Electronic Supplementary Information (ESI)

Nanocomposites with both structural and porous hierarchy synthesized from Pickering emulsions – Towards conductive capsules

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Scanning electrochemical microscopy (SECM)

Electrochemical measurements were performed using an Ameteck commercial scanning electrochemical microscope (SECM). A three electrode setup was employed: a Pt wire was used as auxiliary electrode; an Ag/AgCl electrode was used as quasi reference electrode and a Pt ultramicroelectrode (UME; radius, a = 25 μm) was used as working electrode. SECM approach curves were recorded in 2 mM ferrocyanide in water using a film of MWCNT-CMC native composite with a weight ratio 1:1 as a substrate (mixing 100 mg MWCNTs and 100 mg NaCMC; composite used in this study to stabilize oil-in-water emulsions). Typically, the Pt ultramicroelectrode was slowly approached toward the substrate. Then, I_t was plotted against the normalized distance L = d/a, where I_t is the normalized current (the current recorded at the ultramicroelectrode, I, divided by the current recorded when the tip is far from the electrode, I_{inf}), *d* is the tip–substrate distance and *a* is the radius of the disc ultramicroelectrode. When the UME is far from the substrate, a steady-state current is recorded. At closer distances, two feedbacks could be obtained. A positive feedback is obtained for conducting substrates. Typically, the substrate regenerates the redox probe (*i.e.* ferrocyanide in our case) providing a new source of ferrocyanide within the UME and increasing the steady-state current. On the contrary, for insulating or nonreactive substrates, the surface blocks the ferrocyanide from diffusing to the tip and the steady-state current decreases. A negative feedback is obtained.

In our case, a positive feedback was detected for a MWCNT-CMC composite film with a weight ratio 1:1. This feature reveals the local availability of multi-walled carbon nanotubes and the related conductivity of the composite. As a counterexample, a negative feedback was detected for a MWCNT-CMC composite film with a weight ratio 1:10 (mixing 100 mg MWCNTs and 1 g NaCMC), confirming a lower conductivity.

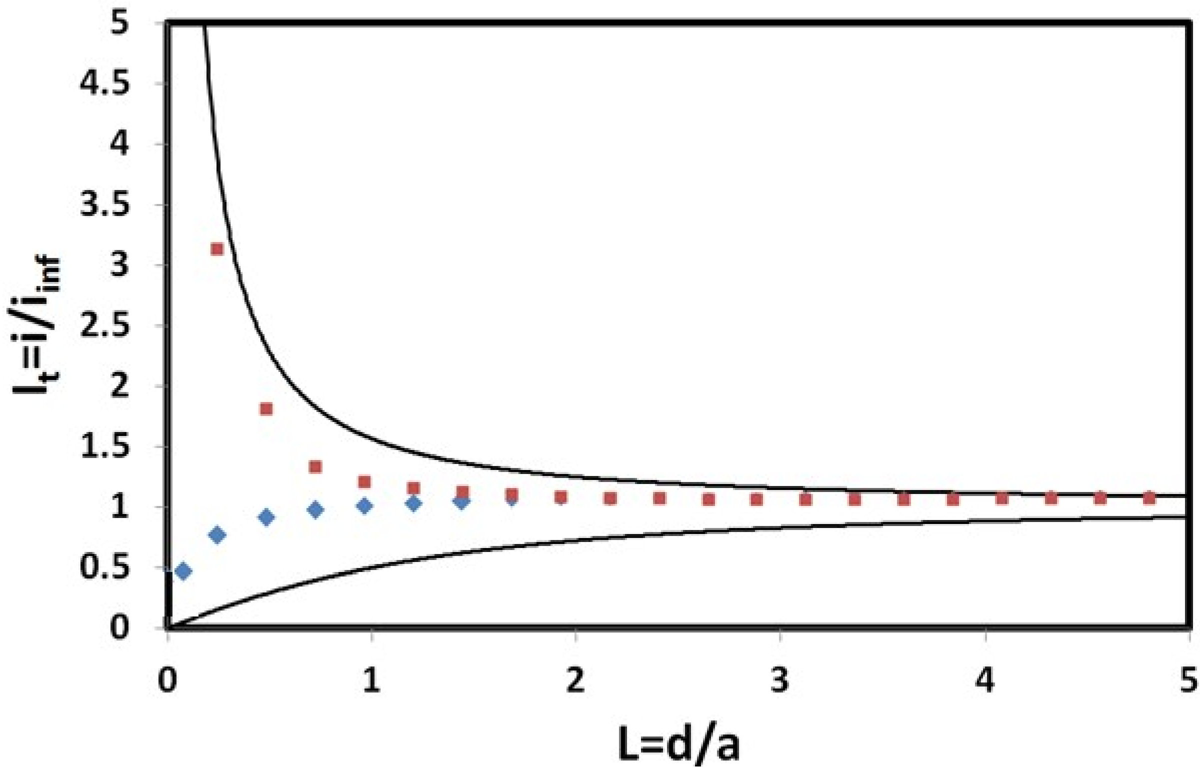

Figure 1S. SECM approach curve recorded with a 25 µm Pt UME tip toward a MWCNT-CMC composite film obtained with a weight ratio 1:1 (red diamond; composites used in this study) and a MWCNT-CMC composite film obtained with a weight ratio 1:10 (blue diamond). The solid line is the theoretical curve for a conducting (positive feedback) and an insulating (negative feedback) substrate. L is the ratio of *d*, distance between the UME and the substrate to *a*, diameter of the UME.

X-ray diffraction (XRD) of pristine MWCNTs

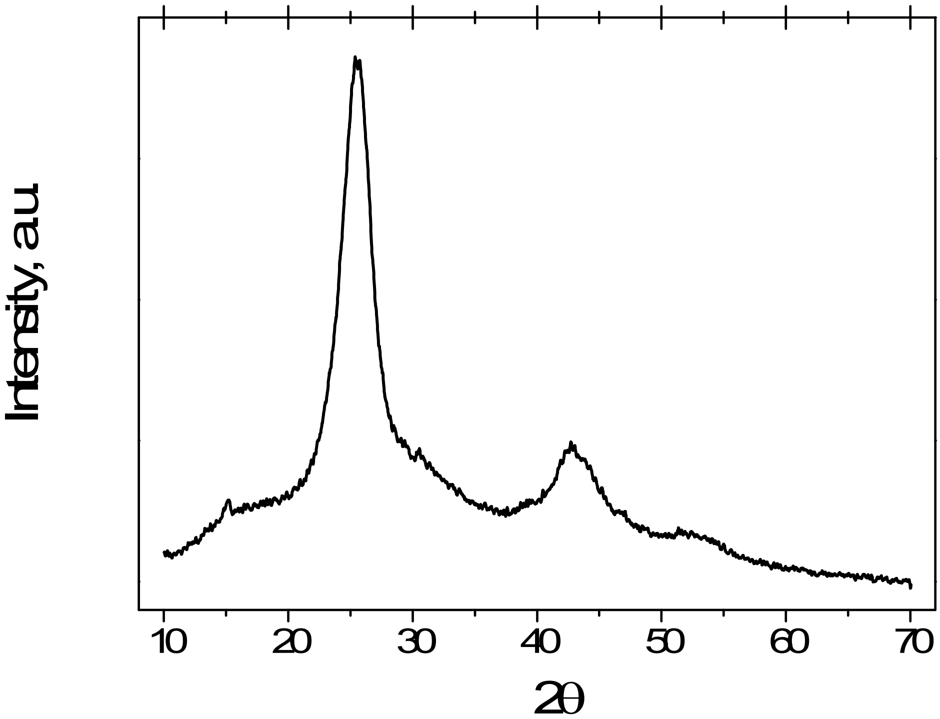

Figure 2S. X-ray diffraction patterns obtained for pristine multi-walled carbon nanotubes.

X-ray photoelectron spectroscopy (XPS)

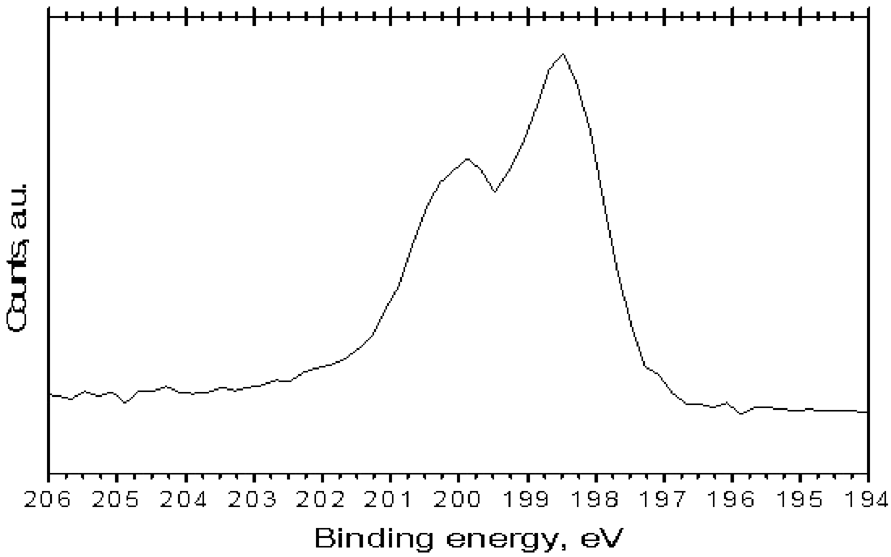

Figure 3S. Cl2p X-ray photoelectron spectroscopy band-like spectrum obtained for MWCNT-CMC-m.

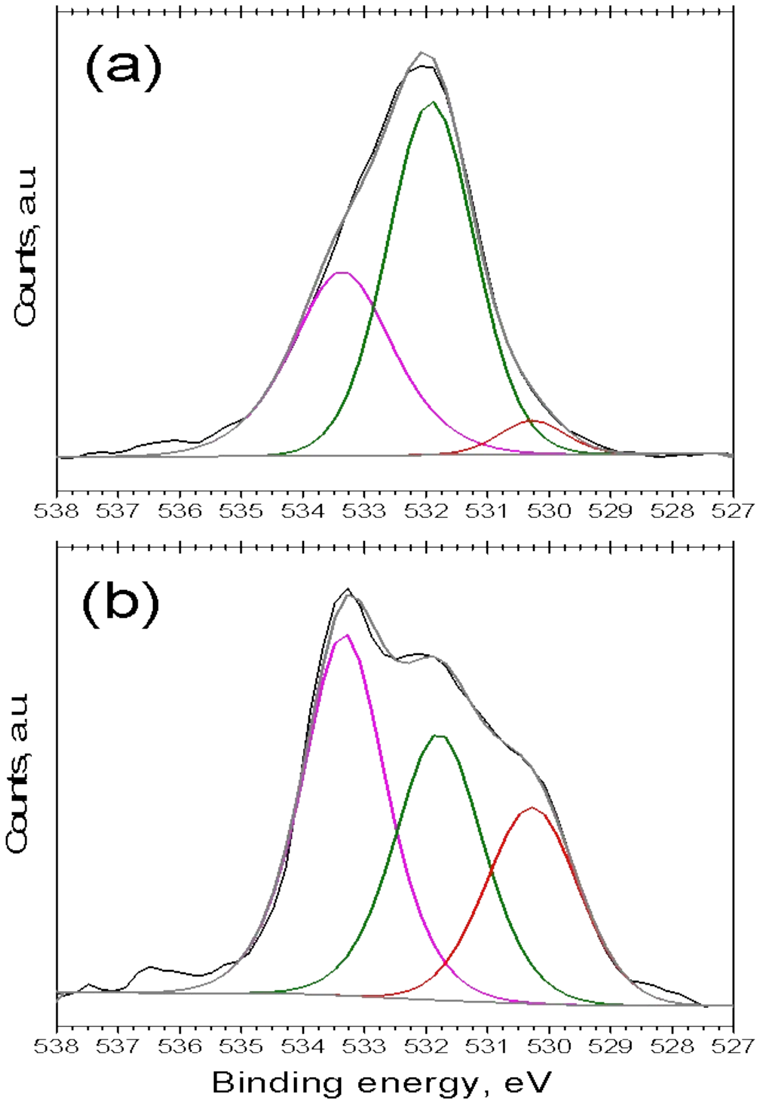

Figure 4S. O1s X-ray photoelectron spectroscopy band-like spectra (black solid lines) and deconvoluted curves (colored solid lines) obtained for (a) **MWCNT-CMC-m** and (b) **MWCNT-CMC-m-550**.

Electrochemical impedance spectroscopy (EIS)

Table 1S. Electrochemical impedance spectroscopy data.

Nomenclature	Thickness (m)	Diameter (m)	Resistance (Ohm)	Conductivity ($S.m^{-1}$)
MWCNT-CMC*	2.10^{-4}	9.10^{-4}	150	2
MWCNT-CMC-m-550	2.10^{-4}	9.10^{-4}	1400	0.2
MWCNT-CMC-m-900	2.10^{-4}	9.10^{-4}	4.6	68

*****native composite