**Supplementary Material**

**Na-doped oriented ZnO nanorod-arrays: Insights into their aqueous growth design, crystal structure and optical properties**

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1. **Cleaning and seeding:**

Zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O), zinc acetate anhydrous (Zn(CH3COO)2), sodium nitrate (NaNO3), and hexamethylenetetramine (HMTA) were all of analytical grade and used without further purification in our experiment. For all the samples substrate preparation was as follows: silicon -Si(100)- substrates were cleaned by performing three 10 minutes steps in an ultrasonic bath with acetone, isopropyl alcohol, and DI water, respectively. A 5 mM solution of 99.98% zinc acetate in pure ethanol was prepared as a seeding solution. The seeding solution was drop casted on substrates for 7 times, followed by a 400 ̊C annealing for 30 minutes so that the zinc acetate decomposed, forming ZnO nanoparticles. The whole process was repeated 2 times for each sample to ensure a full coverage of substrate with ZnO nuclei.

1. **Characterization**

The morphological, structural and optical properties of samples were thoroughly investigated by using different techniques. The pH of the growth solution was measured by an Orion 2 star pH meter with an electrode optimized for measurements at room temperature. The electrode was calibrated for both room temperature and 60 ̊C to minimize the temperature effect error in our pH measurements. A JEOL JSM-7600 FE SEM was employed to image the nanorods from the top and cross section. The crystal structure of the samples was investigated using a PANalytical X’pert MPD Pro diffractometer operated at 40 kV and 40 mA using Ni-filtered Cu Kα irradiation (wavelength 1.5406 Å). Local Raman shifts were measured at room temperature using a Renishaw inVia micro-Raman system, with a 532 nm excitation laser and no polarization detection, in the 0 to 900 cm-1 range. The chemical composition was investigated by X-ray photo-electron spectroscopy (XPS) (Axis UltraDLD, Kratos) with monochromatic aluminium Kα radiation and EDS. An Al X-ray source (1486.6 eV) was used and the spectra were detected in the range from 0 to 1200 eV. The charge calibration was done by setting the C 1s line of adventitious carbon to 284.8 eV to compensate for charge effects. For lower doping concentration Energy-dispersive X-ray spectroscopy (EDS) was used. Finally, room temperature PL spectroscopy was performed with a PTI QM-4 fluorescence spectrophotometer with an excitation wavelength of 340 nm.

1. **Figures:**

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**FIG. S1** Evolution of the pH during the growth as a function of time (temperature up to 65 ̊C).

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**FIG. S2** A) Height and diameter distribution and B) Aspect ratio of undoped and Na-doped ZnO nanorods with different concentrations grown at 60 ˚C on silicon.



**FIG. S3** Plane spacing of undoped and Na-doped ZnO nanorods with different concentration grown at 60 ˚C on silicon.

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**FIG. S4** High-resolution XPS spectra of the O 1s core level of A) undoped ZnO nanorods B) 0.1 M C) 0.25 M D) 0.50 ME) 1 M Na-doped ZnO nanorods grown at 60 ˚C on silicon.

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**FIG. S5** EDS elemental microanalysis of 0.5 M Na-doped ZnO nanorods, showing the presence of Na in the ZnO host lattice.

1. **Tables:**

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| Table SI - Experimental results of crystal characterization of undoped and Na-doped ZnO nanorods | | | | | |
| Sample ID | (002) peak position *2ϴ* ( ̊ ) | Plane spacing (Å) | Lattice constant (Å) | FWHM  ( ̊ ) | Degree of texture |
| Undoped ZnO | 34.52 | 2.594 | 5.189 | 0.3957 | 82% |
| 0.10M NaNO3 | 34.39 | 2.604 | 5.208 | 0.3469 | 83% |
| 0.25M NaNO3 | 34.43 | 2.601 | 5.203 | 0.4021 | 90% |
| 0.50M NaNO3 | 34.37 | 2.606 | 5.212 | 0.4247 | 76% |
| 1M NaNO3 | 34.34 | 2.608 | 5.216 | 0.8338 | 39% |

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| --- | --- | --- | --- | --- | --- | --- |
| Table SII - Experimental XPS measurement results of undoped and Na-doped ZnO nanorods | | | | | | |
| Sample | Zn-2P 3/2  (eV) | Zn-2P 1/2  (eV) | Spin-orbit interaction split | FWHM  (Zn-2p 3/2)  (eV) | Atomic number ratio of O/Zn | OL,OH approximate surface percentage |
| Undoped ZnO | 1021.7 | 1044.8 | 23.1 | 1.85 | 3.8 | 14%, 85% |
| 0.10 M NaNO3 | 1021.6 | 1044.6 | 23 | 1.72 | 1.2 | 53%, 46% |
| 0.25 M NaNO3 | 1021.3 | 1044.4 | 23.1 | 1.82 | 3.3 | 51%, 48% |
| 0.50 M NaNO3 | 1021.6 | 1044.7 | 23.1 | 1.91 | 1.8 | 47%, 52% |
| 1 M NaNO3 | 1021.4 | 1044.5 | 23.1 | 1.73 | 1.4 | 52%, 47% |