Zinc and Copper Oxides Functionalized with Metal Nanoparticles: An Insight Into Their Nano-Organization

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Ag/ZnO and Au/Cu2xO (x = 1, 2) nanocomposites supported on Si(100) and polycrystalline Al2O3 were synthesised by hybrid approaches, combining chemical vapor deposition (either thermal or plasma-assisted) of host oxide matrices and subsequent radio frequency-sputtering of guest metal particles. The influence of the adopted synthetic parameters on the nanocomposite morphological and compositional features was investigated by field emission-scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. Results confirm the synthesis of ZnO and Cu2xO nanoarchitectures, characterized by a tailored morphology and an intimate metal/oxide contact. A careful control of the processing conditions enabled a fine tuning of the mutual constituent distribution, opening thus attractive perspectives for the engineering of advanced nanomaterials.

Keywords: Zinc Oxide, Copper Oxides, Metal Nanoparticles, Chemical Vapor Deposition, Radio Frequency-Sputtering.

1. INTRODUCTION

Nanocomposites combining oxide matrices with metal nanoparticles (NPs) are a fascinating class of materials for several applications, encompassing drug-delivery, optics and optoelectronics, gas sensing, photocatalysis, as well as energy production and storage.1−4 As a matter of fact, their attractive functional properties are influenced not only by the unique features arising from nano-organization, but also from the mutual distribution and synergistic interactions between metal and oxide counterparts.1−3 In this scenario, tailoring composition, size and spatial distribution of each component by suitable synthetic approaches is a strategic goal from both a fundamental and an applicative point of view. An actual open challenge concerns the controllable preparation of nanocomposites supported on selected substrates, which offer enhanced functional properties with respect to the homologous powdered counterparts, allowing a direct integration into advanced devices. In particular, the development of novel high-performance materials relies on nano- to micro-level diagnostics of their structural and morphological features, enabling to interrelate the latter with the synthesis conditions and to optimize their preparation process. In this regard, the complementary use of electron microscopies, such as field emission-scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), can provide crucial information for metal/oxide nanosystem design and implementation.

Among the various oxide semiconductors, ZnO and Cu2xO (x = 1, 2) offer attractive properties in terms of low production cost, biocompatibility and safety, along with size- and shape-dependent properties for a plethora of functional end-uses.5−13 Further considerable interest in these systems is based on the possibility to grow thin films, quantum wells, nanorods, nanoplatelets... with a broad variety of morphological features, rendering zinc and copper oxides interesting platforms for the fabrication of metal/oxide nanocomposites.

Basing on the issues raised above, the present contribution deals with two selected case studies of supported metal/oxide nanocomposites, namely Ag/ZnO and...
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Au/Cu$_x$O ($x = 1, 2$). The target systems have been obtained by joint synthetic strategies based on: (i) the initial chemical vapor deposition (CVD) [either thermal or plasma-assisted (PA-CVD)] of the oxide platform; (ii) the radio frequency (RF)-sputtering of the corresponding metal component. These original routes exploit the versatility of CVD processes to synthesise \textit{host} oxides with tailored structure and morphology, along with the infiltration power of RF-sputtering to disperse \textit{guest} metal NPs with controlled features.$^{14-17}$

This paper attempts to offer an insight into the system nano-organization, highlighting the complementary use of FE-SEM and TEM as powerful and strategic investigation tools. Additional information on the system composition and structure was gained by energy dispersive X-ray spectroscopy (EDXS), X-ray photoelectron spectroscopy (XPS) and glancing incidence X-ray diffraction (GIXRD). Rather than offering a systematic characterization, selected data are presented and critically discussed, in an effort to provide a perspective on the potential of the adopted preparation and characterization techniques.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

Ag/ZnO nanosystems were obtained by a two-step route (PA-CVD+RF-sputtering) on suitably pre-cleaned $p$-type Si(100) and Al$_2$O$_3$ substrates.$^{14,15}$ The initial growth of columnar ZnO arrays was performed by PA-CVD ($\nu = 13.56$ MHz) under Ar/O$_2$ plasmas from a Zn(II) bis(ketoiminate) precursor, $\text{Zn[CH}_3\text{O(CH}_2\text{)}_3\text{NC(CH}_3\text{)}_2\text{CHC(CH}_3\text{)}_2\text{O]}_2$, adopting the following experimental settings: substrate temperature = 300 °C; total pressure = 1.0 mbar; RF-power = 20 W; duration = 60 min. Sequentially, Ag NPs were deposited over ZnO nanosystems by RF-sputtering (Ar plasmas; total pressure = 0.3 mbar; RF-power = 5 W; substrate temperature = 60 °C) from a silver target (0.1 mm thick; BAL-TEC AG$^\circledR$, purity = 99.9%). The Ag loading onto ZnO matrices was tuned by using two different RF-sputtering deposition times, 30 and 90 min. The effect of thermal treatment in air (400 °C, 1 h) on the system characteristics was also investigated.

Au/Cu$_x$O ($x = 1, 2$) systems were prepared as follows. Initially, copper oxide nanostructures were grown on pre-cleaned $p$-type Si(100) substrates (see above) using a cold-wall thermal CVD apparatus. The chosen precursor, Cu(hfa)$_2$TMEDA (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; TMEDA = $N,N,N',N'$-tetramethylethylenediamine), was vaporized under flowing O$_2$ at 70 °C. An additional O$_2$ flow passing through a water reservoir maintained at 50 °C was separately introduced into the reaction chamber. The synthesis of pure Cu$_2$O and CuO nanostructures was performed for 120 min at temperatures of 400 and 550 °C, with total pressures of 3.0 and 10.0 mbar, respectively.$^{16,17}$ Finally, Au deposition on Cu$_x$O matrices was carried out by RF-sputtering from a gold target (0.1 mm thick; BAL-TEC AG$^\circledR$).

![Fig. 1. FE-SEM BSE and SE plane-view (a,d) and cross-sectional (b,e) images for an Ag/ZnO nanocomposite on Si(100), obtained with a silver sputtering time of 30 min. (a,b,c) and (d,e,f) refer to as-prepared and annealed specimens, respectively. EDXS line-scans (c,f) were recorded along the lines marked in cross-sectional micrographs. Arrows indicate the direction of abscissa increase. Representative Ag NPs are highlighted by red circles in plane-view FE-SEM micrographs.](image-url)
AG®, purity = 99.99%), under similar conditions to those adopted for silver (Ar plasmas; total pressure = 0.4 mbar; RF-power = 5 W; substrate temperature = 60 °C; experiment duration = 10 min).

2.2. Characterization

FE-SEM images were recorded collecting secondary and back-scattered electron signals (SE and BSE, respectively) by means of a Zeiss SUPRA 40VP instrument, equipped with an Oxford INCA x-sight X-ray detector for EDXS investigation. Plane-view and cross-sectional micrographs were taken using primary beam voltages between 10 and 20 kV.

TEM and high resolution-TEM (HR-TEM) experiments were carried out on a Tecnai G2 30 UT microscope operated at 300 kV with a 0.17 nm point resolution. Cross-sectional specimens for TEM were prepared by mechanically grinding down to the thickness of approximately 20 μm, followed by Ar+ ion-beam milling using a Balzers RES 101 GVN apparatus.

GIXRD patterns were collected at a constant incidence angle of 1° by a Bruker D8 Advance diffractometer equipped with a Göbel mirror, using a CuKα X-ray source.

XPS analyses were carried out by a Perkin-Elmer Phi5600ci spectrometer at pressures lower than 1×10⁻⁸ mbar, using non-monochromatized AlKα radiation. Quantitation was performed using sensitivity factors provided by Phi V5.4 A software. In-depth analyses were carried out by Ar⁺ sputtering (energy = 4.5 kV; partial pressure = 5 × 10⁻⁸ mbar).

3. RESULTS AND DISCUSSION

3.1. Ag/ZnO Nanosystems

In this work, the attention was initially devoted to the analysis of Ag/ZnO structure and composition both before and after thermal treatment. The obtained data demonstrated the formation of (001)-oriented wurtzite ZnO, along with partially oxidized silver species. In order to investigate the annealing effect on Ag NP distribution in ZnO host matrices, FE-SEM and EDXS analyses were performed. Figures 1(a and d) display plane-view micrographs collected both in SE and BSE modes for Ag/ZnO systems obtained with a silver sputtering time of 30 min. For both as-prepared and annealed samples, the chemical contrast provided by BSE imaging revealed the presence of brighter...
spots, ascribable to small Ag NPs uniformly decorating the outermost system layers. Cross-sectional FE-SEM observations (Figs. 1(b and e)) showed the presence of homogeneously columnar ZnO arrays perpendicular to the substrate surface, whose spatial organization was maintained upon annealing.

In the as-prepared samples, silver nanoaggregates had mean diameter values of ≈ 10 nm and were homogeneously distributed over ZnO column tops, whereas upon annealing a decrease of Ag NP density could be observed. This evidence could be traced back to two different phenomena induced by thermal treatment: (i) the coalescence of some metal NPs, which tended to merge into larger aggregates at ZnO grain boundaries; (ii) an in-depth Ag distribution into the metal oxide host matrix. In order to attain a deeper insight into the latter phenomenon, EDXS line-scan analyses were performed along sample cross-sections, monitoring OK/Slα1, ZnK/Slα1 and AgL/Slα1 signals throughout the whole deposit thickness. As can be noticed, the as-prepared composite (Fig. 1(c)) showed an Ag accumulation in the outermost region (see the Ag signal maximum at ≈ 190 nm). Conversely, for the annealed system (Fig. 1(f)) this phenomenon was not evident due to an in-depth silver diffusion throughout the host ZnO matrix, highlighting that this effect was predominant over thermally-induced particle coalescence.

Further important information on the system nanostructure after annealing was gained by TEM and HR-TEM studies (Fig. 2). In line with Figure 1(d), this investigation confirmed that, beyond small NPs, Ag was also present in form of larger aggregates (diameter values ≈ 40 nm), possessing an intimate contact with zinc oxide (Fig. 2(b)). In addition, HR-TEM imaging (Fig. 2(c)) evidenced that the Si(100) substrate was covered by a uniform SiO2 layer ≈ 4 nm thick. The in-depth diffusion of silver throughout the ZnO host material was demonstrated by the presence of Ag NPs up to the interface with the substrate (see Fig. 2(a) and white arrows in Fig. 2(c)). These results, unambiguously confirming FE-SEM and

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**Fig. 3.** FE-SEM cross-sectional images (a, c) and EDXS line-scans (b, d) for annealed Ag/ZnO nanocomposites obtained with a silver sputtering time of 90 min on Si(100) (a, b) and Al2O3 (c, d) substrates. EDXS line-scans were recorded along the lines marked in cross-sectional micrographs. Arrows indicate the direction of abscissa increase.

**Fig. 4.** (a) Typical GIXRD patterns for Au/CuO nanocomposites supported on Si(100). Vertical lines mark peak positions expected for Cu2O (black) and CuO (red) phases. (b) Au/Cu atomic percentage ratio, obtained by XPS analyses, vs. sputtering time for Au/CuO nanocomposites supported on Si(100). The inset reports a higher magnification corresponding to low atomic ratio values.
EDXS data, evidenced that the adopted annealing procedure was effective in modifying the in-depth silver NP distribution.

Figure 3 displays FE-SEM and EDXS data for two samples obtained after 90 min of silver sputtering on both Si(100) and polycrystalline Al₂O₃. Irrespective of the used substrate, ZnO growth was always characterized by well defined columnar arrays with a similar overall length (compare Figs. 3(a and c)). In this case, cross-sectional EDXS line-scans revealed a silver distribution different from the one observed for a shorter sputtering time. In fact, Ag EDXS trends (Figs. 3(b and d)) showed a limited, though still detectable, Ag amount diffused throughout the specimen section, along with a well evident silver accumulation in the outermost region. Such a behavior suggested that, for higher silver loading, ZnO matrices were capable of hosting only a limited metal amount in the inner layers, and a concomitant out-diffusion of excess Ag took place. Correspondingly, the formation of large spherical particles (\( \varnothing \approx 70–80 \text{ nm} \)) on the deposit surface was observed, as shown by a careful inspection of Figures 3(a and c).

3.2. Au/CuₓO Nanosystems

Basing on our previous results,⁷ copper oxide synthesis enabled to selectively obtain either Cu₂O or CuO phases at 400 or 550 °C, respectively, as confirmed by GIXRD analysis (Fig. 4(a)). In fact, for CuₓO-based samples the peaks located at 29.6°, 36.4° and 42.3° were assigned to (110), (111) and (200) reflections of the cuprite phase.¹⁸ In the case of CuO-containing systems, peaks at 32.5°, 35.5°, 38.7°, 46.3° and 48.8° were related to (110), (002)/(111), (111)/(200), (112) and (202) tenorite planes.¹⁹ As a matter of fact, no gold diffraction peaks could be observed in GIXRD patterns, due to the high dispersion and low amount of the deposited metal.¹⁶,¹⁷

In order to attain further information on gold chemical state and dispersion, XPS analyses were carried out. As a general rule, metallic Au was always detected [BE(Au 4f/2) = 84.4 eV], with surface atomic percentages of 25.0% and 13.0% on CuₓO and CuO host matrices, respectively. Depth profile investigation (Fig. 4(b)) evidenced significant differences on the metal in-depth distribution in the two cases. For Au/Cu₂O nanomaterials, the Au/Cu atomic ratio values evidenced a gold accumulation on the system surface and a subsequent fast decrease upon erosion, pointing out to a scarce metal penetration into copper(I) oxide. For Au/CuO samples, the gold-to-copper ratio on the system surface was lower than in the previous case, and underwent a slower decrease than for Au/Cu₂O upon Ar⁺ sputtering. Since gold deposition

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Fig. 5. Plane-view FE-SEM micrographs of: (a) bare Cu₂O and (d) CuO matrices supported on Si(100); (b) Au/Cu₂O and (e) Au/CuO nanocomposites, along with higher magnification images. Cross-sectional micrographs for (c) Au/Cu₂O and (f) Au/CuO nanosystems.
was performed under the same experimental conditions on both Cu$_2$O and CuO (i.e., Au loading was the same on both systems), the present data suggested an enhanced gold distribution inside copper(II) oxide matrices. Such an observation was corroborated by the study of the system morphology, undertaken by plane-view and cross-sectional FE-SEM analyses (Fig. 5). The inspection of images pertaining to bare CuO and Cu$_2$O (Figs. 5(a and d)) evidenced a completely different morphology for the two matrices. Copper(I) oxide was in fact characterized by well-interconnected pyramidal aggregates (average dimensions $\approx 120$ nm), producing a rather compact deposit. In a different way, CuO systems were formed by the interconnection of multi-granular flower-like nanostructures, resulting in a higher system porosity. Upon gold deposition (Figs. 5(b and e)), the morphology of the pristine materials did not undergo remarkable changes, pointing out that the adopted RF-sputtering conditions were mild enough to prevent undesired alterations. The higher magnification image in Figure 5(b) revealed a uniform distribution of Au particles ($\approx 6$ nm) decorating Cu$_2$O nanopysramid surface. In the case of CuO, the more porous structure, as also evidenced by cross-sectional observations (compare Figs. 5(c and f)) was likely responsible for an enhanced in-depth gold dispersion, in line with Figure 4(b). To further investigate the spatial distribution of gold NPs, TEM analyses were also carried out on these composites. Cross-sectional micrographs (Fig. 6(a)) displayed the formation of porous structures for CuO-based systems, in agreement with FE-SEM observations (see Fig. 5(f)). Most importantly, these studies confirmed the occurrence of highly dispersed Au nanoggregates into copper(II) oxide matrices. In particular, HR-TEM images (Fig. 6(b)) revealed the presence of spherical gold NPs, having a mean diameter of $7 \pm 2$ nm, in close contact with CuO. A careful inspection enabled to discern that some of these NPs were twinned or characterized by stacking faults.

Overall, the present data highlight the importance of material morphological design as one of the key parameters in the development of composite nanosystems. This issue, pointing out to the possibility of oxide matrix functionalization with controlled metal loadings, is of great interest in various applicative fields.

4. CONCLUSIONS

Ag/ZnO and Au/Cu$_x$O ($x = 1/2$) nanosystems have been synthesized by original two-step approaches, involving the growth of host oxide matrices by CVD techniques and the subsequent deposition of guest metal NPs by RF-sputtering. In this work, particular attention has been devoted to a detailed investigation of the system nanoorganization, with special focus on metal NP distribution as a function of the adopted synthetic conditions and of the host matrix features. The versatility of the adopted routes has enabled to tailor NP size and dispersion by a proper setting of experimental parameters, taking advantage of RF-sputtering infiltration power and of eventual thermal treatments. As a result, nanocomposites endowed with an intimate metal/oxide intermixing have been fabricated. The adopted investigation has highlighted the crucial role played by a multi-technique characterization approach in achieving a thorough mapping of the system properties. Taken together, these results pave the way to the design and engineering of metal/oxide nanocomposites for advanced technological applications.

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References and Notes

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