Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

Supplementary Information

NiCo nanotubes plated on Pd seeds as a designed magnetically recollectable catalyst with high noble metal utilisation

S. Schaefer*[a], E.-M. Felix[a], F. Muench[a], M. Antoni[a], C. Lohaus[a], J. Brötz[a], U. Kunz[a], I. Gärtner[b] and W. Ensinger[a]

[a]Technische Universität Darmstadt, Department of Materials Science, Alarich-Weiss-Straße 2, 64287 Darmstadt, Germany

[b]Technische Universität Darmstadt, MPA / IfW Darmstadt, Grafenstraße 2, 64283 Darmstadt, Germany

*E-mail: schaefer@ma.tu-darmstadt.de

Morphology determination by TEM

For more detailed information on the morphology of the Nanotubes, TEM measurements were performed. Therefore, a new batch of sample were synthesised and prepared for the TEM measurements. Sadly, the wall thickness is too high, so that it is impossible to visualise the seeding particles on the surface of the Nanotube (fig. S1). The amount of Pd is too small and the seeds are completely embedded in the tube walls, therefore it is hard to make them visible in a TEM-image.

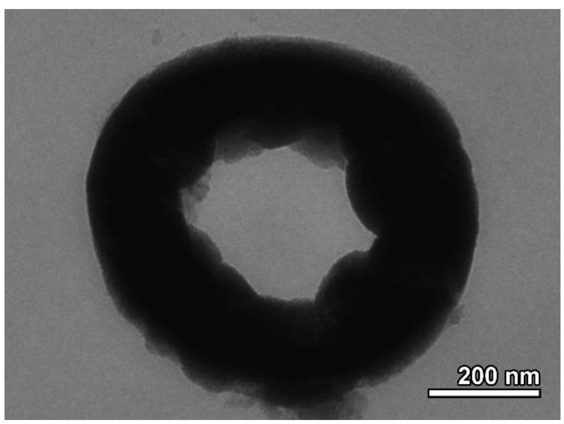

Fig. S1: Crosssection TEM-image of one NiCo NT.

Composition analysis by EDX

To provide more information about the composition of the NTs, EDX measurements were conducted. As shown in fig. S2 only signals of Ni and Co can be observed. Due to the synthesis method also Pd would be expected, but the amount is too small, so it cannot be detected by EDX. Only a slight increase of the background signal between 2 keV and 6 keV could possibly indicate be a sign for the presence of further elements in the composition such as Pd. The signals of Pd would normally appear at energies of $L_{\alpha1}$ = 2.839 keV, $L_{\alpha2}$ = 2.883 keV, $L_{\beta1}$ = 2.99 keV, $L_{\beta2}$ = 3.171 keV and $L_{\gamma1}$ = 3.329 keV and are marked by a star in fig. S2.

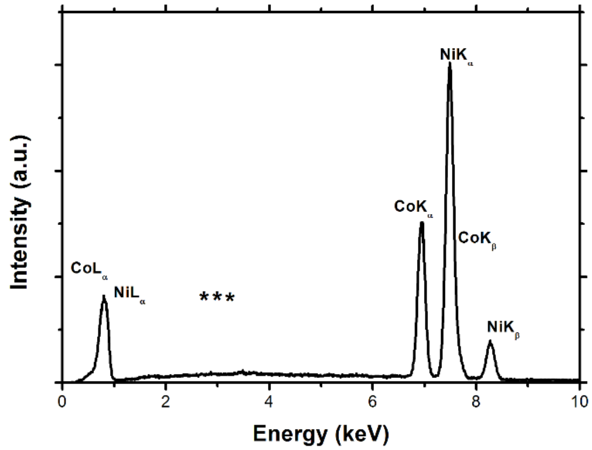

Fig. S2: EDX spectra of NiCo NTs for the composition analysis. No Pd could be detected.

Magnetic Properties of Ni NTs

The Pd seeding particles could also been produced on Ni NTs instead of NiCo NTs. This would be easier for the synthesis because only one metal salt would have been used in the plating solution but, unfortunately, the Ni NTs are paramagnetic. The paramagnetic behaviour is proven by the lack of hysteresis behaviour as it is depicted in fig. S3 On these grounds, those structures are not suitable for the design of magnetically recollectable catalysts.

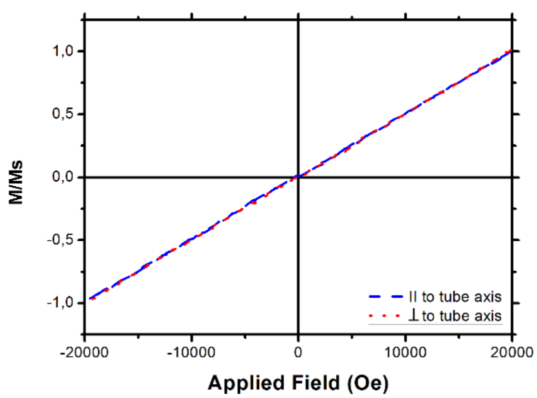

Fig. S3: Magnetic behaviour of Ni NTs measured by VSM once parallel and once perpendicular to the tube axis.

Catalytic activity of NiCo NWs

Electrodeposited NiCo NWs were used to determine the influence of the support material on the catalytic activity towards the hydrogenation of 4-NP. Those NWs can be synthesised without any seed particles on the surface, due to the plating process. Therefore, an electrodeposition electrolyte was prepared with the same metal salt ratio as for the electroless plating solution of NiCo NTs. The NWs were tested as catalyst under the same circumstances as the NTs but nearly no activity could be observed. Even after 30 min reaction time, just a small absorbance decrease at a wavelength of 400 nm could be observed (fig. S4).

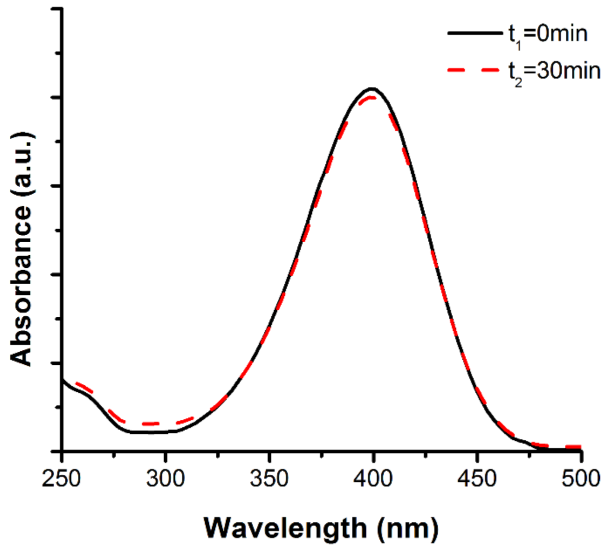

Fig. S4: UV-Vis spectra at two different stages during the reduction reaction of 4-NP by $NaBH_4$ to 4-AP in the presence of the NiCo NWs as catalyst.

Catalytic activity of recollected NT-catalyst

After the catalytic reduction of 4-NP to 4-AP the catalyst material is recollected by applying an external magnetic field and is reused. The activity of the catalyst does not decrease in the second cycle. Therefore, the plots of ln(A/A0) versus reaction time of the two cycles were compared as shown in fig. S5. Hence, there is nearly no difference in the behaviour and therefore the activity for both cycles is nearly identical.

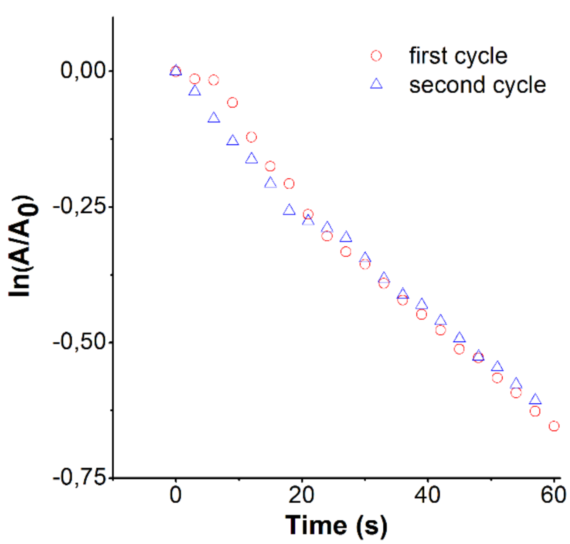

Fig. S5: Plot of $\ln(A/A_0)$ versus reaction time of the reduction reaction of 4-NP by $NaBH_4$ to 4-AP in the presence of the NiCo NTs for two cycles.

Catalytic activity of the same material as thin film

To prove the advantage of one-dimensional hollow nanostructures, a thin film, fabricated under the same conditions, is prepared for comparison. This material is then used as catalyst for the 4-NP reduction reaction with the same parameters as the nanotubes. The results of this measurement are shown in fig. S6. In comparison to the nanotubes, the thin film exhibits no activity towards the reduction reaction, even though the compositions of the two materials are similar. Therefore, it is possible to say that the shape of a nanotube is favourable compared to a thin film (bulk material), due to their behaviour as semi-homogeneous catalysts.

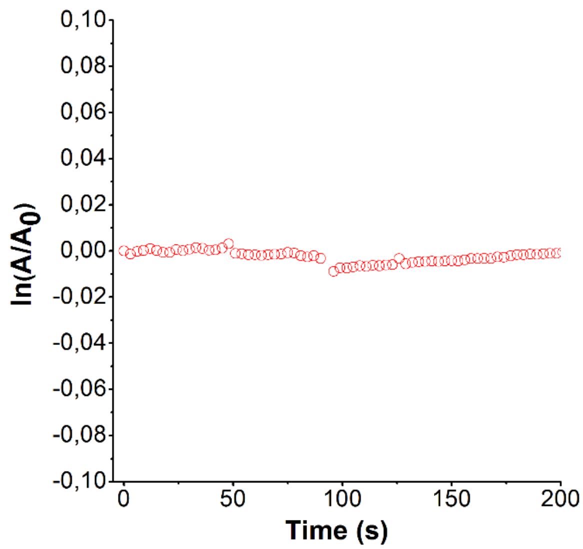

Fig. S6: Plot of $\ln(A/A_0)$ versus reaction time of the reduction reaction of 4-NP by $NaBH_4$ to 4-AP in the presence of the NiCo thin film with Pd seeds.