The growth of one-dimensional (1D) semiconducting materials for advanced functional applications is the current focus of various cutting-edge research activities. In this context, 1D ZnO nanosystems, such as nanowires and nanorods (NRs), are extremely appealing targets due to their broad variety of attractive properties, resulting from the synergy between their ultra-high surface-to-volume ratio, inherent anisotropy and quantum confinement of charge carriers. Such unique characteristics render 1D ZnO nanosystems appealing multi-functional modules for various utilizations, such as electron field emitters, gas sensors, lasers, piezoelectrics and photovoltaic cells. Recently, ZnO NR arrays have also received considerable attention for their advanced photo-activated functions, regarding, in particular, photo-induced superhydrophilicity (PSH) and photocatalysis (PC), that pave the way to the development of stimuli-responsive systems. In this context, the growth of supported ZnO NRs with tailored properties plays a strategic role, since such arrays represent very favorable architectures for light trapping and reduce undesired particle aggregation frequently observed for powdered materials. In addition, for PSH and PC applications, a high surface-to-volume ratio enables a faster arrival of photo-generated electrons and holes to the NRs surface, reducing detrimental recombination phenomena.

The functional performance of ZnO NRs is directly dependent on the availability of proper synthetic strategies enabling a fine control of their morphology and spatial organization. Among the various approaches, chemical vapor deposition (CVD) is one of the most versatile techniques due to its intrinsic experimental flexibility and to the use of metal-organic precursors endowed with ad hoc chemical and physical properties. In particular, activation of both gas-phase and surface processes by means of non-equilibrium plasmas (plasma-enhanced CVD, PE-CVD) promotes alternative reaction pathways under softer conditions than in thermal CVD, enabling one to modulate deposition surface chemistry and to obtain 1D nanostructures with tailored properties.

Herein, we report on the PE-CVD of supported ZnO nanorod arrays on Si(100) substrates from two recently developed bis-(ketoiminato) zinc (II) compounds, Zn(R’NC(CH2)nC=O)2 with R’ = -(CH2)2OCH3 (1) or -(CH2)3OCH3 (2). The selective growth of ZnO NR arrays was performed from Ar/O2 plasmas at 200 and 300 °C (see Figure 1, Table 1 and Supporting Information), the lowest temperatures reported in the literature for the PE-CVD of such 1D architectures. Special attention was devoted to the interrelations between PSH and PC activity of the obtained 1D ZnO systems and their morphological characteristics. PSH properties were analyzed by monitoring the evolution of water contact angle (CA) as a function of the UV irradiation time. The self-cleaning activity of the synthesized NRs was investigated through a novel quantitative and highly sensitive PC method recently developed by some of us, consisting of the determination of a terephthalic acid (TPA) oxidation product, that is, hydroxyterephthalic acid (HOTPA).

| Table 1. ZnO nanorods length (uncertainty=±12 nm) and numerical density per unit area as a function of the adopted growth temperature and the used precursor. |
|----------------|----------------|----------------|----------------|
| Sample | Growth temperature [°C] | precursor | NRs length [nm] | NRs density [NRs/μm²] |
| ZnO1 | 200 | 1 | 248 | 1440 |
| ZnO2 | 2 | 356 | 710 |
| ZnO3 | 300 | 1 | 405 | 950 |
| ZnO4 | 2 | 504 | 620 |

Figures 1a,b display cross-section transmission electron microscopy (TEM) images for representative ZnO specimens synthesized from compounds 1 and 2, respectively. The systems...
were characterized by a well-developed 1D morphology, consisting of aligned ZnO NR arrays oriented perpendicularly to the substrate surface. In both cases, high-resolution (HR) TEM images demonstrated that NRs preferentially grew along the \(<001>\) direction, as also confirmed by fast Fourier transform (FFT) (Figure 1c). Such a c-axis growth was a common feature for all samples, as confirmed by X-ray diffraction (XRD) investigation (see Figure S1 of the Supporting Information). The system surface topography was characterized by a highly homogeneous array of protruding NRs, as evidenced by scanning electron microscopy (SEM, Figure 1d and e).

Interestingly, the length and surface density of such 1D nanostructures could be tailored as a function of both the growth temperature and the adopted precursor (see Figure 1). In particular, the NR length increased with the growth temperature and also upon using precursor 2 rather than 1, all the other parameters being constant. The former effect could be attributed to a more efficient precursor decomposition at higher temperatures, as frequently observed in CVD processes. A further contribution arose from the appreciably higher volatility of compound 2 with respect to 1, although their molecular structures differ by just a CH₂ moiety in the ketoiminate ligands. As a consequence, an improved mass supply to the growth substrate and a higher growth rate were achieved using precursor 2.

As regards PSH properties, specimen ZnO1 (see Table 1) presented the lowest activity among the analyzed samples. Such an effect was ascribed both to the reduced NR length, responsible for less efficient light absorption, and to the relatively compact cross-sectional structure, resulting in a lower active area. In a different way, ZnO NR arrays thicker than 300 nm (samples ZnO2–ZnO4, Table 1) presented remarkable PSH performances, with a very fast hydrophobic-to-superhydrophilic conversion upon UV exposure (Figure 2a). The initial hydrophobic CA value was close to 120° for all samples, in agreement with previous reports. This phenomenon was mainly attributed to adventitious carbon contamination, as evidenced by X-ray photoelectron spectroscopy (XPS) (see Figure S2 of the Supporting Information).

![Figure 1. Cross-section TEM images for samples: a) ZnO1; b) ZnO2; c) HRTEM micrograph for ZnO2; Inset: FFT along the [010] zone axis. Plane-view SEM micrographs for: d) ZnO1; e) ZnO2.](image)

![Figure 2. PSH behavior of Si-supported ZnO nanorods: a) water CA as a function of irradiation time. Photographs of H₂O droplets on sample ZnO4: b) before and c) after UV irradiation, 150 min. d) AFM image for ZnO4. e) Morphological evolution of ZnO 1D NR arrays. Denser arrays present a lower surface roughness and a more compact cross-section, whereas a rougher surface texture and an increased active area are obtained for lower NR densities.](image)
Upon UV irradiation, a fast CA decrease was observed. The present performances were significantly better than those of Activ glass (Pilkington), the benchmark TiO$_2$ material, and also higher than those of ZnO films and of the best performing ZnO nanoplatelets reported by us under similar operating conditions.$^{[10]}$ It is worth observing that, for specimens ZnO2–ZnO4 (Figure 2 a), the hydrophobic-to-supersuperhydrophobic conversion kinetics did not improve in the same order of the NR length. In fact, the performances of the sample with shortest NRs, that is, ZnO2, were intermediate between those of ZnO3 and ZnO4. Such results suggest that, although an increase in the NR length may result in more efficient light harvesting, other parameters concur in determining the system PSH activity, such as surface chemical composition and topology.$^{[2a, 3a, 6b, 7a]}

To elucidate the interrelations between their PSH behaviour and surface morphology, atomic force microscopy (AFM) analyses were performed for samples reported in Figure 2 a. The recorded micrographs (Figure 2 d) confirmed the presence of homogeneously protruding and aligned NRs, in line with Figures 1 d,e. Interestingly, these analyses provided root-mean-square (RMS) roughness values increasing in the same order of the PSH activity, that is, ZnO3 < ZnO2 < ZnO4 (see Table 2), indicating that surface corrugation was the main factor affecting the PSH properties of the present ZnO systems.$^{[5a]}

Table 2. RMS roughness values for ZnO2–ZnO4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS roughness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO2</td>
<td>3.2</td>
</tr>
<tr>
<td>ZnO3</td>
<td>2.6</td>
</tr>
<tr>
<td>ZnO4</td>
<td>5.8</td>
</tr>
</tbody>
</table>

In order to explain the influence of the sample morphology on functional behavior, a simple pictorial model has been proposed in Figure 2 e. For all specimens, the first deposition steps lead to the nucleation of small ZnO nanocrystals, producing a rather compact seed layer. During the subsequent growth stages, such crystallites self-catalyze the formation of ZnO nanorods that mainly develop perpendicularly to the substrate surface with a ZnO nanorods that mainly develop perpendicularly to the sub- growth stages, such crystallites self-catalyze the formation of ZnO nanorods that mainly develop perpendicularly to the surface. The typical NR diameter ranged between 25 and 40 nm. When the adopted process parameters led to a lower NR density, the obtained 1D arrays were characterized by a higher surface roughness due to the higher spacing between individual NRs (Figure 2 e). This effect, further enhanced by an increase of NRs length, likely resulted in a higher active area and in improved PSH behavior.

It is also worthwhile observing that all nanodeposits were characterized by a high surface –OH content, as evidenced by XPS (see Figure S3, Supporting Information).$^{[4a, 7a]}$ The formation of hydroxyl species could be mainly traced back to the dissociative chemisorption of atmospheric H$_2$O on surface oxygen vacancies, whose content is reasonably enhanced by plasma bombardment effects during PE-CVD.$^{[3a, 4]}$ Upon UV irradiation, photogenerated holes can react with lattice O species to form new oxygen vacancies. This phenomenon further promotes water chemisorption, increasing the surface –OH amount and resulting in a superhydrophilic behaviour due to an increased wettability.$^{[2a, 5a]}$ For ZnO NR arrays, an RMS roughness increase could be related to a higher active surface area (see Figure 2 e).$^{[11a]}$ On this basis, it is reasonable to suppose that the overall hydroxyl group content increased in the same order of RMS values, that is, ZnO3 < ZnO2 < ZnO4, further supporting the PSH trends reported in Figure 2 a.

As regards the PC behaviour, for all ZnO samples a progressive increase of the HOTPA concentration vs irradiation time was observed (Figure 3 a). Under the present conditions, TPA degradation and, consequently, HOTPA formation followed pseudo-zero-order kinetics (rate constant = $k_1$).

![Figure 3.](image-url) a) PC behavior of specimen ZnO4: HOTPA concentration as a function of irradiation time. b) Rate-constant ($k_2$) dependence on RMS roughness for samples ZnO2–ZnO4.

Considering that HOTPA degradation should also be taken into account (rate constant = $k_3$), HOTPA concentration vs time dependence could be described by Equations (1) and (2):$^{[9]}

$$\frac{d[HOTP A]}{dt} = k_1 - k_2[HOTP A]$$

$$[HOTP A] = \frac{k_1}{k_2} \left(1 - e^{-k_2 t}\right)$$

The trend in Figure 3 a could be fitted by Equation (2). Similarly to PSH behavior, systems with the highest RMS surface roughness also displayed improved PC performances. In fact, an increase of the $k_1$ reaction rate constant proportional to RMS roughness was detected for specimens ZnO2–ZnO4 (Figure 3 b). The reasons explaining this trend are in line with previous considerations on PSH data, as well as with the pictorial model reported in Figure 2. Specifically, on going from sample ZnO3 to ZnO2 and, finally, to ZnO4, the progressive RMS enhancement and the concomitant increase of the active area have a promotional effect on the PC processes involved. In particular, the large content of surface O vacancies, acting as capturing centres for photogenerated electrons, minimizes charge-carrier recombination phenomena. As a consequence, photo-generated holes are more readily available for the oxidation of organic pollutants. Furthermore, oxygen vacancies also assist the generation of active species, such as ‘OH and O$_2^*$’.
on the surface on ZnO NRs, providing thus a two-fold beneficial contribution to PC activity.[2b, 4c, 6a]

For the best-performing sample (ZnO4), the analyses yielded $k_i = 9.5 \times 10^{-9}$ mol L$^{-1}$ min$^{-1}$, a value five times higher than Pilkington Activ glass, the benchmark reference material. This difference is likely dependent on several parameters, including the higher roughness and overall deposit thickness of specimen ZnO4 with respect to that of Pilkington Activ glass.[9, 10a, 11]

In conclusion, highly oriented ZnO NR arrays were synthesised on Si(100) by PE-CVD at 200–300 °C from Ar/O$_2$, starting from ketoiminato Zn (II) precursors. The morphological features of the obtained ZnO NR arrays (RMS roughness, NR length and density) could be tailored by controlling both the precursor nature and the growth temperature, rendering the PSH and PC properties tunable as a function of the system characteristics. These features pave the way to self-cleaning and anti-fogging applications, as well as to utilization in environmental remediation and microfluidic switches.[2a, 3a, 4a, 6a] To this aim, future efforts will be devoted to the PE-CVD of ZnO NRs on transparent substrates for the production of advanced light-activated smart materials.

Experimental Section

ZnO nanorods were synthesised on p-type Si(100) substrates (MEMC, Merano, Italy) by a custom-built PE-CVD apparatus.[6] Precursors 1–2 were vaporized at 140 °C and delivered to the reaction chamber by a 60 sccm Ar flow. Two further auxiliary gas lines were used to introduce Ar (15 sccm) and O$_2$ (20 sccm) gases directly into the reactor. The deposition time, total pressure and RF power for all experiments were 1 h, 1.0 mbar and 20 W, respectively.

TEM and HRTEM analyses were carried out using a JEOL 4000EX microscope operated at 400 kV and having a 0.17 nm point resolution. Samples for observations were prepared by focused ion beam (FIB) techniques, using a FEI Nova 200 Nanolab DualBeam SEM/FIB system. A dual-cap C–Pt protection layer was used to protect ZnO nanorod arrays from ion milling damage.

SEM measurements were carried out by a Zeiss SUPRA 40VP field-emission instrument, using primary beam voltages of 10–20 kV.

AFM analyses were performed using a NT-MDT SPM Solver P47H-Pro instrument operating in tapping mode and in air. RMS roughness values were obtained from 1 x 1 μm$^2$ images.

Investigation of PSH properties was performed by UV irradiation of as-grown ZnO samples and measuring water CA values vs time (also see the Supporting Information).[11b]

Before PC measurements, ZnO NR arrays were pre-irradiated for 24 h and subsequently dipped in a sodium terephthalate (NaTPA)/hydroxyethyl cellulose (HEC) solution. Solvent evaporation produced a transparent organic coating on the ZnO NRs surface. Subsequently, samples were irradiated under the same conditions adopted for PSH tests and the reaction kinetics was studied by high-performance liquid chromatography with fluorescence detection.[6]

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