A novel approach to grow ZnO nanowires and nanoholes by combined colloidal lithography and MOCVD deposition[†]

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A hybrid approach of colloidal lithography and metalorganic chemical vapour deposition (MOCVD) has been used to fabricate ZnO nanowire bundles and nanoholes by using a silver metalorganic precursor as the growth catalyst.

The synthesis and size control of multidimensional composite materials is receiving growing attention due to potential applications in catalysis and gas sensing.¹ Metallic nanoring and nanohole arrays are particularly attractive for their unique optical properties, persistent currents, and multiple magnetic states.^{2–4} ZnO nanostructures, especially nanowires and nanorods, offer remarkable physical and chemical properties, with potential applications as nanoscale electronic, photonic, field emission, sensing, and energy conversion devices.^{5,6}

The common vapour transport deposition methods usually grow ZnO nanowires on silicon, sapphire, or nitride substrates coated with Au catalytic nanoparticles.⁷ Nanorods placement can be predefined via location of metal catalyst islands or particles.⁸ Au is the most used catalyst for ZnO nanowires growth, since the use of Ag as an alternative metal has the drawback of temperature limitation (up to 500 °C) related to fast Ag oxidation which results in low-quality nanowires.⁹ Here we present an original method to grow ZnO nanowires by using a new Ag catalyst obtained from thermal reduction of silver(I) hexafluoroacetylacetonate tetraglyme [Ag(hfa)tetraglyme] metalorganic complex.^{10,11} This precursor has been already successfully applied to deposit silver films, silver nanoparticles embedded in polymeric and silica thin films or silver nanorods through a single-step route involving its thermal reduction to metallic silver.^{12–14} The main advantage of this approach is the employment of liquid precursor solutions that can be easily deposited by spin coating on any type of substrate as films. Moreover, no Ag₂O formation is detected after the ZnO deposition by MOCVD performed at reduced pressure in an Ar-O₂ atmosphere and temperatures up to 700 °C. The fabrication of a nanostructured ZnO layer is

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† Electronic supplementary information (ESI) available: (1) Lengthy experimental details; (2) AFM images of dense PS monolayer array, Ag precursor-coated PS monolayer, Ag precursor-coated quartz;
(3) EDX spectra of ZnO nanowires grown on different Ag films;
(4) XRD patterns of ZnO nanowires grown on different Ag films. See DOI: 10.1039/b816251d

simply obtained by combined use of colloidal lithography. A silver film is deposited on two-dimensional arrays of colloidal polystyrene nanospheres self-assembled by dewetting.¹⁵ The Ag(hfa)tetraglyme precursor has been dissolved in EtOH–H₂O 1 : 1 solution to obtain 0.1 M and 0.05 M concentrations, respectively.

Two types of substrates have been prepared by spin coating of an Ag precursor solution, respectively on (1) quartz substrates (homogeneous Ag film, h-Ag) and (2) PS monolayers transferred on quartz substrates (nanostructured Ag film, ns-Ag). The preparation of a PS monolayer by dewetting driven self-assembly is described elsewhere.¹⁵ After spin coating, the samples have been thermally treated for 30 min in a MOCVD hot wall tubular reactor, under an Ar flow (100 sccm, P = 1 Torr) at T = 150 °C. XRD analysis performed after thermal treatment (not shown here) confirms the presence of metallic silver (111 preferentially oriented) on both substrates. AFM analysis reveals that Ag precursor solution fully incorporates the PS monolayer array with the formation of very tiny nanoneedle grains, while the layer deposited on quartz exhibits a regular distribution of large grains (height = 60 ± 40 nm, diameter = 94 ± 27 nm) (see Fig. S1 ESI[†]). Fig. 1 shows the AFM images of ns-Ag films obtained after the PS colloidal mask removal, for the two concentrations of investigated precursor solution. The ns-Ag layer deposited from 0.1 M solution exhibits a dual grain size distribution, which consists of circular patterns of large grains (height = 3.8 ± 1 nm, diameter = 114 ± 10 nm) and tiny nanoneedles (height = 1.4 ± 0.3 nm, diameter = $12.5 \pm$ 1.3 nm) in the centre, corresponding to the PS sphere masked area. On the other hand, the ns-Ag layer deposited from



Fig. 1 AFM images and section analysis of Ag nanostructures from 0.1 M (upper panels) and 0.05 M (lower panels) precursor solutions. $(1 \times 1) \ \mu m^2$ scan area.

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0.05 M solution presents a ring pattern with a wider Ag grain size distribution (height = 15 ± 3 nm, diameter = 22 ± 10 nm).

ZnO has been deposited from a Zn(tta)₂tmeda metalorganic precursor^{16,17} using standard deposition conditions (70 min at 600 °C under Ar-O2 gas flows). Fig. 2 shows high yield nanowires formation, whose length is >10 µm, obtained for ZnO films grown both on ns-Ag and h-Ag substrates (0.1 M Ag precursor concentration). On ns-Ag (Fig. 2a) nanowire diameters range from 100 to 200 nm and bundle formation is observed. The insert shows a magnified bundle area with a circular pattern having almost 300 nm diameter (comparable with the spheres' dimensions). These features are likely related to the local enhancement of a silver catalytic effect, in turn due to a high concentration of silver catalyst in the large grains formed around the circular sphere area (see Fig. 1). EDX analysis (see Fig. S2a ESI[†]) confirms the presence of ZnO, while no Ag peaks are detected. This finding can be explained by the simultaneous occurrence of polystyrene calcination and ZnO growth during the deposition process, which helps the formation of locally depleted silver areas. On the other hand, the ZnO layer deposited on h-Ag (Fig. 2b) exhibits thinner wires (~ 20 nm) homogeneously distributed over the whole surface area. A small Ag peak is detected by EDX analysis (see Fig. S2b ESI⁺) in addition to Zn and O related signals. It is to stress that the comparable deposition conditions used for ZnO growth on the two



Fig. 2 SEM images of ZnO films grown on ns-Ag (a) and h-Ag (b) substrates.

substrates as well as the relative intensity of substrate and overlayer related peaks observed in the EDX spectra, indicate that the detection of Ag on ZnO films deposited on h-Ag substrates cannot be related to a film thickness lower than that of the film deposited on ns-Ag.

XRD analysis (Fig. 3) confirms the polycrystalline nature of the ZnO nanowires and the diffraction peaks are consistent with values indexed for the wurtzite in the standard card (JCPDS 36-1451). The Ag peaks 111 and 200 are visible in the spectrum of ZnO grown on spin coated film (h-Ag) and confirm that silver is not oxidised during ZnO deposition at T = 600 °C (using O₂ flows). The ZnO peak intensity ratios slightly change for the two samples: in particular in the case of ZnO nanowires grown on h-Ag, a small increase of the 002 reflection is observed with respect to the one on ns-Ag (the latter well matching the bulk ZnO spectrum). This observation points to a modest preferential growth orientation of thinner nanowires along the 002 direction. Further studies focused on growth mechanisms of ZnO nanowires as a function of different Ag catalyst morphology (in terms of height and particle distribution rather than particle dimensions) are in progress.

It must be noted that the patterning shown in Fig. 1 is covered by the massive ZnO nanowire growth induced by the enhanced catalytic effect of ns-Ag. Milder deposition conditions need to be defined to observe the nano-patterning effect.

Preliminary results obtained by using shorter time (30 min) and lower temperature (500 $^{\circ}$ C) deposition conditions are shown in Fig. 4. An ordered nanoring "Cheerios-like" array is visible, confirming the dual role of silver as catalyst and patterning agent.

Semi-quantitative analysis of EDX data (Fig. 5) indicates a reduced ZnO deposition yield with respect to the previously discussed samples (while no Ag peak is present).

The XRD analysis (see Fig. S3 ESI[†]) confirms formation of the ZnO crystalline phases showing a predominant 002 orientation, typical of ZnO nanostructured layers, while the 002 preferential orientation is lost and the 100 and 101 peaks become predominant when long nanowires are formed (Fig. 3).

We have shown an original method to grow highly crystalline ZnO nanostructures (nanowires and nanoholes) *via* MOCVD combined with colloidal lithography methods.



Fig. 3 XRD patterns of ZnO nanowires grown on h-Ag and ns-Ag.



Fig. 4 SEM image of a ZnO nanoholes array on ns-Ag obtained using low temperature and short time deposition conditions.



Fig. 5 EDX spectrum of ZnO nanohole array on ns-Ag.

The Ag(hfa)tetraglyme metalorganic precursor, used as an alternative Ag catalyst source, exhibits a very efficient catalytic activity, which is locally enhanced with respect to the homogeneous silver layer. Extensive and uniform nanowires growth is observed using standard ZnO deposition conditions (generally required to grow a 100 nm thick ZnO layer in the absence of catalyst). Nanowire lengths are $>10 \mu m$ and their diameters range from a few nm to 200 nm. Nanowire bundles are observed only when ns-Ag substrates are used, and no significant Ag signal is detected. This finding points to the possibility of competition between ZnO nucleation and PS/Ag sphere calcination when PS colloids are mixed with precursor solution.

The combined use of closely packed PS self-assembled colloids and Ag(t) metalorganic precursor offers the advantage of growing "Ag free" ZnO nanowire bundles (at higher temperature and time), characterised by very large surface areas, or "Cheerios-like" nanohole arrays (at lower temperatures and times), which replicate the template of the PS monolayer assembly.

This approach leads to formation of porous materials having a wide variety of applications in bioengineering, catalysis, environmental engineering, and sensor systems because of their high surface-to-volume ratio.

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