ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Magnetic Mesoporous Nanocarriers for Drug Delivery with Improved Therapeutic Efficacy

*Albert Serrà, Núria Gimeno, Elvira Gómez, Margarita Mora, Maria Lluïsa Sagristá, and Elisa Vallés**

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Cyclic voltammetries

Voltammetric curves were recorded on Si / Ti (15 nm) / Au (100 nm) substrates (**Figure 1S**) in order to interpret the CoNi electrodeposition process in the microemulsion and to select the potentials able to form the CoNi mesostructures over gold surfaces. The blue curve (Figure 1Sa) corresponds to the typical profile of a CoNi deposition process in an aqueous solution: with the nucleation and the growth loop in the cathodic scan, and the oxidation peak corresponding to the alloy oxidation. When both surfactant and ionic liquid are added to the aqueous solution to form the microemulsion, the voltammetric profile changes. To justify this change, cyclic voltammetries of aqueous solution containing surfactant (Figure 1Sb) and of the microemulsion at different cathodic limits (Figure 1Sc) were recorded. The presence of the surfactant in the CoNi aqueous solution leads to a small reduction peak prior to the main alloy deposition current (Figure 1Sb, cathodic limit -0.8 V). We can assign this first reduction peak to the initial deposition of nickel or nickel-rich deposit, over which the anomalous codeposition of CoNi takes place. The presence of the surfactant hinders the adsorption of the Co (II) species proposed in the mechanism of the anomalous CoNi electrodeposition, [1] as the manner that the initial step of normal electrodeposition is detected.

The voltammetries in the ionic liquid-in-CoNi aqueous solution microemulsion also shows a first reduction peak at around -0.6 V, assigned to the initial nickel deposition, followed by a main reduction peak assigned to the CoNi deposition. In the first reduction peak, the accumulation of deposit by means of a hold allows detecting the oxidation peak corresponding to the first nickel-rich deposit formed at potentials prior to the oxidation of the CoNi alloy.

When deposits were prepared from the three electrodeposition media (CoNi aqueous solution -W-, solution containing surfactant -W+S-, and IL/W microemulsion) the previous proposal is corroborated. In both W+S and IL/W systems, the obtained deposits at low deposition potentials (-650 mV) are nickel-rich, which is justified by the nobler character of this metal

respect to the cobalt (**Table 1S**). At more negative potentials, the CoNi alloy is already formed, and anomalous codeposition takes place, because the composition of the deposits are cobalt richer than that of the obtained in CoNi solution. In the case of the W system, the initial nickel deposition is not observed, as has been found previously.

From the performed voltammetric study, we can select potentials equal or more negative than -900 mV to assure the formation of the CoNi alloy from the IL/W microemulsion. In order to obtain the same composition of the CoNi structures from aqueous solution W (compact structures) or IL/W microemulsion (mesoporous structures) over gold substrate, a potential of -1000 mV was selected to form the deposits.

Table 1S: Elemental composition of CoNi deposits (1.6 C cm^{-2}) on Si / Ti (15 nm) / Au (100 nm) substrates prepared at different potentials in non-stirring conditions.

			W	W + S	IL/W microemulsion
Elemental Composition / wt. %	-650 mV	Co	-	7 ± 2	6 ± 1
		Ni		93 ± 2	94 ± 1
	-900 mV	Co	45 ± 2	34 ± 2	30 ± 1
		Ni	55 ± 2	66 ± 2	70 ± 1
	-1000 mV	Co	49 ± 1	49 ± 3	49 ± 3
		Ni	51 ± 1	51 ± 3	51 ± 3

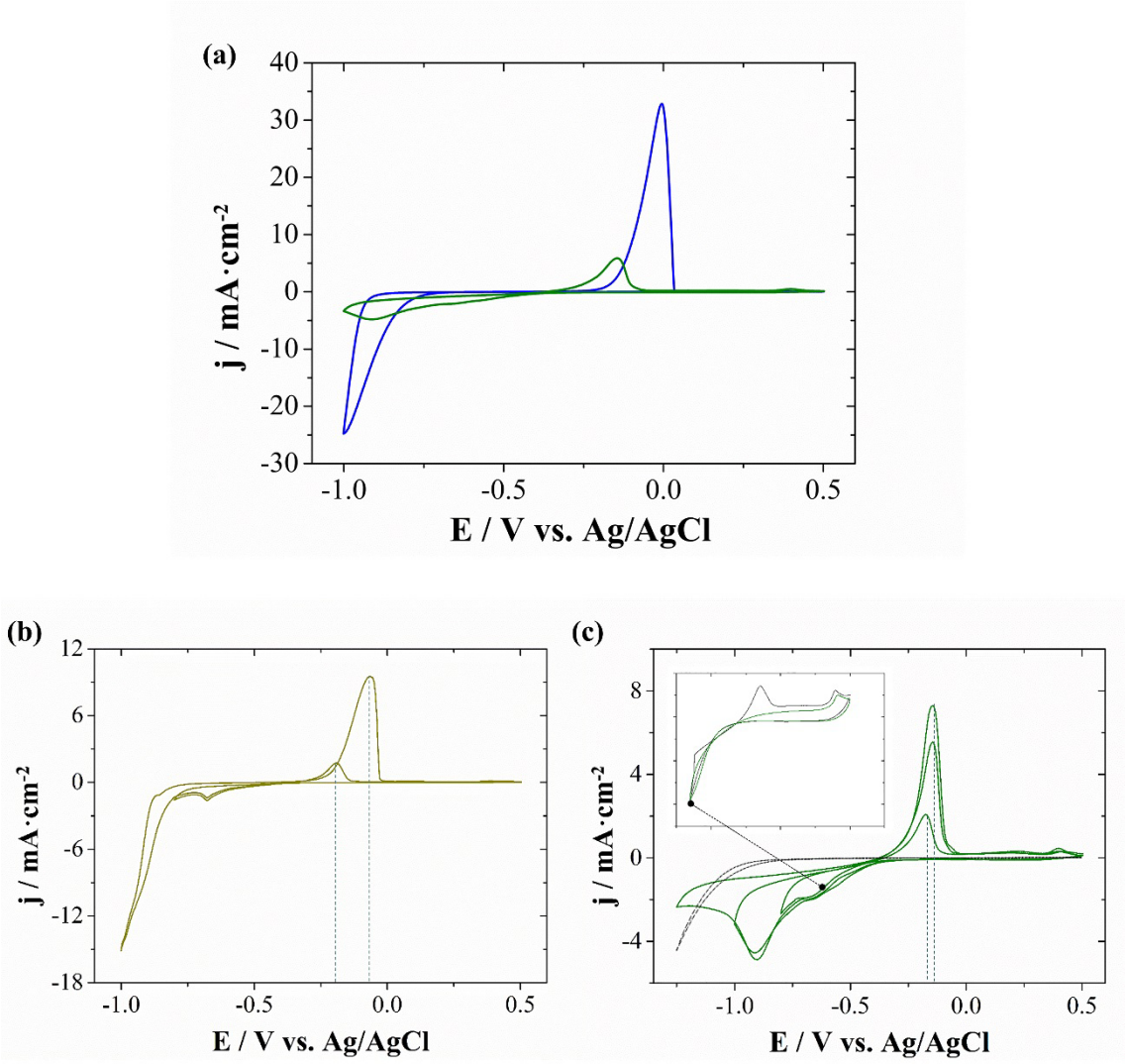

Figure 1S: Cyclic voltammetry under stationary conditions at 50 mV s^{-1} of (a) aqueous solution (blue line) and IL/W microemulsion (green line); (b) 84.9 wt. % of aqueous solution + 15.1 of Triton X-100; and (c) IL/W microemulsion with (green line) and without (black line) Co(II) and Ni(II) species.

Conductivity, surface tension and viscosity of various electrochemical media

Table 2S: Conductivity, surface tension and viscosity of the different electrochemical media: aqueous solution (W), aqueous solution + surfactant (W+S) and IL/W microemulsion.

	W	W + S	IL/W microemulsion
Conductivity / mS cm^{-1}	104	77.7	67.9
Surface Tension / mN m^{-1}	75	32	32
Viscosity / mPa s^{-1}	1.43	11.1	37.5

Cronoamperometric curves, SEM characterization and length distribution of synthesized coni nanorods

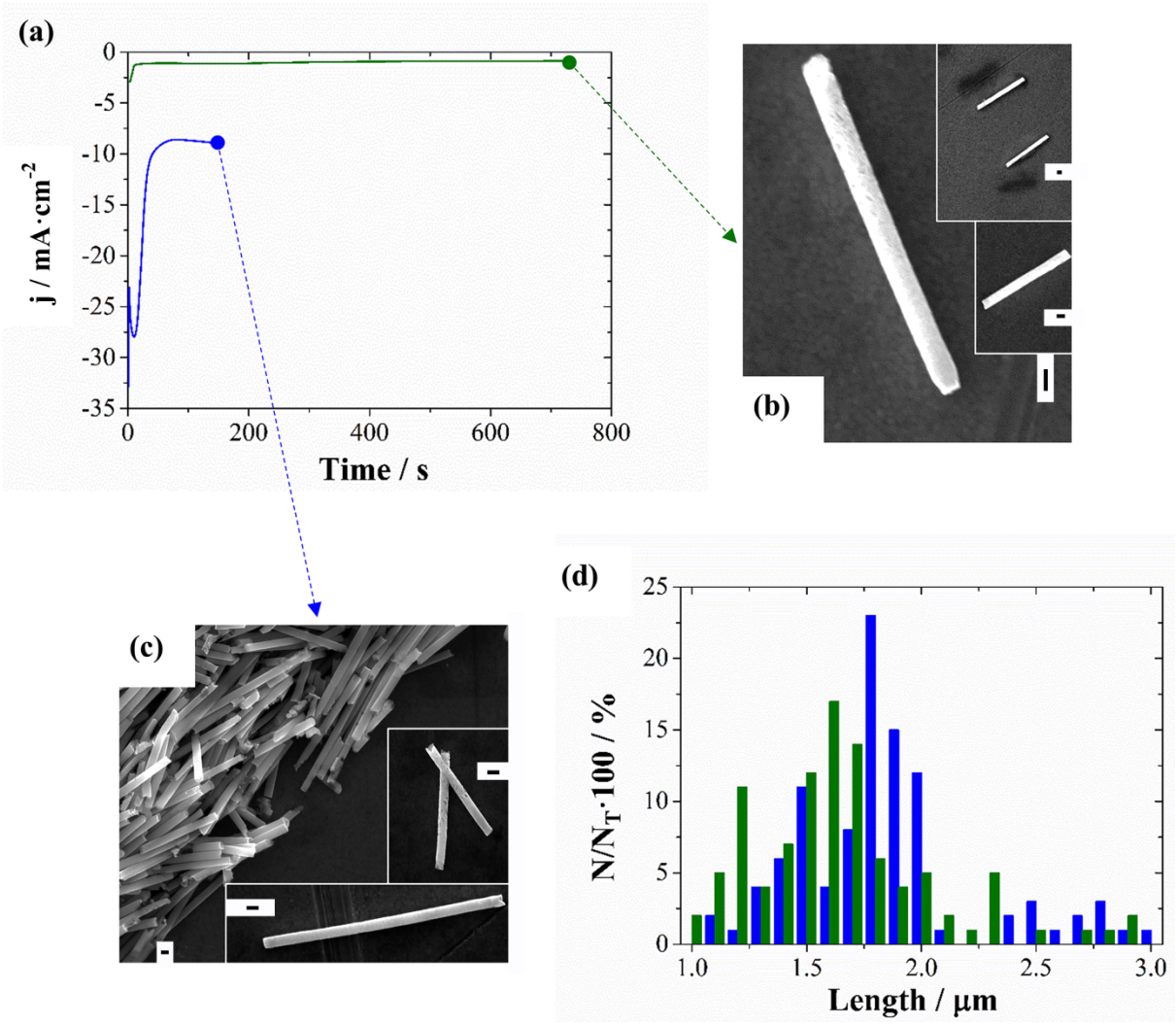

Figure 2S: Chronoamperometric curves (a), SEM images (b, c) and length distribution (d) of CoNi NRs obtained at -1000 mV on PC membranes at 25 ºC in aqueous solution (blue) and ionic liquid-in-aqueous microemulsion (green). Scale bar: 100 nm.

X-Ray Diffraction

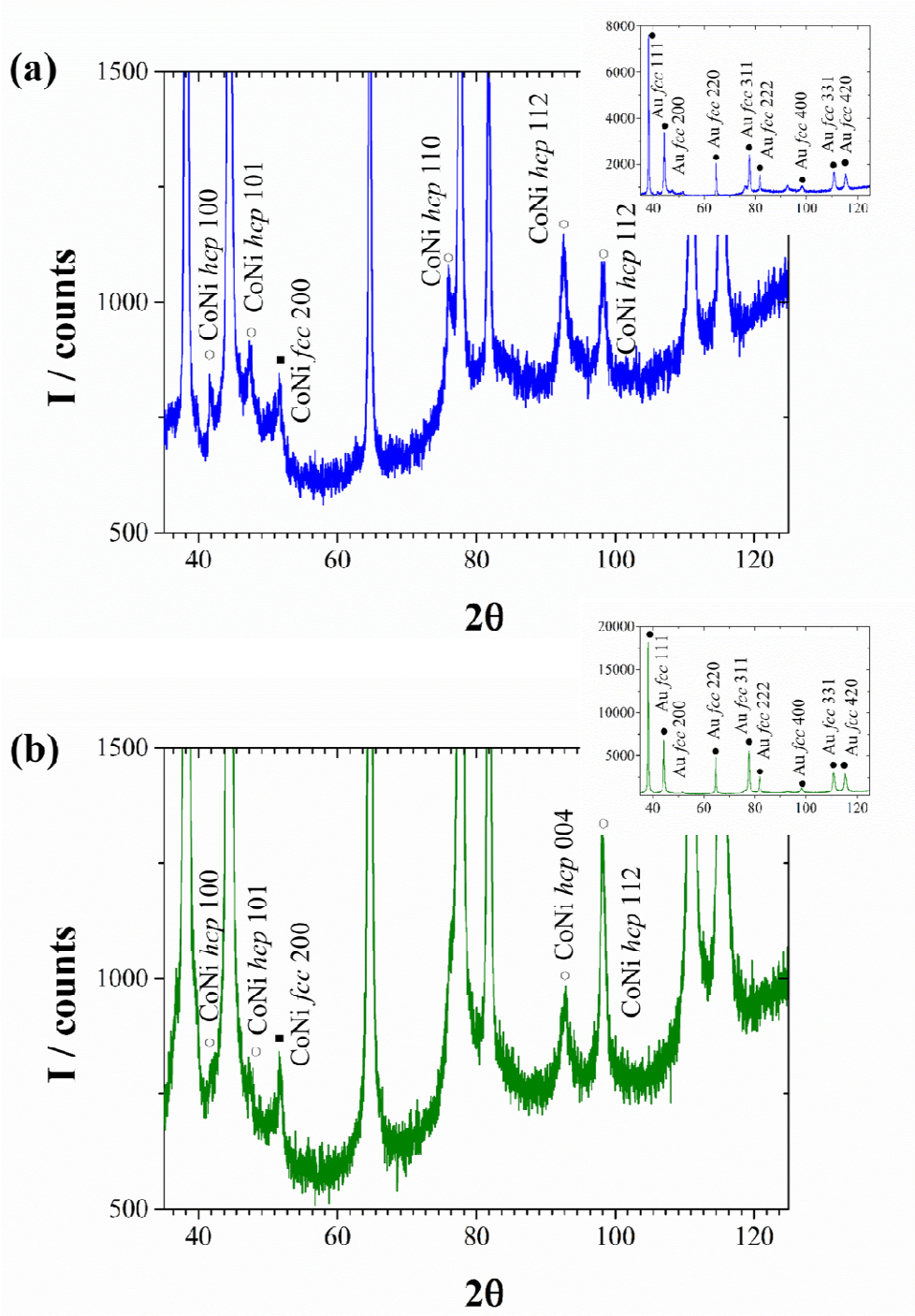

Figure 3S: XRD patterns for (a) compact and (b) mesoporous CoNi@Au nanorods.

Selected area electron diffraction patterns and magnetic properties

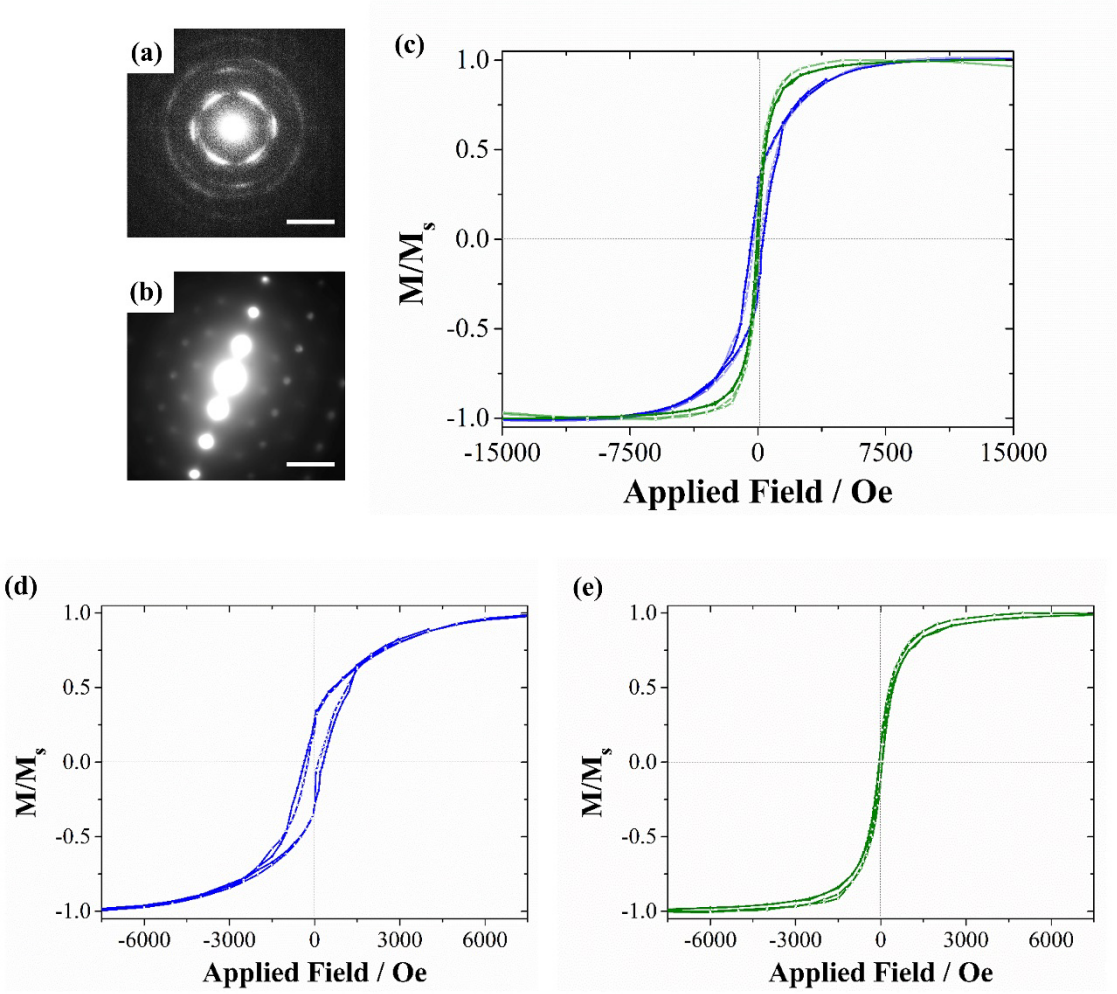

Figure 4S: Representative Selected Area Electron Diffraction (SAED) of compact (a) and mesoporous (b) CoNi@Au NRs. Room-temperature in-plane hysteresis loops of compact CoNi@Au (c and d, continuous blue line) and CoNi@Au-SH-PEG (c and d, dashed blue line) nanorods and mesoporous CoNi@Au (c and e, continuous green line) and CoNi@Au-SH-PEG (c and e, dashed green line). Scale bar: 4 nm^{-1}.

Cytotoxic activity of CoNi@Au-SH-PEG nanorods

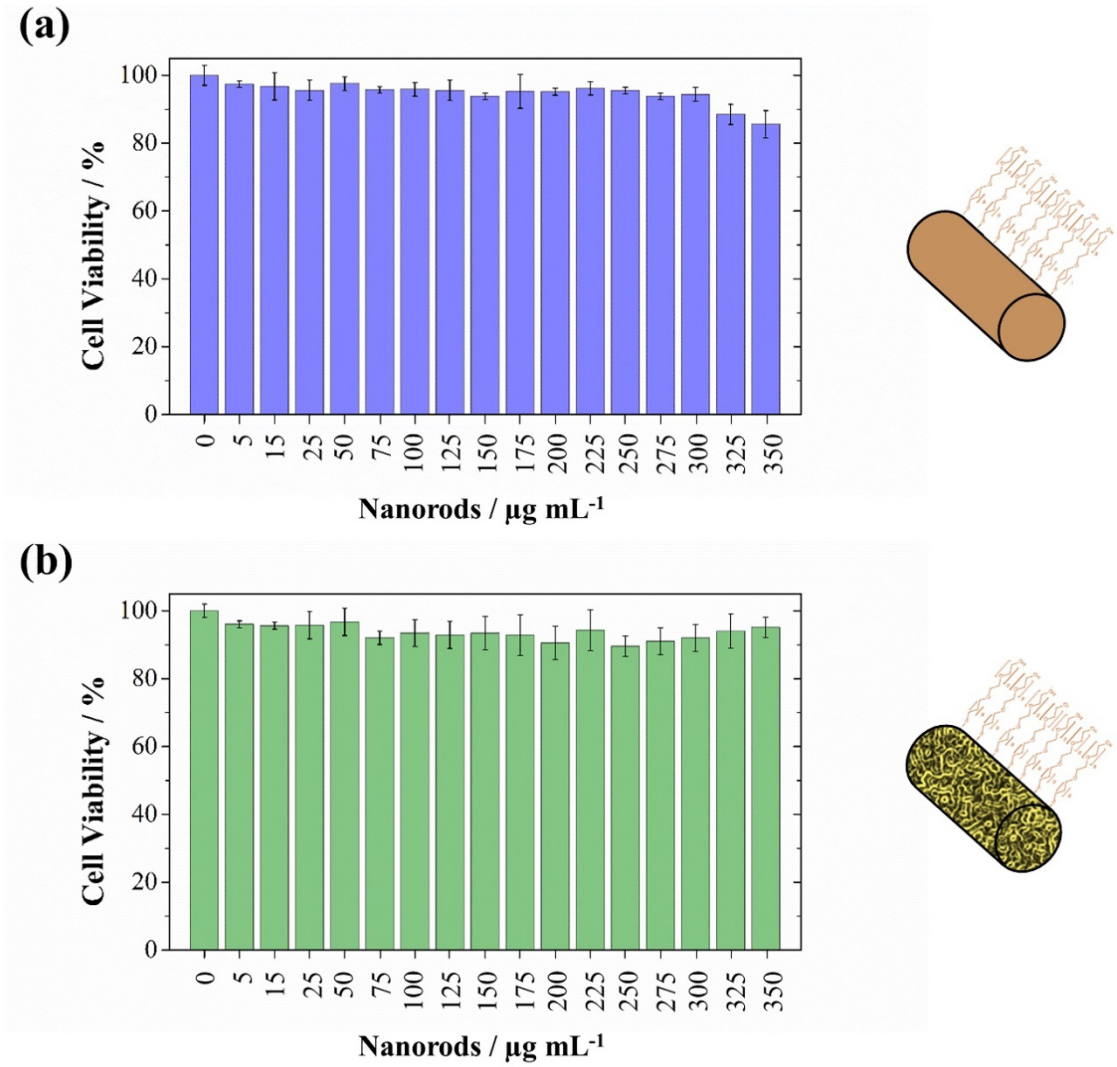

Figure 5S: HeLa cell viability after incubation for 24 h with functionalized compact (a) and mesoporous (b) CoNi@Au-SH-PEG nanorods at the amounts indicated in the figure, followed by 24 h additional incubation with fresh culture medium.

Nanorods uptake by HeLa cells

Video 6S. Three-dimensional reconstruction of alive HeLa cells containing compact nanorods in the cytoplasm, demonstrating the internalization of the carriers. See the attached video file for compact NRs.

Video 7S. Three-dimensional reconstruction of alive HeLa cells containing mesoporous nanorods in the cytoplasm, demonstrating the internalization of the carriers. See the attached video file for mesoporous NRs.

References

1. A) N. Zech, E.J. Podlaha, D. Landolt, *J. Electrochem. Soc*. **1999**, 146, 2886; b) E. Gómez, J. Ramírez, E. Vallés*J. Appl. Electrochem.* **1997**, 28, 71.