## **Supplementary information**

## Scalable chemical synthesis of doped silicon nanowires as a powder for energy applications

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Figure S1: SEM images of undoped SiNW product showing plates of packed SiNWs grown on direct contact with the salt particle support. The top-left image shows a typical  $20\mu$ m-sized cubic void remaining after NaCl dissolution.



Figure S2: SEM images of undoped SiNWs grown from a 30mL glass reactor (A) and from a 150mL steel reactor (B). Scales are the same. (C): corresponding SiNW diameter histograms. (D): photograph of a typical 500mg batch of undoped SiNWs produced in a 150mL steel reactor.



Figure S3: X-ray scattering spectra of undoped and 1%P SiNWs (Cu K $\alpha$  source, lambda=15.41Å). Vertical lines show indexation of Si (black, PDF file 00-005-0565) and Au (orange, PDF file 00-004-0784).

Powder X-ray diffraction has been carried out on a Panalytical X'Pert powder diffractometer equipped with a copper anode ( $\lambda K\alpha 1$ = 1.5406 Å,  $\lambda K\alpha 2$ = 1.5444 Å) and an X'Celerator 1D detector. It was configured in Bragg-Brentano geometry, with a variable divergence slit on the primary beam path and a set of anti-scattering slits positioned before and after the sample. Axial divergence was limited by 0.02 rad Soller slits. Data analysis were performed using the Fullprof and Panalytical Highscore softwares.



Figure S4: Left: Raman spectra of undoped SiNWs at various laser intensities (excitation 532nm). Right: map of peak width versus peak position of undoped (black dots), SiNWs at 0.2%P (blue diamonds), 0.4%P (green squares), 0.6%P (yellow circles), 0.8%P (orange down

triangles) and 1%P (red up triangles). The bottom-right star shows the reference Si bulk signal.



Figure S5: thermogravimetry (TG) and TG effluent mass spectroscopy (MS) of undoped and 1%P-SiNWs under argon (A,B,C) and oxygen (D,E,F). A, D: mass variation for undoped (red) and doped (black) SiNWs and temperature program (thin line) as a function of time. B, C, E, F: MS signals at m/z=2 (H2, triangles), m/z=44 (CO2, crosses) and m/z=78 (benzene, circles), time derivative of mass variation (black line) and heat flow signal (light blue, bold line) as a function of temperature. MS signal at m/z=78 was scaled by a factor of 6 for clarity.



Figure S6: typical EDX spectrum for SiNW pellet (0.6%P-SiNWs). Inset shows an enhanced view with peak attribution and deconvolution.

Table S1: Elemental analysis of SiNWs by EDX. Quantitative analysis was obtained with standards of SiC, MgO and GaP. EDX spectra have been recorded from the horizontal, flat surface of pressed pellets of SiNWs of compactness >80%.

atom%			
C/Si	O/Si	P/Si	Au/Si
24 ± 2	12 ± 2	$0.00 \pm 0.02$	0.5 ± 0.1
19 ± 2	27 ± 1	0.35 ± 0.05	0.8 ± 0.1
12 ± 5	20 ± 5	0.36 ± 0.15	0.7 ± 0.2
12 ± 2	32 ± 4	0.97 ± 0.29	0.8 ± 0.2
	atom% C/Si 24 ± 2 19 ± 2 12 ± 5 12 ± 2	atom%C/SiO/Si $24 \pm 2$ $12 \pm 2$ $19 \pm 2$ $27 \pm 1$ $12 \pm 5$ $20 \pm 5$ $12 \pm 2$ $32 \pm 4$	atom%C/SiO/SiP/Si $24 \pm 2$ $12 \pm 2$ $0.00 \pm 0.02$ $19 \pm 2$ $27 \pm 1$ $0.35 \pm 0.05$ $12 \pm 5$ $20 \pm 5$ $0.36 \pm 0.15$ $12 \pm 2$ $32 \pm 4$ $0.97 \pm 0.29$



Figure S7: typical STEM image of 1%P-SiNWs showing different P/Si ratios in crystalline SiNW and amorphous connection zones. EDX images acquired at 200kV on a Thermo Scientific Titan Themis S/TEM equipped with 4 silicon drift detectors.



Figure S8: Electron spin resonance (ESR) spectra of SiNWs with growing content of P (initial P/Si content from 0.2% to 1%).



Figure S9: CV curve at a scan of 0.01Vs<sup>-1</sup> to 100Vs<sup>-1</sup> and b) Average capacitive current density versus scan rate for doped SiNWs.



Figure S10: GCD cycles of 1%P-SiNW SCs at current densities of 0.14 to 4.5mA/cm<sup>2</sup>.