhanced spectroscopies.[5,17,40,41] In this regard, island-like gold NP arrays have been produced by sputtering on SiO_2 under very mild conditions (Fig. 2a), tuning their organization by variations of the sole deposition time. Such a morphology is preserved upon coverage with a SiO_2 layer, a transparent and protective hosting medium for NP arrays (Fig. 2b).[15,42] The role of metal–oxide interactions is well evidenced by the effect of the surrounding matrix on the optical response and, in particular, on the surface plasmon resonance (SPR) peak shape and position (Fig. 2c).[5,13,34,35,38] In particular, the red-shift of the SPR band upon embedding Au NPs in SiO_2 could be attributed to an increase of the surrounding dielectric constant due to Au/SiO_2 interfacial interactions. These results, along with calculations of M/O optical responses performed through a combination of Maxwell-Garnett model and Mie theory,[43] indicate the possibility of tuning optical properties for specific

Eugenio Tondello

Eugenio Tondello is Full Professor of Inorganic Chemistry at the Faculty of Science, Padova University, Italy, from 1975. His research activity has been mainly devoted to the study of structure–property relationships of molecular systems, as well as inorganic and hybrid nanomaterials and surfaces. He has co-authored more than 210 scientific papers on international journals.

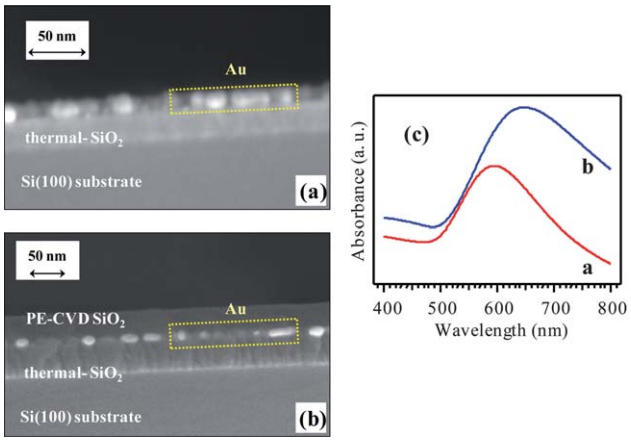

Fig. 2 Morphology of Au NP arrays on SiO_2 obtained at 60 °C after 60 min sputtering: (a) as such; (b) upon coverage with a SiO_2 layer by plasma enhanced-chemical vapor deposition (PE-CVD) at 60 °C. (c) Optical spectra of Au NP arrays depicted in (a) and (b) (adapted from ref. 41).

applications.[5,44] Nevertheless, the detailed nature of the involved M/O electronic interactions, especially at the nanometre scale, has still to be unraveled. To this regard, the use of advanced Scanning Tunnelling Microscopy (STM) and Scanning Tunnelling Spectroscopy (STS) could be extremely useful, despite the sample electrical properties render their application a hard task.

Intermediate cases between outside and inside NPs are represented by M/TiO_2 (M = Au, Ag) nanomaterials obtained by hybrid sputtering/sol–gel approaches.[7,24,45,46] Thanks to the peculiarity of the adopted synthetic routes, an intimate M–O contact, crucial for eventual functional applications, can be achieved (Fig. 3a and b). Whereas only Au^0 could be detected in the former case, the higher Ag *vs.* Au reactivity towards oxidation is responsible for a different behavior. In fact, for Ag/TiO_2 composites, $Ag^0 \rightarrow Ag^I$ oxidation, whose entity depended on the adopted annealing conditions, took place at the interface with the TiO_2 matrix. This phenomenon was likely responsible for an enhanced dragging of Ag NPs even in the inner TiO_2 layers.

In both cases, photocatalytic performances were significantly influenced by M/O interactions. For Au/TiO_2 composites, the activity enhancement with respect to pure TiO_2 has been ascribed to the Schottky barrier character of M–O junctions,[24] resulting in an electron drawing effect by gold NPs that favors light-induced charge carrier separation. Concerning Ag/TiO_2 nanomaterials, the best performances were obtained upon annealing at 400 °C, corresponding to the highest interfacial content of Ag^I,[45] a strong oxidizing agent. But once again, the question arises: which phenomena do exactly occur? And what is the mutual role of physical *vs.* chemical interactions in this context? The answer to these questions might be partially provided by Scanning Transmission Electron Microscopy–Electron Energy Loss Spectroscopy (STEM–EELS), representing a powerful chemical probe with high sensitivity to the sampled environment. Yet, the attainment of a nanometre spatial resolution is directly dependent on the availability of an HR-TEM facility.

Core–shell NPs

In relation to the above topics, a large amount of literature can be found on photocatalytic applications not only of classical core–shell M/O NPs (Fig. 1c), but also of porous nanocages (Fig. 1d). Zeng *et al.*[25] have developed Pt/ZnO porous nanocages (Fig. 4a) by laser ablation synthesis of Zn(core)/ZnO(shell) NPs, followed by Pt introduction from H_2PtCl_6 and a mild acidic etching of the metal core. Reaction of Zn metal cores with Pt^{IV} centers yields Zn^{II} (hollowing of the core part) and Pt^0, deposited *in situ* in the ZnO shell[12] (Fig. 4b). As a result, a large number of Pt/ZnO Schottky barriers are formed in the final nanocages, suggesting a better separation of photogenerated charges.[12,24,25]

Indeed, the photocatalytic activity (Fig. 4c) was significantly improved with

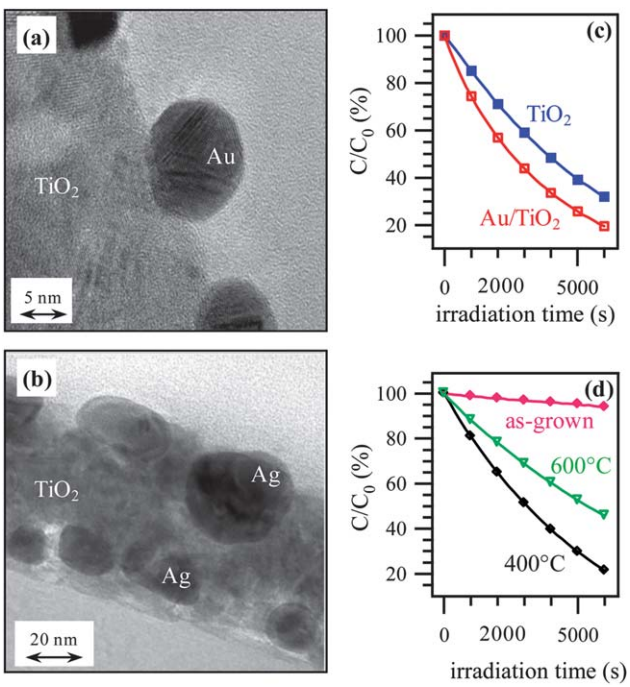

Fig. 3 TEM images of M/TiO_2 nanosystems, with (a) M = Au and (b) M = Ag, after annealing at 600 °C. Photobleaching of Plasmocorinth B (PB) aqueous solutions by: (c) pure TiO_2 and Au/TiO_2 nanosystems annealed at 600 °C; (d) as-grown and annealed Ag/TiO_2 nanocomposites (adapted from ref. 7, 24, 45, and 46).

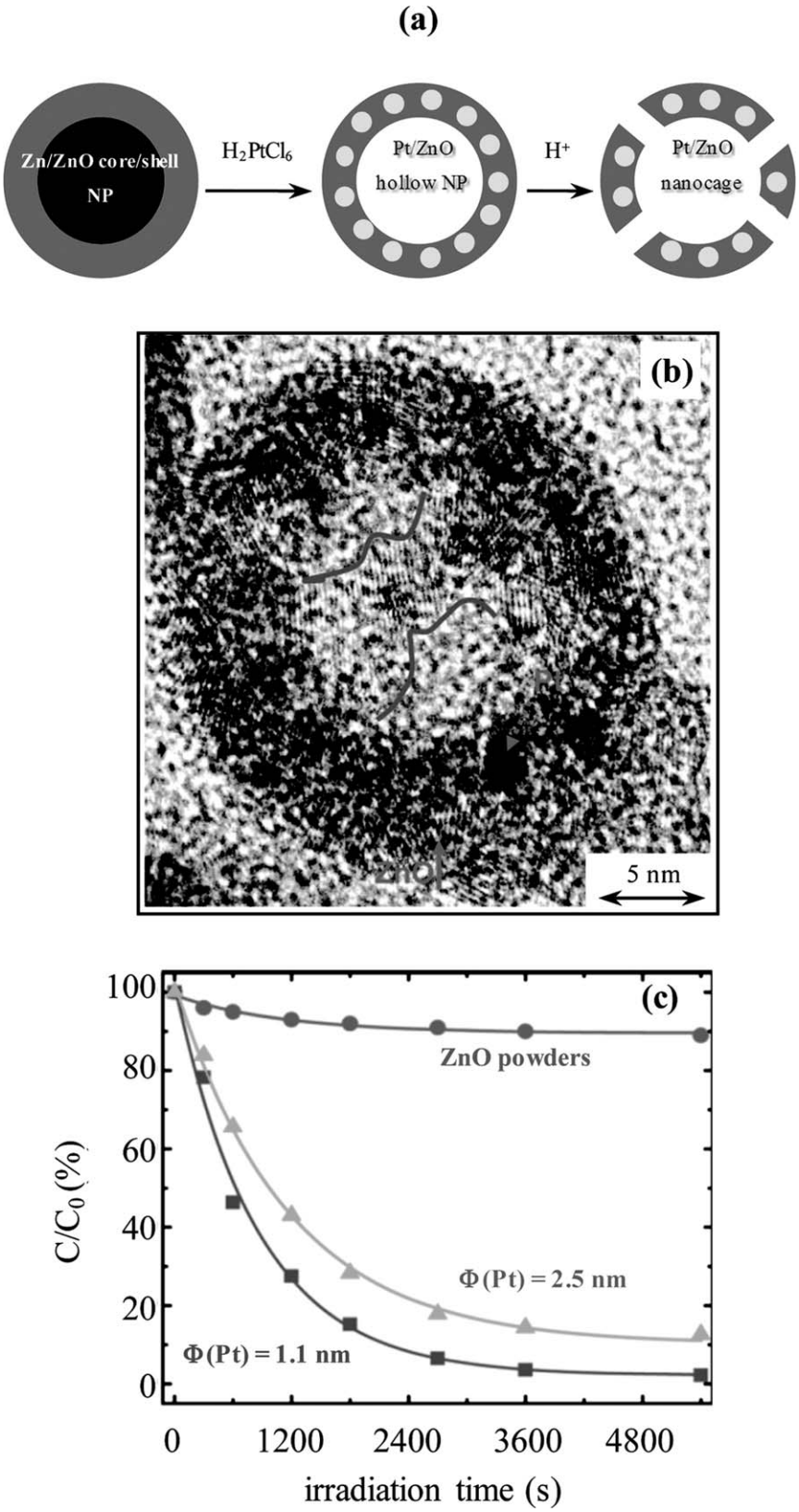

Fig. 4 (a) Synthesis route to porous Pt/ZnO nanocages and (b) representative HR-TEM image. ZnO crystals in the center of the particle joining the opposite cage walls have been marked. (c) Photodegradation of methyl orange solutions by ZnO powders and Pt/ZnO nanocages containing Pt NPs of different sizes (adapted from ref. 25).

respect to conventional ZnO powders, thanks to the synergy between the peculiar large area morphology and the Pt embedding state in the porous ZnO nanocages. In fact, the performances are further increased by reducing the Pt NPs size, implying an enhanced M–O contact. Nevertheless, we are ultimately confronted with the question of whether or not the simple M/O contact is the key influencing factor. What about the occurrence of interfacial chemical interactions? An interesting insight might be provided by the choice of proper synchrotron-based X-ray techniques with suitable spatial and energy resolution, such as X-ray Absorption Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS).

Concerning photo-activated applications, noble metals (*e.g.*, Pt, Rh, Au, and Ag) on various oxide substrates have also been proposed as promoters of water splitting[47] towards the evolution of H_2 as an attractive energy vector, whose production has been a fascinating dream since the publication of the "Misterious Island" by J. Verne (1874). In particular, Rh/Cr_2O_3 core–shell NPs have been successfully dispersed on GaN–ZnO solid solutions, achieving improved performances for visible-light activated H_2O splitting. In fact, the Cr_2O_3 shell prevents the backward reaction ($2H_2 + O_2 \rightarrow H_2O$) over Rh.[48] Nevertheless, the precise control of shell thickness and its influence on the system behavior remain open issues. Furthermore, the authors only reported that Rh/Cr_2O_3 NPs dispersion on the photocatalyst improves the electron transfer efficiency and that the $H^+ \rightarrow H_2$ reduction took place at the Rh/Cr_2O_3 interface,[47] but the exact occurring mechanism is still unknown.

Besides hydrogen photo-production,[49] further applications of core–shell systems obtained by confining metal NPs in inorganic cavities (Fig. 1e) fall into other areas of heterogeneous catalysis,[6] from preferential CO oxidation[50] to ammonia decomposition,[51] from water-gas-shift[52] to reforming reactions.[53] As a representative example, porous nanocages, for instance of Pd/CeO_2, have been proposed as an amenable path to avoid the formation of noble metal aggregates, with consequent catalyst deactivation.[54] Yet, it is worth highlighting that

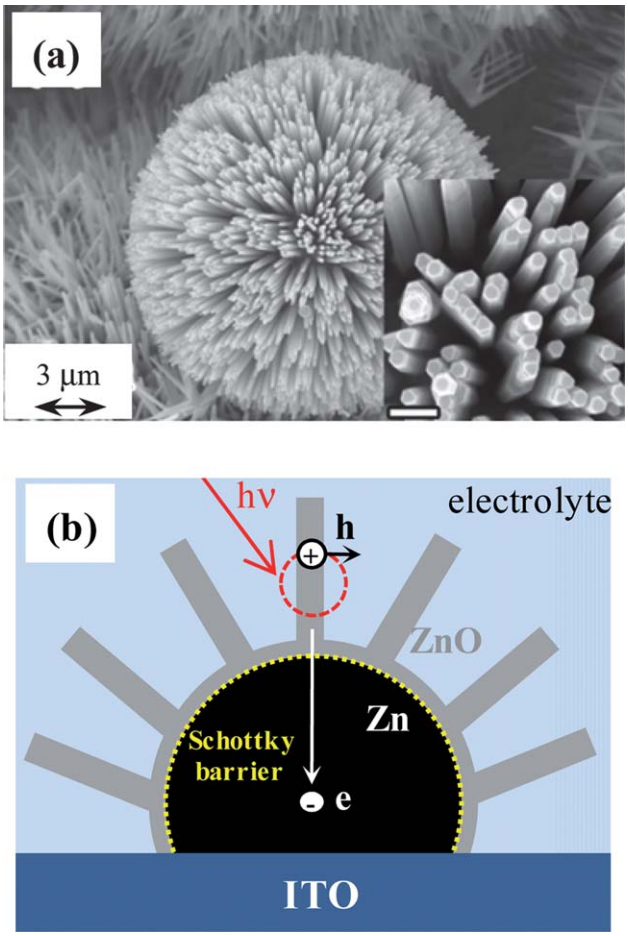

Fig. 5 (a) Representative SEM micrograph of urchin-like Zn/ZnO structures (inset scale bar: 400 nm). (b) Sketch of the generation, separation and transport of photo-induced charge carriers at the Zn/ZnO interface in the above structures (adapted from ref. 19).

a possible drawback of an intimate contact between Pd and the reducible CeO_2 support is a facile, though reversible, catalyst deactivation under reducing conditions.[52] Despite the accessibility of peripheral metal NP sites and the occurrence of interfacial M/O electron transfers facilitating CeO_2 redox properties have been demonstrated, the site-sensitive investigation of interfacial reactivity is still far from being elucidated. A similar observation holds even for the significance of such catalysts with respect to traditional ones possessing exposed metal–CeO_2 interface.[55] It is also worthwhile observing that all the above catalytic processes involve reactions of small molecules, which do not suffer from large diffusion limitations. Nevertheless, the use of porous core–shell structures may turn out to be unsuccessful if large organic molecules need to be converted.

Most of the systems examined up to now are targeted for optical/photocatalytic applications. Further interesting examples of the interface role concern coupled magnetic/optical applications, such as in the case of Co-core, concentric CoO–Au core–shell NPs.[56] In fact, ferromagnetic Co particles tend to oxidize in air to the non-passivating CoO. To prevent this problem, a protective Au shell was introduced from a solution route on the external CoO interface. As a consequence, the SPR gold peak was shifted with respect to that of pure Au NPs of the same diameter, due to Au/CoO interactions. These characteristics might play a significant role in coupling optical and magnetic applications, despite the nature of interfacial interactions has not yet been unraveled. Will high-resolution XAS and XPS techniques be a key tool in proving an answer to these questions?

A further interesting example of M–O heterojunctions concerns urchin-like Zn/ZnO core–shell NPs, composed by single-crystalline ZnO nanorods protruding from a central Zn core (Fig. 5a).[18] Such materials, that represent a *trait d'union* between core–shell 0D NPs and 1D M/O nanosystems, have been obtained by vapor transport through the initial nucleation of Zn nanospheres, subsequently oxidized to ZnO. A large lattice mismatch in the basal (0002) plane between Zn and ZnO results in ZnO nanorods grown epitaxially from the central core, in line with other reports.[57] The outstanding photoelectrochemical performances of such materials, that candidate them as promising anodes in solar energy conversion devices, were related to their unique structure (Fig. 5b). After hole and electron photo-generation in ZnO nanorods, the latter diffuse in the radial direction towards the Zn/ZnO interface, and finally to the indium tin oxide (ITO) substrate. Single crystalline ZnO rods provide direct channels for electron transport and can supply a sufficient space charge layer even at high applied potentials, resulting in a high photocurrent density. The efficiency of the Zn/ZnO interface in acting as electron sink is synergistically superimposed with a facilitated hole transport towards the electrolyte, thanks to the unique urchin-like morphology.

1D M/O nanosystems

At variance with previous cases, 1D-like M/O systems are by far the least explored,[1] especially regarding the nature of M–O interfacial interactions. The topology of such materials can be extremely different as a function of their assembly. Beyond the rational design of core–shell 1D M/O systems (Fig. 1f) for various applications,[1,4,11,15,57–59] we focus herein on the two cases depicted in Fig. 1g and h, *i.e.* metal NPs *in* or *on* 1D oxide structures, that represent the cutting-edge frontier of research activities in the field. An innovative type of heterojunction has been developed by the periodical encapsulation of Au NPs in Ga_2O_3 nanowires (Fig. 6a) by vapor–liquid–solid (VLS) growth.[18,60] This method provides a particular example of interface in M–O system assembly, in which metal droplet serves as soft templates to limit nanowire

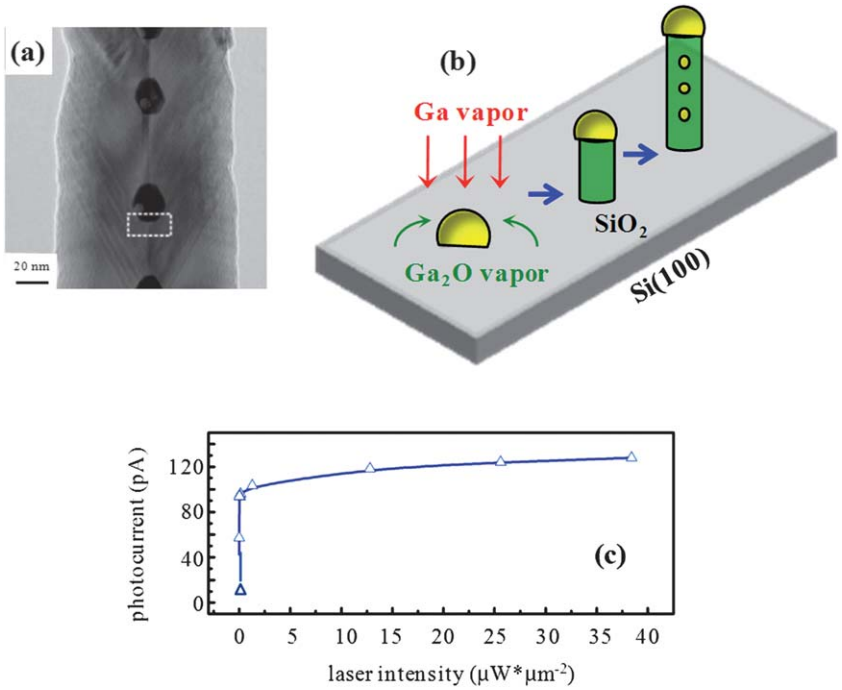

Fig. 6 (a) TEM image of an individual Ga_2O_3 nanowire embedding discrete Au NPs. The high quality M/O interface is framed. (b) Sketch of the corresponding growth mechanism. (c) Device photoresponse as a function of pumping power (adapted from ref. 18).

lateral growth. Once M liquid is supersaturated with the target oxide, 1D anisotropic formation starts to occur at the solid–liquid interface.[9] In this peculiar case, the growth is initiated by gallium incorporation from the vapor phase in a gold NP (Fig. 6b). For $T \geq 800$ °C, the supersaturation prevails around the droplet edge rather than in its central area, forming a Ga_2O_3 nanowire with an internal twin boundary. This twinned growth reflects the difference in the nucleation rate due to the non-homogeneous concentration of Ga_2O initially formed at the Ga droplet interface. Consequently, 1D Ga_2O_3 nanorods embedding Au NPs crystallize under the fluctuations of Ga_2O concentration and twin boundary formation. The remarkable system photoelectric response (Fig. 6c), similarly to the case of Au-in-SiO_2 nanofibers,[10] was explained by SPR effects of embedded gold NPs, and, in particular, to the large electromagnetic field at the interface of Au NPs, amplifying their third-order non-linear susceptibility.

Furthermore, the photoresponse is dominated by the generation of "hot" electrons in Au NPs and their tunnelling through Ga_2O_3 barrier, resulting in a direct proportionality with pumping power. The detailed understanding of underlying electron transfer processes might be valuable not only to improve the system response, but also to develop diverse optoelectronic devices by synthetic tailoring. For instance, a similar growth procedure has led to Au/Ga_2O_3 core–shell nanowires for high-frequency logic nanoelectronics.[60] For both preparation and application, advanced electrochemical investigations might be of help to unravel the involved electron transfer phenomena.

A different case regards the organization of M NPs *on* the surface of 1D oxides. For instance, Ag NPs have been immobilized on ZnO whiskers incorporated in a paper matrix for antibacterial applications, with 1D zinc oxide structures acting as selective supports for Ag nanoaggregates.[14] The excellent system antibacterial activity was interpreted basing on the synergy between their peculiar nanomorphology and the possible interfacial presence of Ag^I, a strong oxidizing agent.[45] Nonetheless, the impact of Ag/ZnO interfacial assembly on the system functional properties was not thoroughly investigated. A detailed insight into the material structural organization might be provided by Reflection High Energy Electron Diffraction (RHEED), a powerful analytical tool to elucidate the nucleation and growth processes.

Further interesting applications of M-on-O 1D systems concern the fields of sensing and energetics. In particular, Au and Pt NPs have been used to functionalize the surface of CuO nanoribbons, achieving attractive gas sensing performances for the detection of volatile organic compounds.[61] Yet, such enhancement was ascribed to the catalytic activity of metal NPs, without any further explanation. The chemical and physical properties beneath these processes might strongly benefit from the use of STEM-EELS and synchrotron XAS characterization.

Conclusions and perspectives

Thanks to the remarkable progresses in the synthesis techniques, M/O nanostructures with various degrees of complexity and programmable performances have shown a bright promise for technological advancements. Nevertheless, the examples provided above demonstrate that, even if tailoring of M/O system properties is possible as a function of the desired applications, a complete understanding of M/O interfacial interactions does not yet exist at this stage. That is, the question '*Quo vadis*?' (where do we go from here?) in these areas is still far from receiving an appropriate answer. Further advancements in the related fields can no more be based on a '*proof-of-concept*' approach,[2] and a quantitative assessment on how and why chemical and physical interfacial interactions impact the system organization and properties is imperative. This insight can be derived on an experimental basis through the joint use of advanced characterization techniques providing complementary information, some of which have been mentioned in this paper. A deeper understanding can be also corroborated by a reliable and flexible theoretical modeling capable of bridging the interface role with M/O nanosystem properties as a function of their length scale. Only on this basis, the highway towards "what's next?" in M/O systems development for the science and technology of the future will finally be taken.

Acknowledgements

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References

1 S. J. Limmer, T. P. Chou and G. Cao, *J. Phys. Chem. B*, 2003, **107**, 13313–13318.
2 Z. Nie, A. Petukhova and E. Kumacheva, *Nat. Nanotechnol.*, 2010, **5**, 15–25.
3 D. Buso, M. Post, C. Cantalini, P. Mulvaney and A. Martucci, *Adv. Funct. Mater.*, 2008, **18**, 3843–3849.
4 X. Y. Kong, Y. Ding and Z. L. Wang, *J. Phys. Chem. B*, 2004, **108**, 570–574.
5 A. Seyed-Razavi, I. K. Snook and A. S. Barnard, *J. Mater. Chem.*, 2010, **20**, 416–421.
6 L. De Rogatis, M. Cargnello, V. Gombac, B. Lorenzut, T. Montini and P. Fornasiero, *ChemSusChem*, 2010, **3**, 24–42.
7 L. Armelao, D. Barreca, G. Bottaro, A. Gasparotto, S. Gross, C. Maragno and E. Tondello, *Coord. Chem. Rev.*, 2006, **250**, 1294–1314.
8 M. Acciarri, C. Canevali, C. M. Mari, M. Mattoni, R. Ruffo, R. Scotti, F. Morazzoni, D. Barreca, L. Armelao, E. Tondello, E. Bontempi and L. E. Depero, *Chem. Mater.*, 2003, **15**, 2646–2650.
9 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353–389.
10 W. Shi, W. Lu and L. Jiang, *J. Colloid Interface Sci.*, 2009, **340**, 291–297.
11 Y.-H. Wong and Q. Li, *J. Mater. Chem.*, 2004, **14**, 1413–1418.
12 H. Zeng, W. Cai, P. Liu, X. Xu, H. Zhou, C. Klingshirn and H. Kalt, *ACS Nano*, 2008, **2**, 1661–1670.
13 S. Liu and Z. Tang, *J. Mater. Chem.*, 2010, **20**, 24–35.
14 H. Koga, T. Kitakoa and H. Wariishi, *J. Mater. Chem.*, 2009, **19**, 2135–2140.
15 A. Guerrero-Martínez, J. Pérez-Juste and L. M. Liz-Marzán, *Adv. Mater.*, 2010, **22**, 1182–1195.
16 G. A. Ozin and L. Cademartiri, *Small*, 2009, **11**, 1240–1244.
17 S. M. Prokes, O. J. Glembocki, R. W. Wendell and M. G. Ancona, *Appl. Phys. Lett.*, 2007, **90**, 093105.
18 C.-H. Hsieh, L.-J. Chou, G.-R. Lin, Y. Bando and D. Goldberg, *Nano Lett.*, 2008, **8**, 3081–3085.
19 D.-M. Tang, G. Liu, F. Li, J. Tan, C. Liu, G. Q. Lu and H.-M. Cheng, *J. Phys. Chem. C*, 2009, **113**, 11035–11040.
20 G. A. Ozin, K. Hou, B. V. Lotsch, L. Cademartiri, D. P. Puzzo, F. Scotognella, A. Ghadimi and J. Thomson, *Mater. Today*, 2009, **12**, 12–23.
21 J. Mannhart and D. G. Schlom, *Science*, 2010, **327**, 1607–1611.
22 A. D. Caviglia, S. Gariglio, N. Reyren, D. Jaccard, T. Schneider, M. Gabay, S. Thiel, G. Hammerl, J. Mannhart and J.-M. Triscone, *Nature*, 2008, **456**, 624–626.
23 M. Chiesa, E. Giamello, C. Di Valentin, G. Pacchioni, Z. Sojka and S. Van Doorslaer, *J. Am. Chem. Soc.*, 2005, **127**, 16935–16944.
24 L. Armelao, D. Barreca, G. Bottaro, A. Gasparotto, C. Maccato, C. Maragno, E. Tondello, U. Lavrenčič Štangar, M. Bergant and D. Mahne, *Nanotechnology*, 2007, **18**, 375709.
25 H. Zeng, P. Liu, W. Cai, S. Yang and X. Xu, *J. Phys. Chem. C*, 2008, **112**, 19620–19624.
26 D. R. Baer, J. E. Amonette, M. H. Engelhard, D. J. Gaspar, A. S. Karakoti, S. Kuchibhatla, P. Nachimuthu, J. T. Nurmi, Y. Qiang, V. Sarathy, S. Seal, A. Sharma, P. G. Tratnyek and C.-M. Wang, *Surf. Interface Anal.*, 2008, **40**, 529–537.
27 H. Fan, K. Yang, D. M. Boyle, T. Sigmon, K. J. Malloy, H. Xu, G. P. López and C. Jeffrey Brinker, *Science*, 2004, **304**, 567–571.
28 M. Amft and N. V. Skorodumova, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 195443.
29 L. Armelao, D. Barreca, G. Bottaro, G. Bruno, A. Gasparotto, M. Losurdo and E. Tondello, *Mater. Sci. Eng., C*, 2005, **25**, 599–603.
30 J. K. Edwards, B. Solsona, P. Landon, A. F. Carley, A. Herzing, M. Watanabe, C. J. Kiely and G. Hutchings, *J. Mater. Chem.*, 2005, **15**, 4595–4600.
31 N. Kamiuchi, T. Matsui, R. Kikuchi and C. Eguchi, *J. Phys. Chem. C*, 2007, **111**, 16470–16476.
32 L. Armelao, D. Belli Dell'Amico, R. Braglia, F. Calderazzo, F. Garbassi, G. Marra and A. Merigo, *Dalton Trans.*, 2009, 5559–5566.
33 L. Abis, L. Armelao, D. Belli Dell'Amico, F. Calderazzo, F. Garbassi, A. Merigo and E. A. Quadrelli, *J. Chem. Soc., Dalton Trans.*, 2001, 2704–2709.
34 D. Barreca, A. Gasparotto, E. Tondello, G. Bruno and M. Losurdo, *J. Appl. Phys.*, 2004, **96**, 1655–1665.
35 D. Barreca, A. Gasparotto, C. Maragno, E. Tondello and S. Gialanella, *J. Appl. Phys.*, 2005, **97**, 054311.
36 S. J. Henley, J. D. Carey and S. R. P. Silva, *Phys. Rev. B: Condens. Matter*, 2005, **72**, 195408.
37 L. Armelao, G. Bottaro, R. Campostrini, S. Gialanella, M. Ischia, F. Poli and E. Tondello, *Nanotechnology*, 2007, **18**, 155606.
38 I. Bannat, K. Wesswels, T. Oekermann, J. Rathousky, D. Bahnemann and M. Wark, *Chem. Mater.*, 2009, **21**, 1645–1653.
39 L. Armelao, R. Bertoncello and M. De Dominicis, *Adv. Mater.*, 1997, **9**, 736–741.
40 D. Li, D.-W. Li, Y. Li, J. S. Fossey and Y.-T. Long, *J. Mater. Chem.*, 2010, **20**, 3688–3693.
41 D. Barreca, A. Gasparotto, C. Maccato and E. Tondello, *Nanotechnology*, 2008, **19**, 255602.
42 L. M. Liz-Marzán and P. Mulvaney, *J. Phys. Chem. B*, 2003, **107**, 7312–7326.
43 D. C. Schinca, L. B. Scaffardi, F. A. Videla, G. A. Torchia, P. Moreno and L. Roso, *J. Phys. D: Appl. Phys.*, 2009, **42**, 215102.
44 I. Pastoriza-Santos, D. Gomez, J. Pérez-Juste, L. M. Liz-Marzán and P. Mulvaney, *Phys. Chem. Chem. Phys.*, 2004, **6**, 5056–5060.
45 L. Armelao, D. Barreca, G. Bottaro, A. Gasparotto, C. Maccato, E. Tondello, O. I. Lebedev, S. Turner, G. Van Tendeloo, C. Sada and U. Lavrenčič Štangar, *ChemPhysChem*, 2009, **10**, 3249–3259.
46 L. Armelao, D. Barreca, G. Bottaro, A. Gasparotto, E. Tondello, M. Ferroni and S. Polizzi, *Chem. Mater.*, 2004, **16**, 3331–3338.
47 K. Maeda, K. Teramura, D. Lu, N. Saito, Y. Inoue and K. Domen, *J. Phys. Chem. C*, 2007, **111**, 7554–7560.
48 N. Sakamoto, H. Ohtsuka, T. Ikeda, K. Maeda, D. Lu, M. Kanehara, K. Teramura, T. Teranishi and K. Domen, *Nanoscale*, 2009, **1**, 106–109.
49 V. Gombac, L. Sordelli, T. Montini, J. J. Delgado, A. Adamski, G. Adami, M. Cargnello, S. Bernal and P. Fornasiero, *J. Phys. Chem. A*, 2010, **114**, 3916–3925.
50 M. Cargnello, C. Gentilini, T. Montini, E. Fonda, S. Mehraeen, M. F. Chi, M. Herrera-Collado, N. D. Browning, S. Polizzi, L. Pasquato and P. Fornasiero, *Chem. Mater.*, 2010, **22**, 4335–4345.
51 T. Montini, C. C. Pavel, M. Comotti, F. Vizza, C. Bianchini and P. Fornasiero, *ChemCatChem*, 2010, **2**, 1096–1106.
52 N. L. Wieder, M. Cargnello, K. Bakhmutsky, T. Montini, P. Fornasiero and R. J. Gorte, *J. Phys. Chem. C*, 2010, DOI: 10.1021/jp102965e, in press.
53 S. Specchia, L. D. Vella, L. De Rogatis, T. Montini, V. Specchia and P. Fornasiero, *Catal. Today*, 2010, **155**, 101–107.
54 M. Cargnello, N. L. Wieder, T. Montini, R. J. Gorte and P. Fornasiero, *J. Am. Chem. Soc.*, 2010, **132**, 1402–1409.
55 C. M. Y. Yeung and S. C. Tsang, *J. Phys. Chem. C*, 2009, **113**, 6074.
56 S. H. Johnson, C. L. Johnson, S. J. May, S. Hirsch, M. W. Cole and J. E. Spanier, *J. Mater. Chem.*, 2010, **20**, 439–443.
57 M. Trejo, P. Santiago, H. Sobral, L. Rendón and U. Pal, *Cryst. Growth Des.*, 2009, **9**, 3024–3030.
58 L. Li, Y.-W. Yang, G.-H. Li and L.-D. Zhang, *Small*, 2006, **2**, 548–533.
59 W. Zhou, G. Wang, X. Hong and X. Shen, *J. Phys. Chem. C*, 2009, **113**, 5450–5454.
60 C.-H. Hsieh, M.-T. Chang, Y.-J. Chien, L.-J. Chou, L.-J. Chen and C.-D. Chen, *Nano Lett.*, 2008, **8**, 3288–3292.
61 X. Gou, G. Wang, J. Yang, J. Park and D. Wexler, *J. Mater. Chem.*, 2008, **18**, 965–969.

