

Supporting online material

**Nanocomposites by the use of Simultaneous Twin Polymerization:
tin alloys in a carbon / silica matrix**

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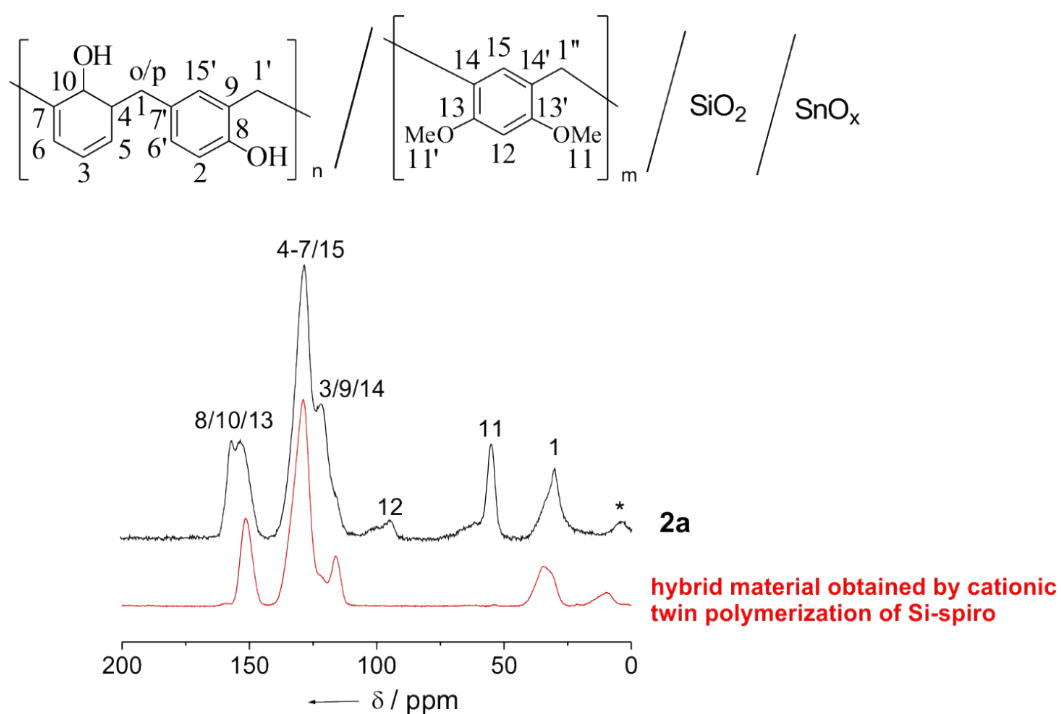


Figure S1. Comparison of the solid state ^{13}C $\{^1\text{H}\}$ CP MAS NMR spectrum of hybrid material **2a** (phenolic resin/ SiO_2 / SnO_x) with the solid state ^{13}C $\{^1\text{H}\}$ CP MAS NMR spectrum of the hybrid material obtained by cationic twin polymerization of Si-Spiro (phenolic resin/ SiO_2).

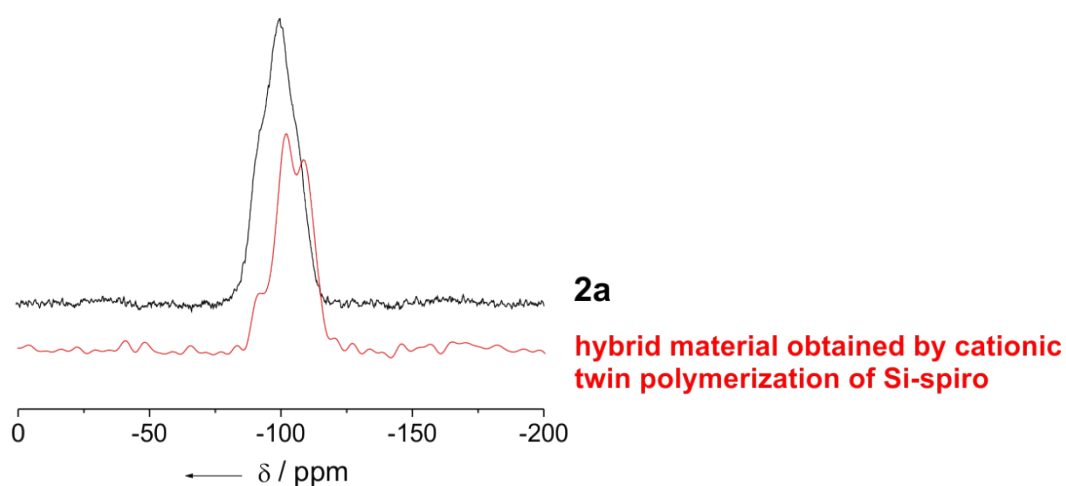


Figure S2. Comparison of the solid state ^{29}Si $\{^1\text{H}\}$ CP MAS NMR spectrum of hybrid material **2a** (phenolic resin/ SiO_2 / SnO_x) with the solid state ^{29}Si MAS NMR (quantitative) spectrum of the hybrid material obtained by cationic twin polymerization of Si-spiro (phenolic resin/ SiO_2).

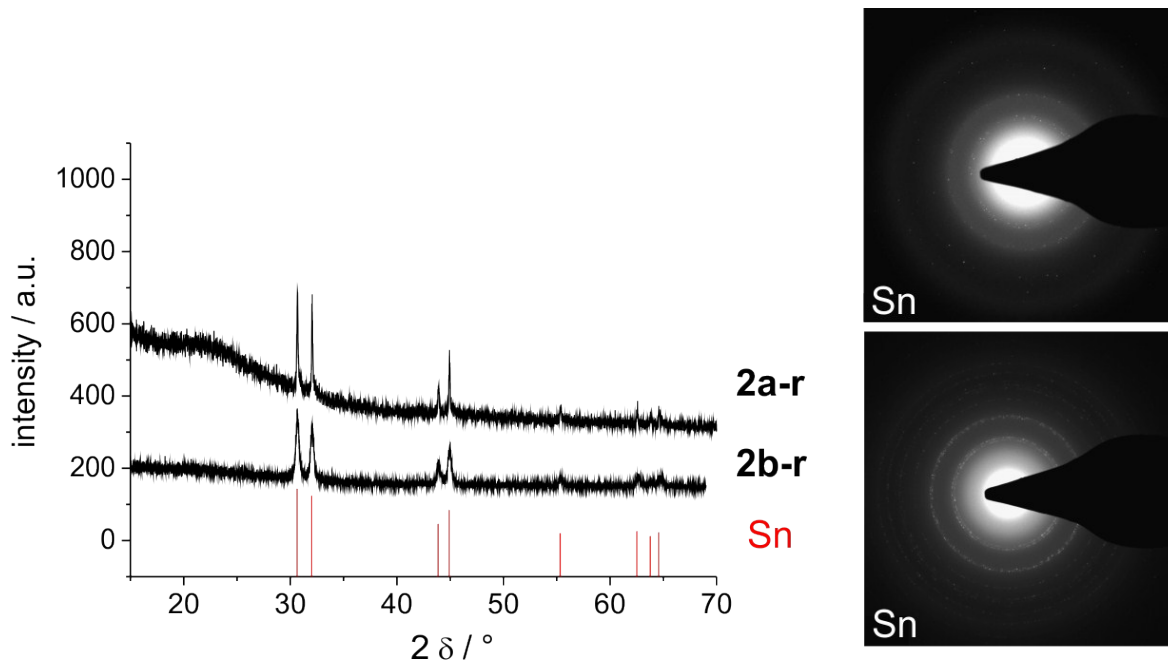


Figure S3. Left: powder X-ray diffraction (PXRD) pattern of the nanocomposites **2a-r** and **2b-r** (argon/ hydrogen (95/5 %); heating rate: 10 K/min, final temperature: 600 °C, time 2 h). (Sn: JCPDS 03-065-0296). Right: Selected area electron diffraction of **2a-r** (top) and **2b-r** (bottom).

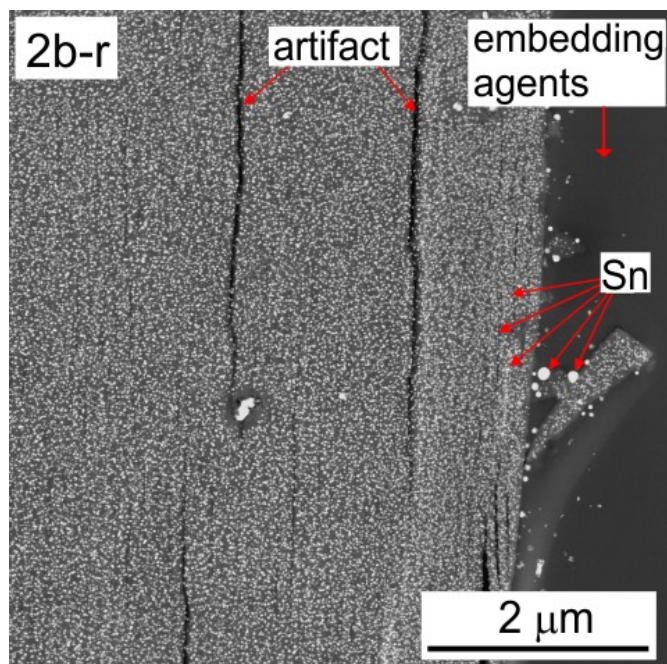


Figure S4. HAADF-STEM image of the nanocomposite Sn/C/SiO₂ **2b-r**.

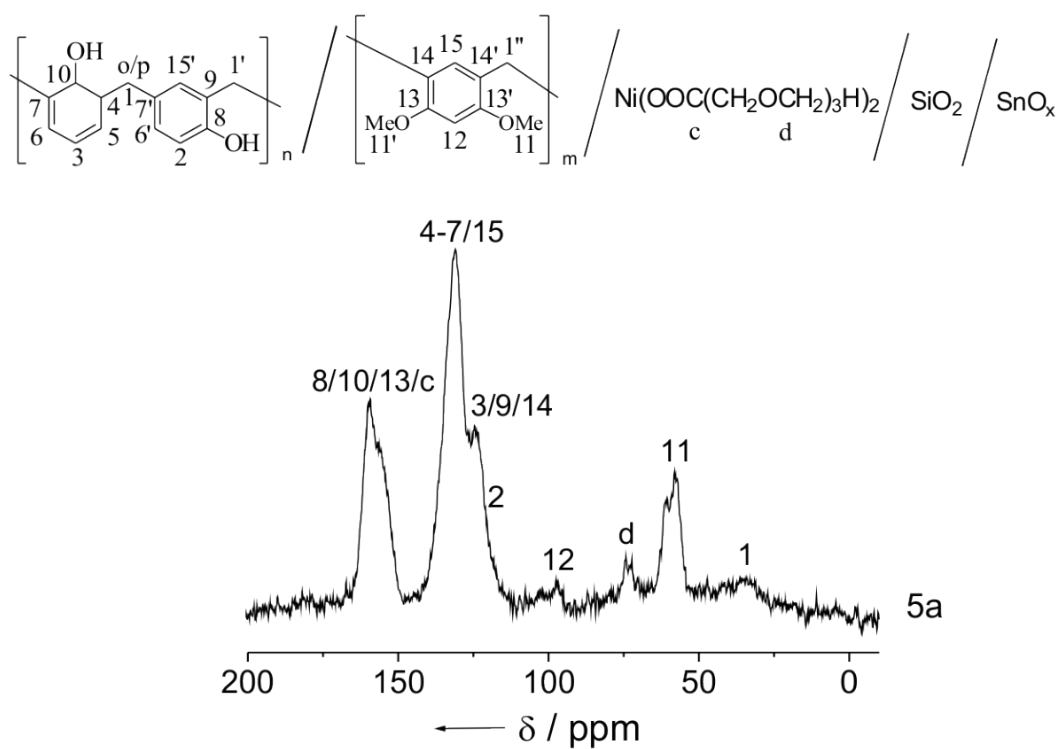


Figure S5. Solid state ^{13}C $\{^1\text{H}\}$ CP MAS NMR spectrum of hybrid material **5a** (phenolic resin/ $\text{Ni}(\text{OOC}(\text{CH}_2\text{OCH}_2)_3\text{H})_2/\text{SiO}_2/\text{SnO}_x$).

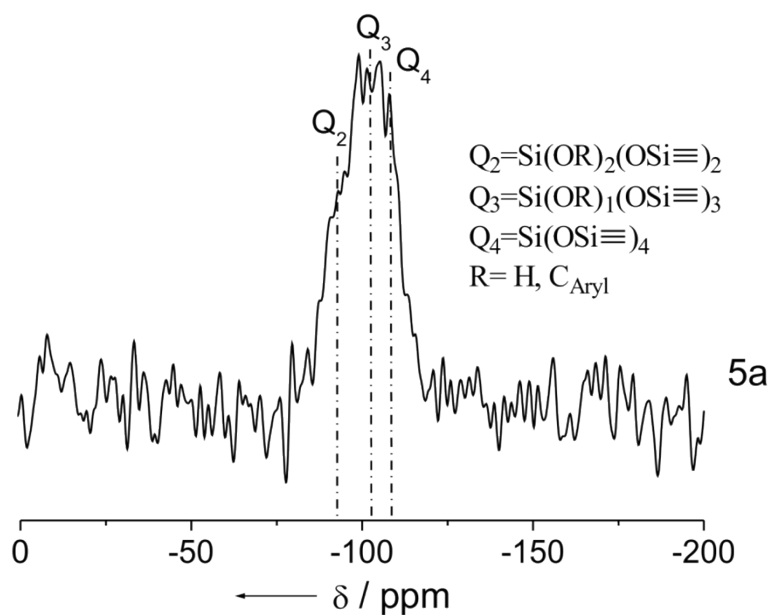


Figure S6. Solid state ^{29}Si $\{^1\text{H}\}$ CP MAS NMR spectrum of hybrid material **5a**.

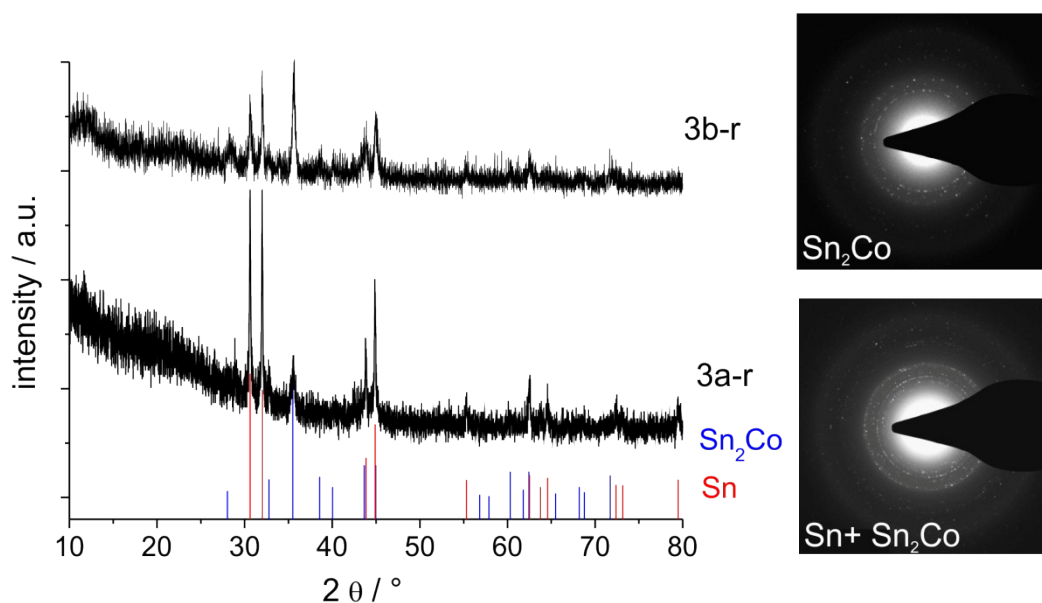


Figure S7. Left: powder X-ray diffraction (PXRD) pattern of the nanocomposites **3b-r** and **3a-r** (argon/ hydrogen (95/5 %); heating rate: 10 K/min, final temperature: 600 °C, time 2 h). (Sn: JCPDS 03-065-0296, Sn₂Co: JCPDS 00-025-0256). Right: Selected area electron diffraction of **3b-r** (top) and **3a-r** (bottom).

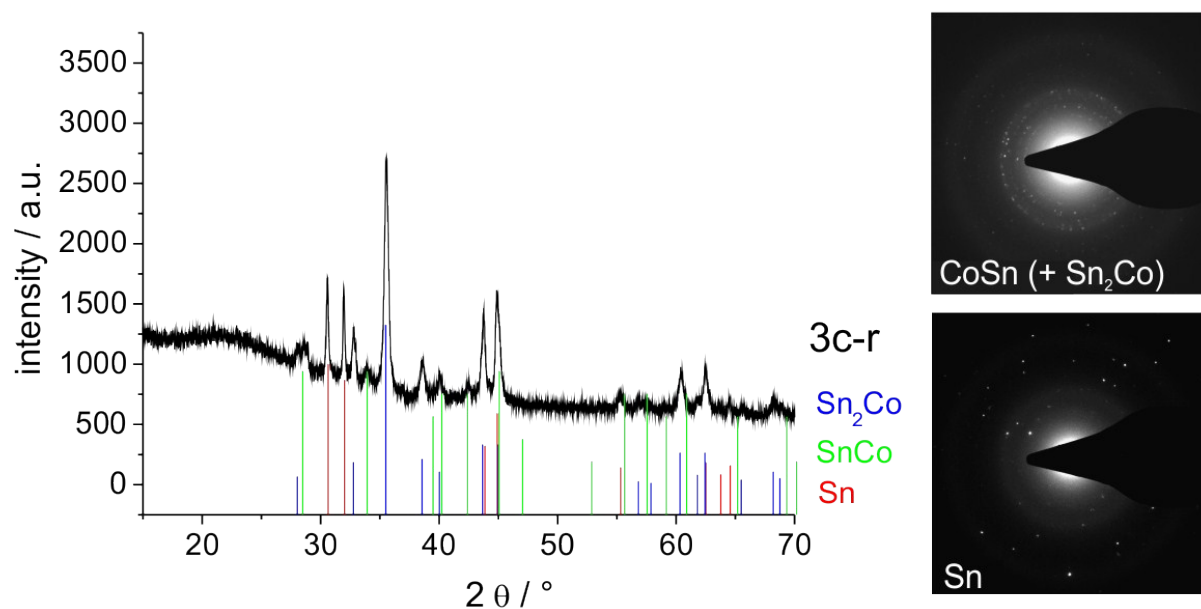


Figure S8. Left: Powder X-ray diffraction (PXRD) pattern of the nanocomposites **3c-r** (argon/ hydrogen (95/5 %); heating rate: 10 K/min, final temperature: 600 °C, time 2 h). (Sn: JCPDS 03-065-0296, Sn₂Co: JCPDS 00-025-0256, SnCo: JCPDS 00-002-0559). Right: Selected area electron diffraction of **3c-r**.

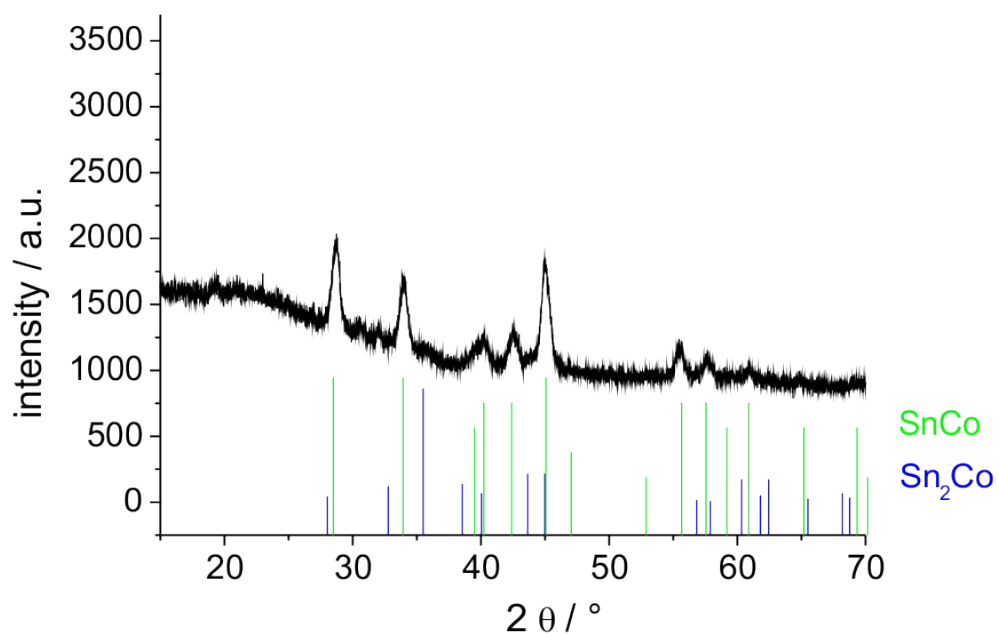


Figure S9. Powder X-ray diffraction (PXRD) pattern of the reduced (argon/ hydrogen (95/5 %)) hybrid material obtained from the twin polymerization of Si-spiro with tin(II)-2,4-dimethoxyphenylmethanolate and cobalt(II)-2-(2-(2-methoxyethoxy)ethoxy)acetate (Si/Sn/Co ratio: 3:1:0.5); heating rate: 10 K/min, final temperature: 800 °C, time 2 h). (Sn₂Co: JCPDS 00-025-0256, SnCo: JCPDS 00-002-0559).

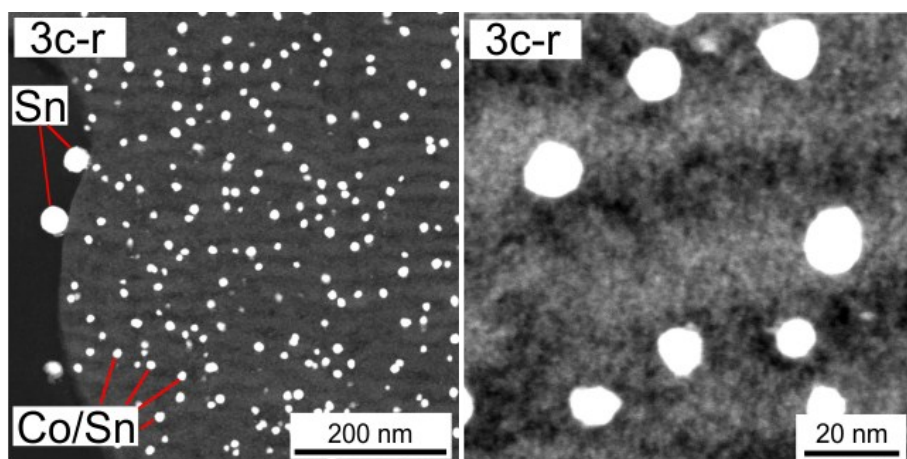


Figure S10. HAADF-STEM images of the nanocomposite Sn₂Co/C/SiO₂ **3c-r**.

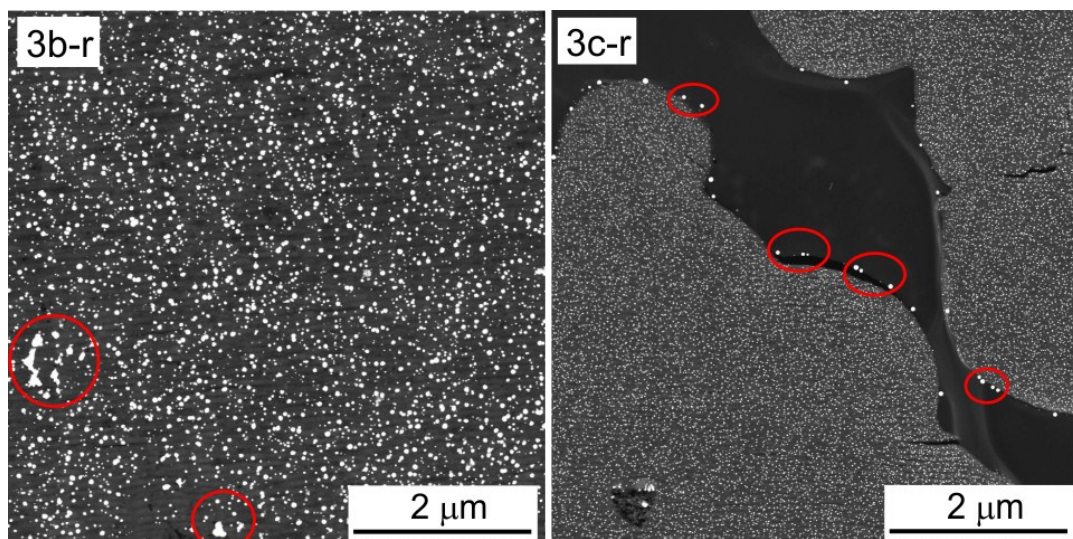


Figure S11. HAADF-STEM images of the nanocomposites $\text{Sn}_2\text{Co}/\text{C}/\text{SiO}_2$ **3b-r** and **3c-r**.

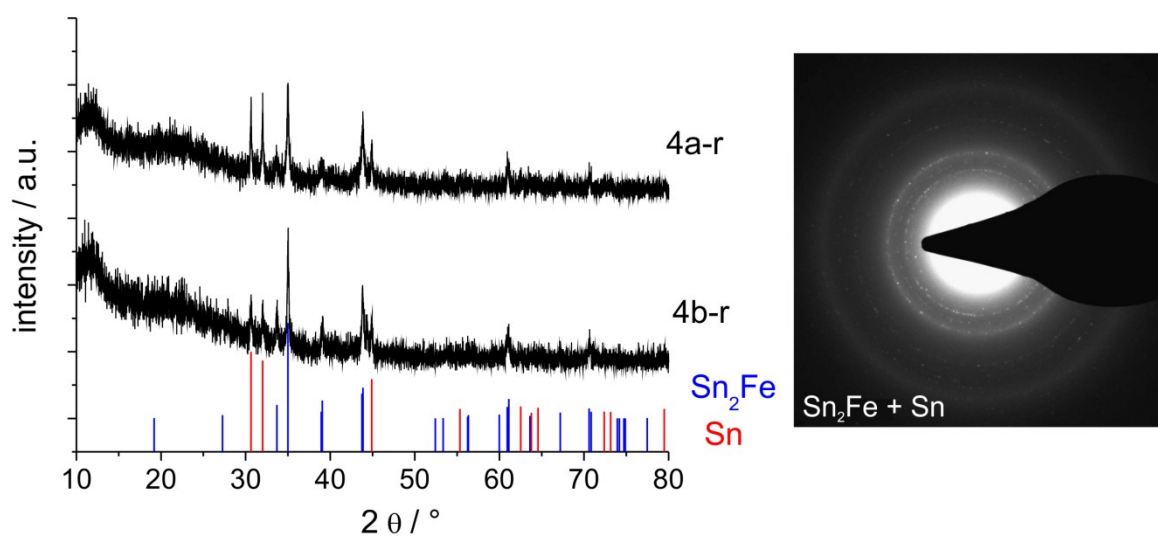


Figure S12. Left: powder X-ray diffraction (PXRD) pattern of nanocomposites **4a-r** and **4b-red** (argon/ hydrogen (95/5 %); heating rate: 10 K/min, final temperature: 600 °C, time 2 h). (Sn: JCPDS 03-065-0296, Sn_2Fe : JCPDS 03-065-0374) Right: Selected area electron diffraction of **4a-r**.

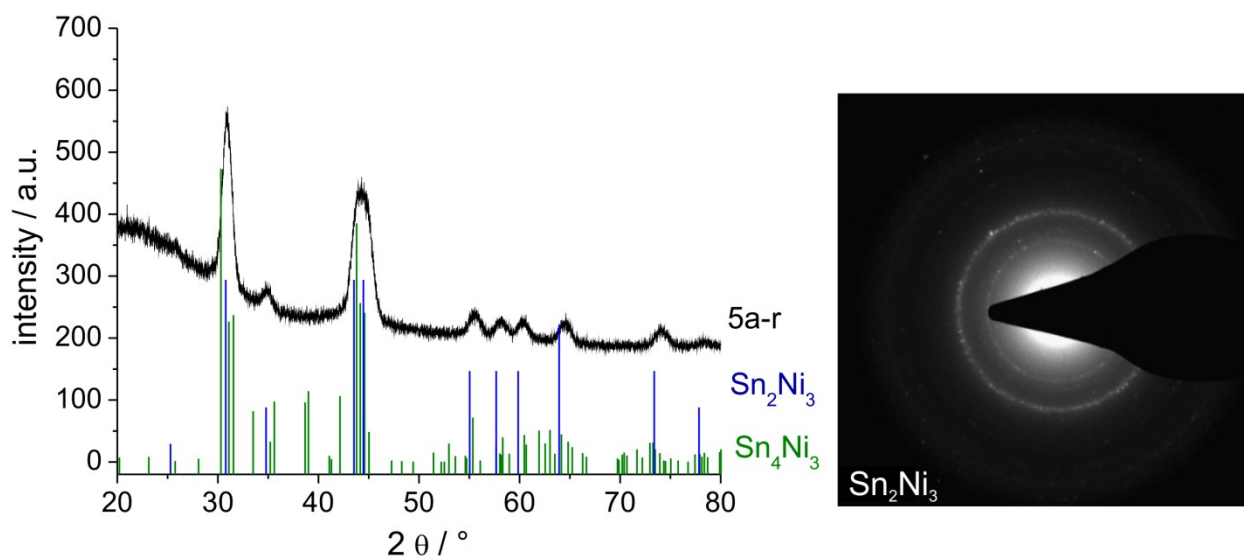


Figure S13. Left: powder X-ray diffraction (PXRD) pattern of nanocomposite **5a-r** (argon/ hydrogen (95/5 %); heating rate: 10 K/min, final temperature: 780 °C, time 3 h). (Sn_4Ni_3 : JCPDS 03-065-2313, Sn_2Ni_3 : JCPDS 00-006-0414). Right: Selected area electron diffraction of **5a-r**.

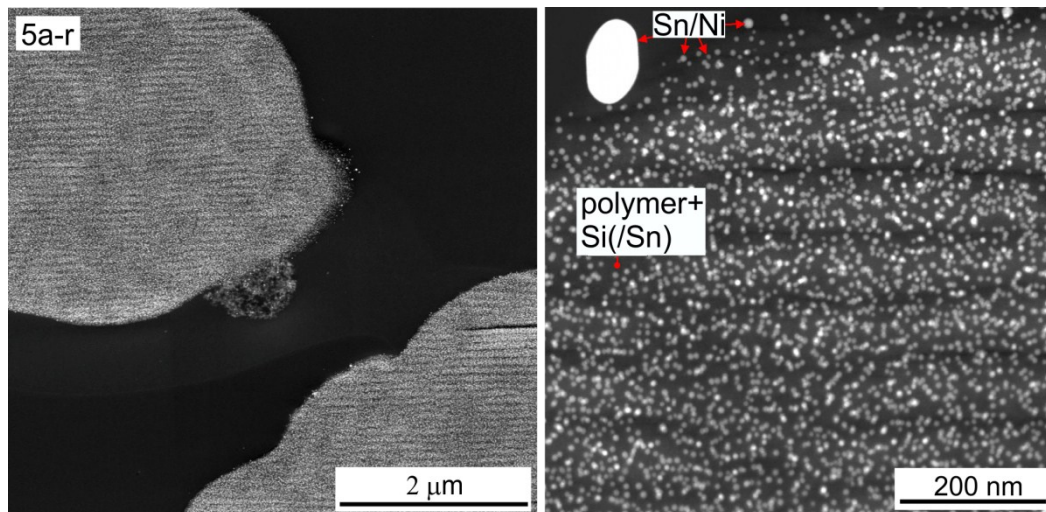


Figure S14. HAADF-STEM images of the nanocomposite $\text{Ni}_3\text{Sn}_2/\text{C}/\text{SiO}_2$ **5a-r**.

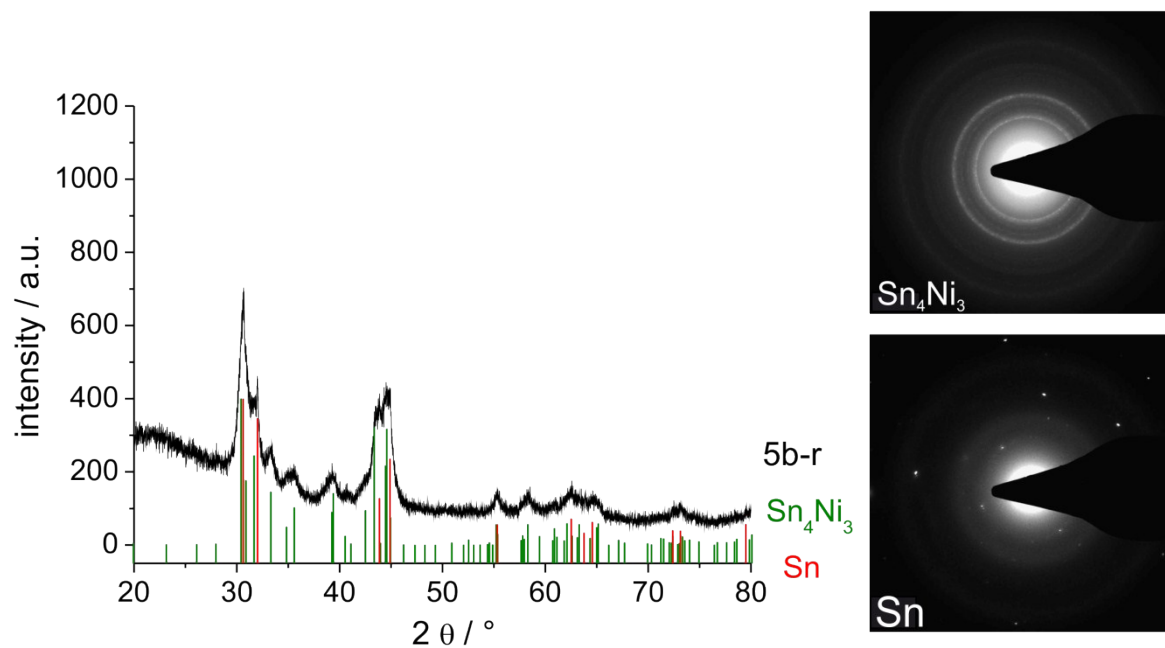


Figure S15. Left: powder X-ray diffraction (PXRD) pattern of nanocomposite **5b-r** (argon/ hydrogen (95/5 %); heating rate: 10 K/min, final temperature: 780 °C, time 3 h). (Sn₄Ni₃: JCPDS 03-065-2313; Sn: JCPDS 03-065-0296) Right: Selected area electron diffraction of **5b-r**.

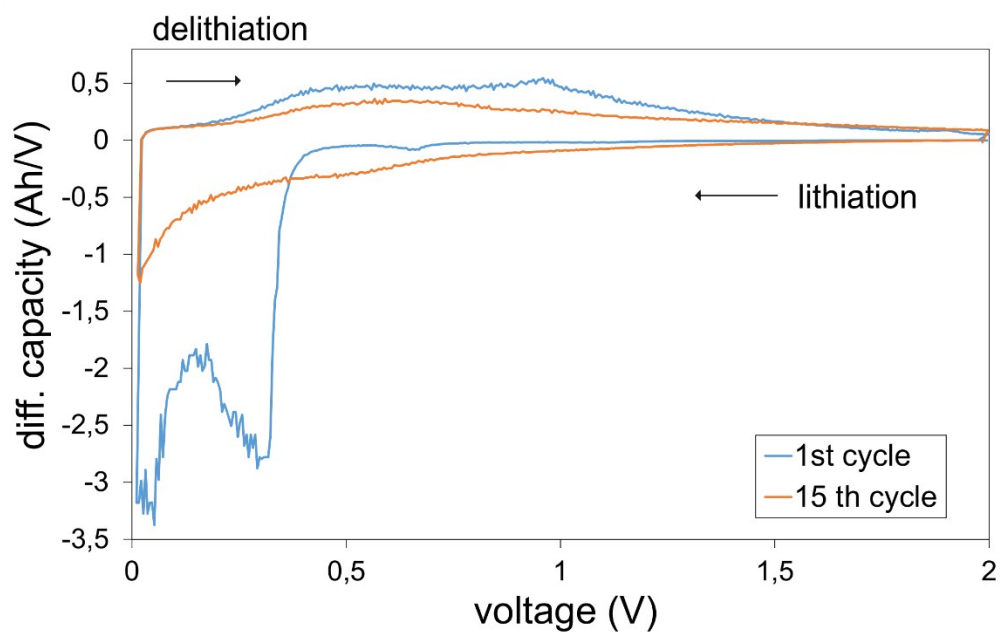
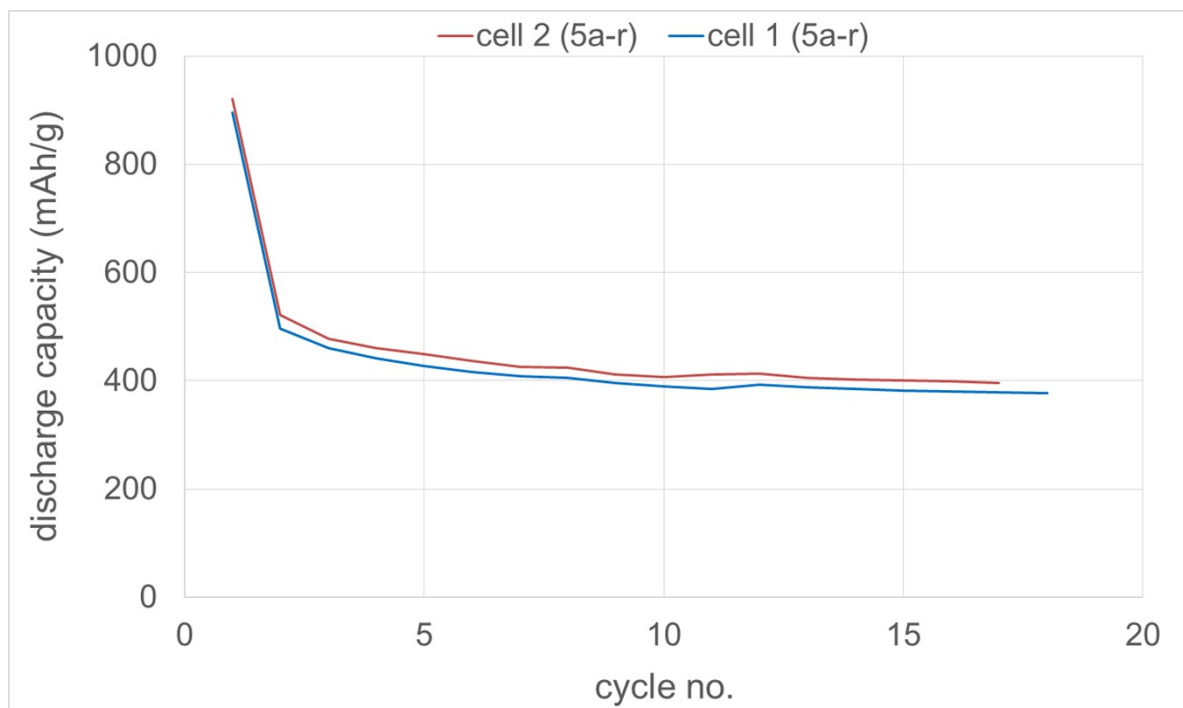


Figure S16. Top: Cycling performance of the nanocomposite **5a-r**. Bottom: The differential capacity of the electrode produced from the nanocomposite **5a-r** at a voltage of 0 to 2 V. The **5a-r** shows the expected curve profile for a tin-nickel-alloy/carbon composite during the lithiation and delithiation of the material.^[1]

[1] a) J. Qin, X. Zhang, N. Zhao, C. Shi, E. Liu, J. Li, C. He, *RSC Adv.* **2014**, *4*, 49247-49256; b) D. Guan, J. Li, X. Gao, C. Yuan, *J. Alloy Compd.* **2014**, *617*, 464-471.

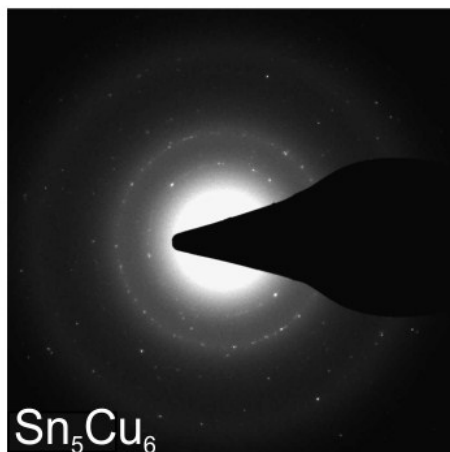


Figure S17. Selected area electron diffraction of the nanocomposite **6-r**.

Synthesis of hybrid materials:

Synthesis of hybrid materials (General method):

In a typical reaction 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] and tin(II)-2,4-dimethoxyphenylmethanolate (**1**) were suspended in toluene and heated to 90 °C. The colorless solution changed to a red color and the metal containing additive was added. The reaction mixture was then heated to 105 °C and after stirring for 12 hours the as obtained precipitate was filtered off, washed three times with acetone (10 ml) and dried in vacuo.

Hybrid material 2a: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (3.0 g, 11.02 mmol) and **1** (1.66 g, 3.67 mmol) in toluene (25 ml) gave 2.98 g (64 wt.%) of a pale violet powder.

Hybrid material 2b: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (0.94 g, 3.45 mmol) and **1** (1.56 g, 3.45 mmol) in toluene (20 ml) gave 1.38 g (55 wt.%) of a pale violet powder.

Hybrid material 3a: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (1.12 g, 4.11 mmol) and **1** (0.62 g, 1.37 mmol) in the presence of cobalt(II)-2-(2-(2-methoxyethoxy)ethoxy)acetate (0.06 g, 0.14 mmol) in toluene (20 ml) gave 1.21 g (67 wt.%) of a pale violet powder.

Hybrid material 3b: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (0.41 g, 1.51 mmol) and **1** (0.68 g, 1.51 mmol) in the presence of cobalt(II)-2-(2-(2-methoxyethoxy)ethoxy)acetate (0.14 g, 0.33 mmol) in toluene (20 ml) gave 0.63 g (51 wt.%) of a pale violet powder.

Hybrid material 3c: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (1.19 g, 4.37 mmol) and **1** (0.66 g, 1.46 mmol) in the presence of cobalt(II)-2-(2-(2-methoxyethoxy)ethoxy)acetate (0.20 g, 0.48 mmol) in toluene (20 ml) gave 1.29 g (63 wt.%) of a pale violet powder.

Hybrid material 4a: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (1.27 g, 4.65 mmol) and **1** (0.7 g, 1.55 mmol) in the presence of iron(III) undecanate (0.28 g, 0.46 mmol) in toluene (25 ml) gave 1.76 g (78 wt.%) of a dark red powder.

Hybrid material 4b: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (1.20 g, 4.39 mmol) and **1** (0.66 g, 1.46 mmol) in the presence of iron(III) undecanate (0.30 g, 0.73 mmol) in toluene (25 ml) gave 1.36 g (63 wt.%) of a dark red powder.

Hybrid material 5a: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (1.64 g, 6.03 mmol) and **1** (0.91 g, 2.01 mmol) in the presence of nickel(II)-2-(2-(2-methoxyethoxy)ethoxy)acetate (0.62 g, 1.51 mmol) in toluene (25 ml) gave 2.16 g (68 wt.%) of a pale green powder.

Hybrid material 5b: Polymerization of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (0.72 g, 2.65 mmol) and **1** (1.20 g, 2.65 mmol) in the presence of nickel(II)-2-(2-(2-methoxyethoxy)ethoxy)acetate (0.33 g, 0.79 mmol) in toluene (20 ml) gave 1.06 g (47 wt.%) of a pale green powder.

Hybrid material 6:

A mixture of 2,2'-spirobi[4*H*-1,3,2-benzodioxasiline] (1.80 g, 6.61 mmol), **1** (1.0 g, 2.20 mmol) and copper(II) undecanate (1.15 g, 2.64 mmol) was dissolved in toluene (25 ml) at 90 °C. To the dark-red solution 0.08 ml (0.66 mmol) SnCl₄ was added. After stirring for 12 hours at 105 °C the as obtained precipitate was filtered off, washed three times with acetone (10 ml) and dried in vacuo to give 2.85 g (72 wt.%) of a pale brown powder.

Production of the test cell

For the electroactive material 87 wt.% of the nanocomposite **5a-r** was mixed with 6 wt.% of conductive black (Super P Li from Timcal) and 7 wt.% binder (polyvinylidene fluoride KYNAR FLEX® 2801) in 125 wt.% N-ethyl-2-pyrrolidone and stirred for 16 h. The coating material was subsequently applied to a copper film of thickness 20 µm (purity 99.9%) using a coating bar and dried at 120 °C under reduced pressure. For the building of the electrochemical test cells (2-electrode test arrangement analogous to a button cell), circular pieces with a diameter of 20 mm were punched out. Lithium foil was used as the counter and reference electrode. A 1 M solution of LiPF₆ in a 1:1 w/w mixture of ethylene carbonate and ethyl methyl carbonate was used as the electrolyte. For electrochemical characterization, the cells were connected to a Maccor Series 4000 battery cycling unit and were cycled at a specific current of 30 mA per gram of electroactive material between 10 mV and 2 V against Li/Li⁺. After 10 mV had been attained, the voltage was kept constant for 30 min. (according to US 20130341559 A1)