Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Magnetic amphiphilic hybrid carbon nanotubes containing N-doped and undoped sections: Powerful tensioactive nanostructures

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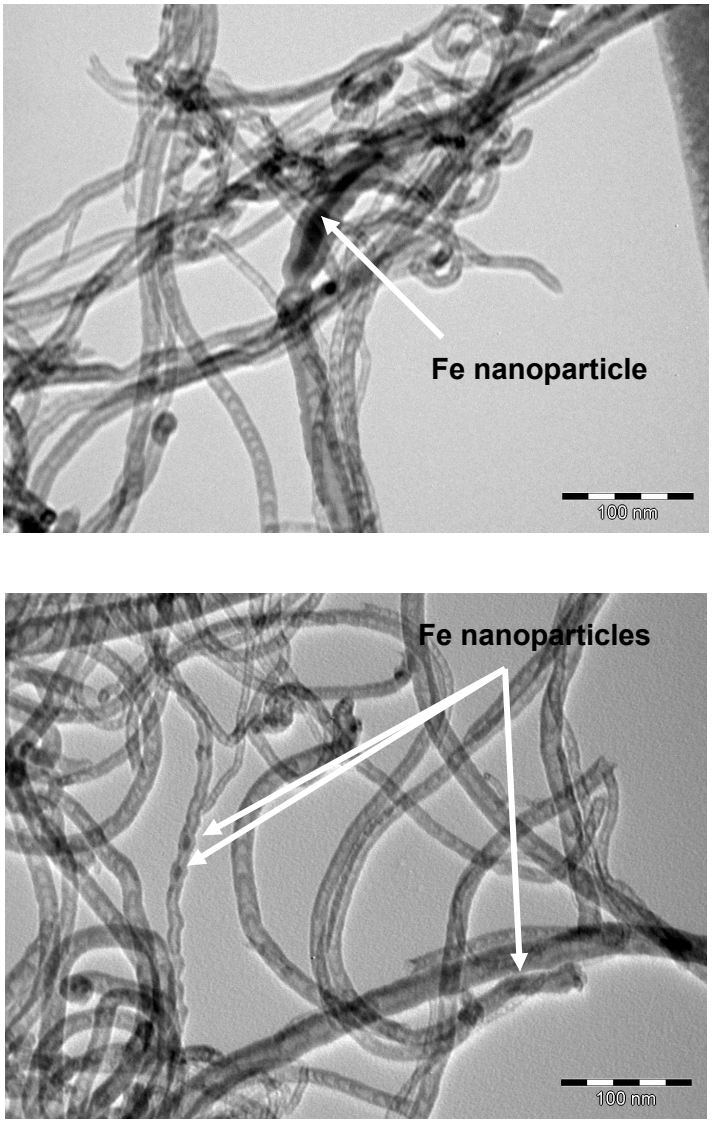


Figure S1. TEM micrographs of sample A20E10.

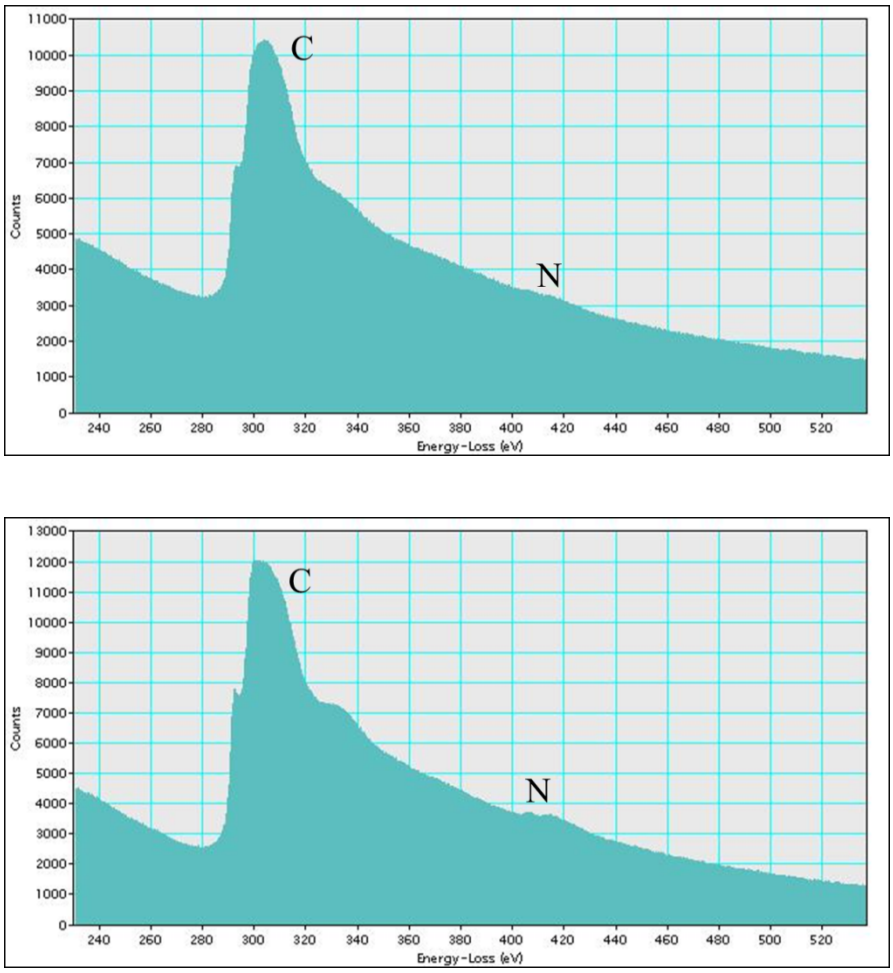
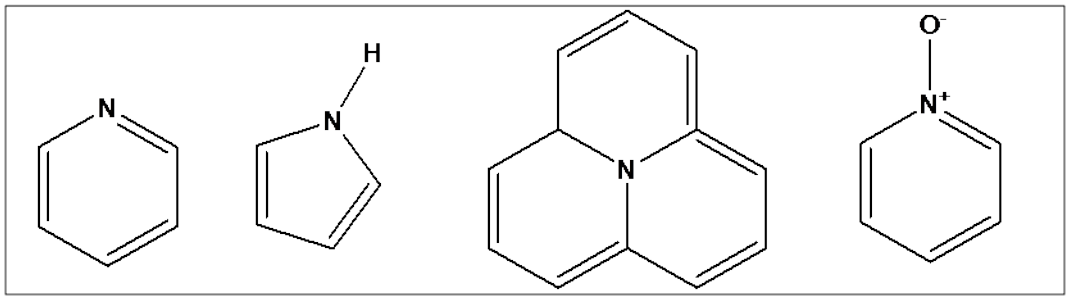


Figure S2. EELS spectra of samples E10A20 (top) and A20E10 (bottom).

Type of nitrogen species found in A30: (A) N_P (pyridinic), (B) N_{PYR} (pyrrolic), (C) N_Q (quaternary) and (D) N_{ox} (oxidized pyridinic).



Sample	XPS			
	%C	B.E Carbon	%N	B.E nitrogen
A30	98.3	284.3	3.8	404

XPS					
Test	% N_P	% N_{PYR}	% N_Q	% N_{ox}	Dominant species
A30	28.8	31.3	12.3	27.6	Pyrrolic

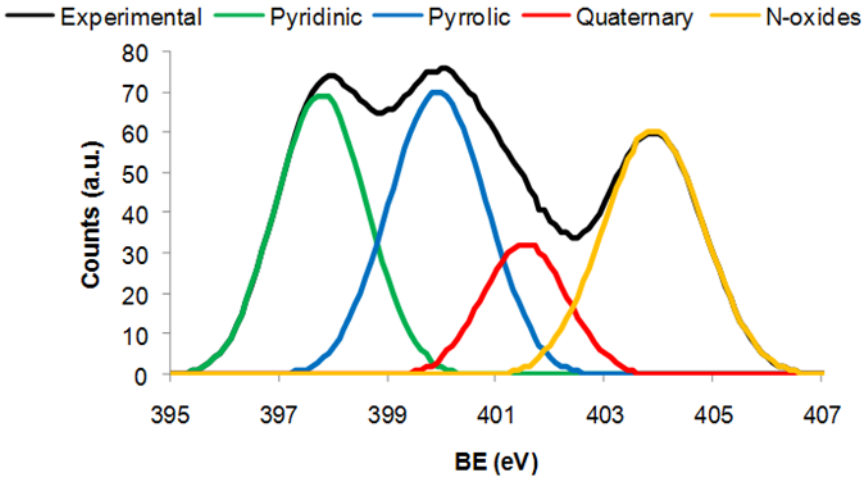
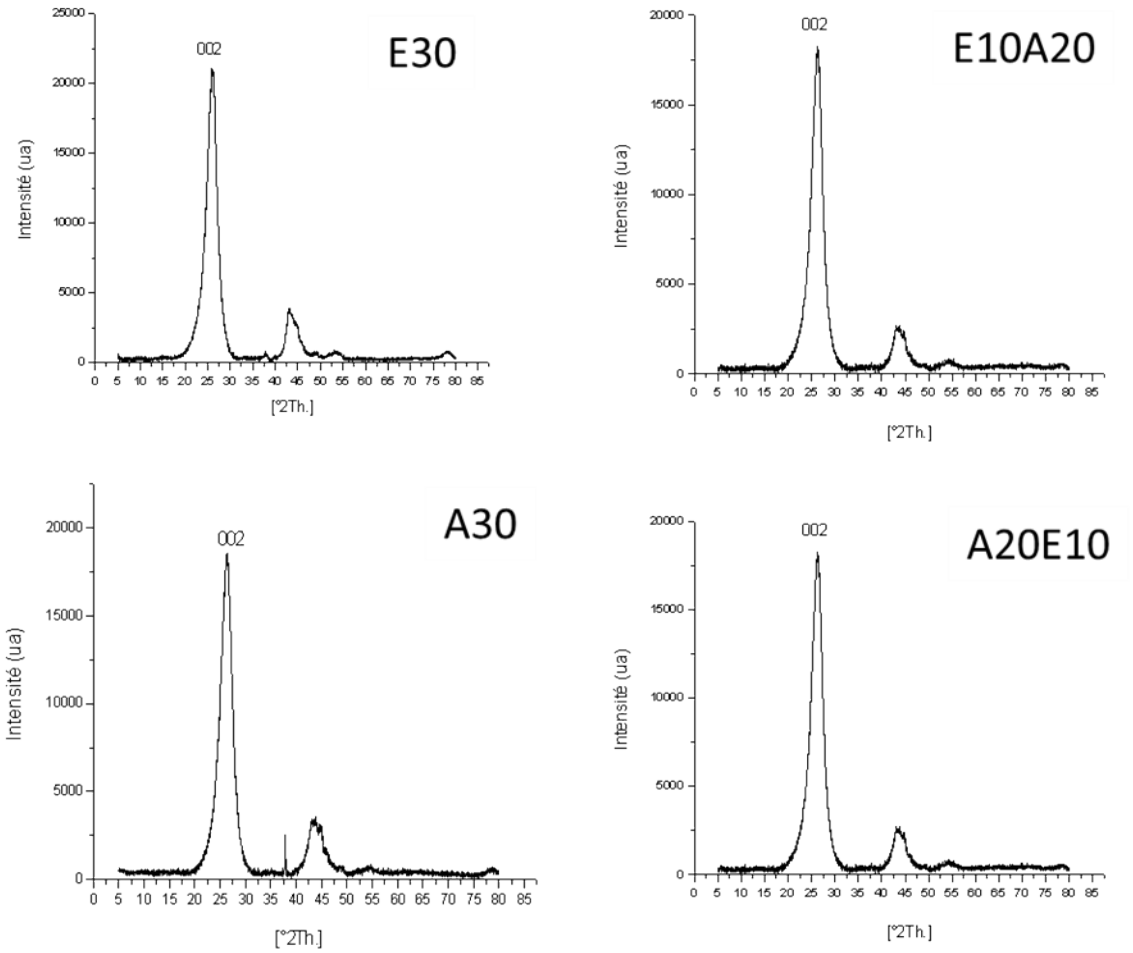


Figure S3. XPS data for sample A30.



Sample	N content (%)	Plane, 2θ (002)	d_{002}(Å)
E30	0	25.62	3.43
E10A20	0.4	25.74	3.44
A20E10	5.0	25.99	3.39
A30	6.1	25.98	3.36

Figure S4. XRD data for the prepared CNTs.

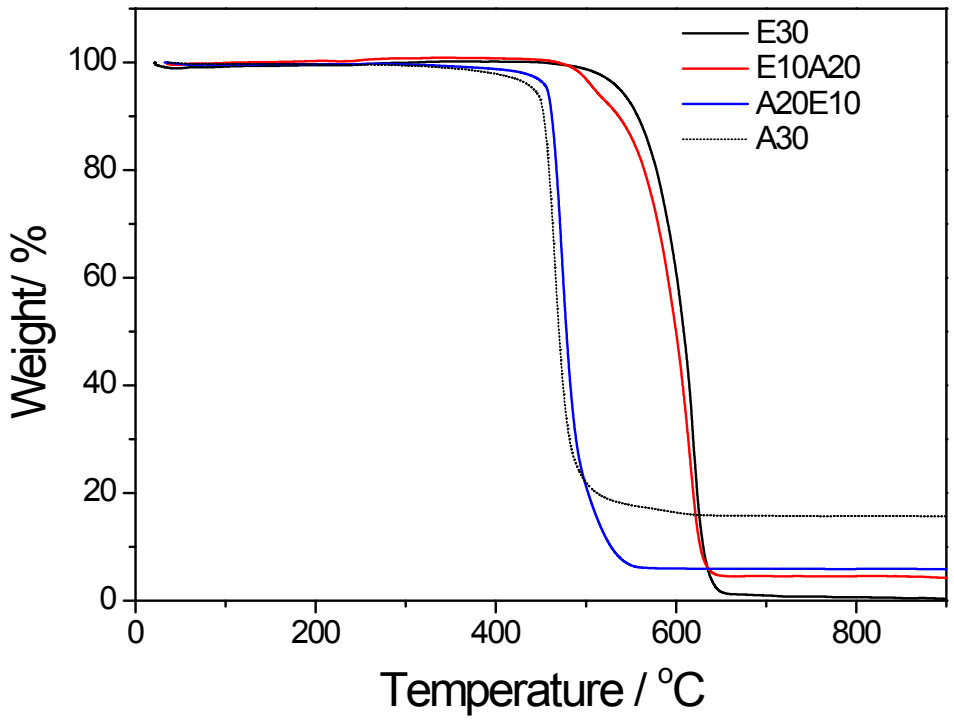
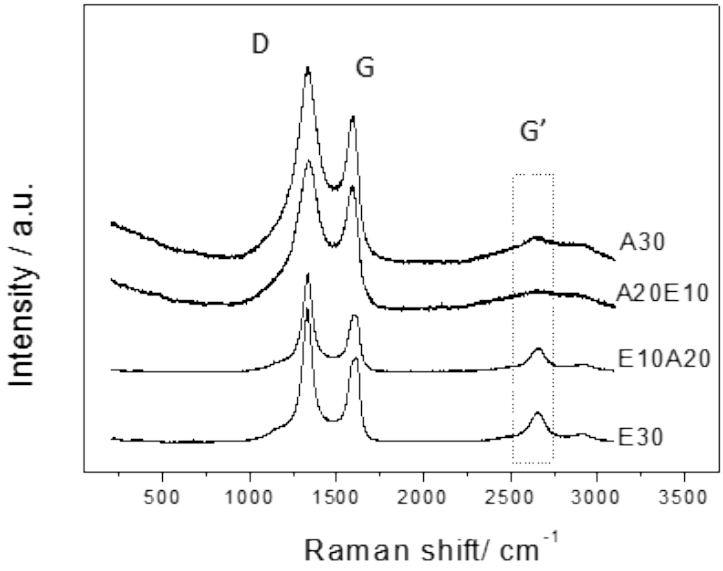


Figure S5. TGA analyses of under air of samples E30, A30, A20E10 and E10A20.



Sample	**I_D/I_G**	**$I_{G'}/I_G$**
E30	0.6	0.2
E10A20	0.6	0.2
A20E10	0.8	0.1
A30	0.8	0.1

Figure S6. Raman spectra of the produced CNTs.

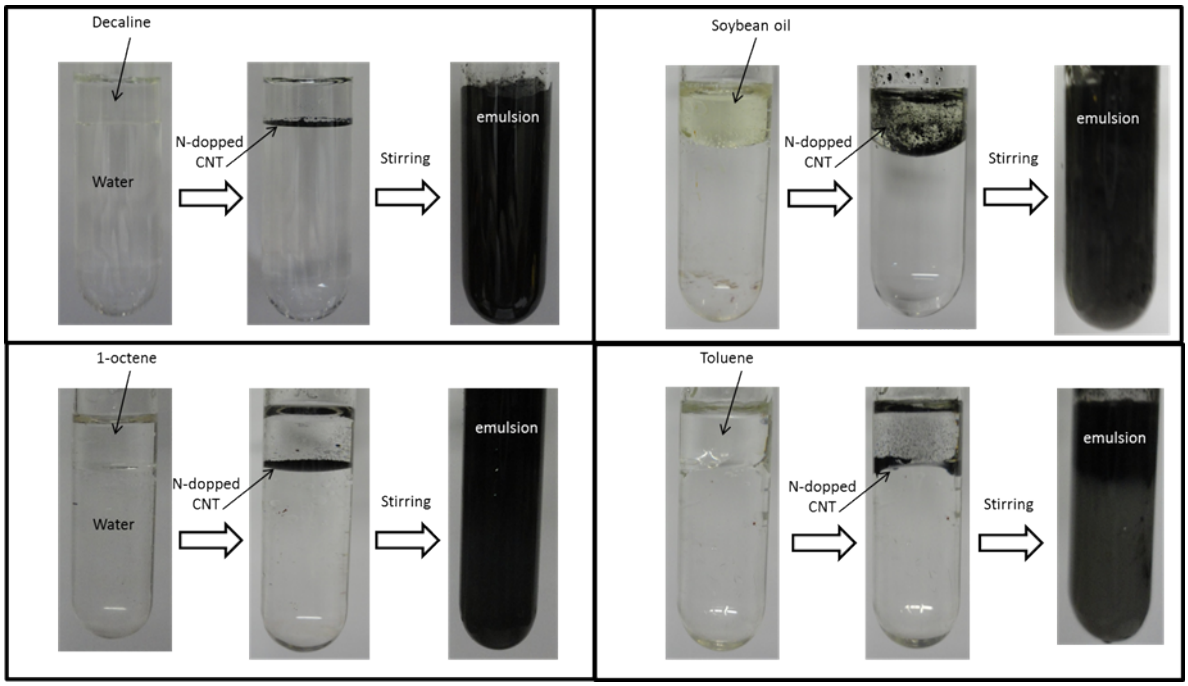


Figure S7. Photographs of biphasic system, emulsified and after magnetic separation in the presence of the sample A10E20.

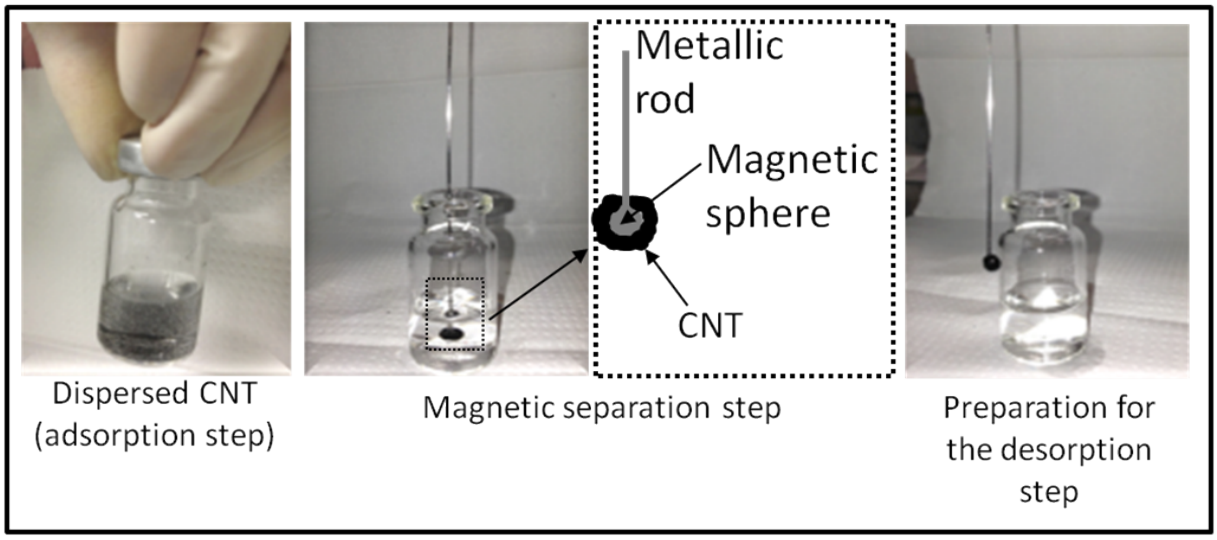


Figure S8. Adsorption of the PAHs and removal of the magnetic CNT from the aqueous sample.

Environmental water sampling of PAHs. US Environmental Protection Agency (EPA) PAH Mix (see Figure S9) containing naphthalene (NA), acenaphthylene (AcPY), acenaphthene (AcP), fluorine (FL), phenanthrene (PHEN), anthracene (Ant), fluoranthene (FLUR), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3-cd]pyrene (IdcP), dibenz[a,h]anthracene (dBAn) and benzo[ghi]perylene (BPe), at 200.00 μg mL^{-1} in methanol: methylene chloride (1:1) was purchased from Supelco (Bellefonte, Pennsylvania, United States).

A stock solution of 1.00 mg L^{-1} was prepared by appropriate dilution in HPLC-grade methanol Sigma-Aldrich (St. Louis, Missouri, United States) and stored at –18.0°C. This stock solution was used for the matrix spike in different concentration levels (5.00 to 80.00 μg L^{-1}) to optimize the extraction conditions during validation study. Calibration standards were prepared at 5.00, 10.00, 20.00, 40.00, 60.00 and 80.00 μg L^{-1} concentrations using ultrapure water produced in a purifier model Purelab UVMK2 from Elga (Marlow, Buckinghamshire, England). HPLC-grade acetone, acetonitrile and toluene were purchased from Sigma-Aldrich (St. Louis, Missouri, United States). Aluminum oxide, and sulfuric acid were purchased from Synth (Diadema, São Paulo, Brazil).

The analysis was performed in a Finnigan Trace DSQ GC/MS equipped with an ion trap mass spectrometer from Thermo Scientific (West Palm Beach, Florida, United States); a capillary column (30 m × 0.25 mm × 0.25 μm) containing 5% diphenyl, 95% dimethylpolysiloxane HP-5MS from Agilent Technology, Inc. (Santa Clara, California, United States) was used.

Aqueous standards of PAH were prepared by injecting an appropriate amount of the working standard to a final concentration of 10.00 μg L^{-1} for all analytes. The conditions for extraction and desorption were based in the study published by Zhao *et al*.[39]. The extraction procedure of the PAH from water with CNT as follows: 2.0 mg of CNT were added to 4.00 mL of water sample in a 10 mL vial, and efficiently dispersed by vortex stirring during 1 min at 25°C. After the CNT dispersion and extraction of the target analytes, a magnet was used to recover the CNT, which were subsequently washed with ultrapure water and dried in nitrogen. Next, the PAH were eluted from the CNT with a mixture of 150 μL of acetone and 50 μL of toluene under heating in an aluminum block at 55°C for 3 min. After cooling to room temperature 1 μL of the final extract is injected in the GC/MS system for analyte determination. All the experiments were conducted in triplicate.

PAH extraction was performed by SPME through the direct immersion (DI) mode. The SPME device with PDMS fibers were obtained from Supelco (Bellefonte, Pennsylvania, United States). The extraction was carried out with a 100 μm polydimethylsiloxane (PDMS) fiber exposed in aqueous solution containing 16 PAH to a final concentration of 10 μg L^{-1} for all analytes. Pyrex vial containing the PAH solution was sealed with silicone/PTFE septa and aluminum caps, and maintained at room temperature and constant stirring for 1 min. After extraction, PAH were desorbed thermally and analyzed by GC/MS. GC/MS analyses showed that the CNT method is more efficient than the use of polydimethylsiloxane (PDMS) with much lower solvent consumption, technical simplicity and time with good linearity (range from 0.18 to 80 μg L^{-1}) and determination coefficient (R^2 0.9810-0.9914). The LOD ranged from 0.05 to 0.42 μg L^{-1} with LOQ from 0.18 to 1.40 μg L^{-1}. Recovery (n = 9) ranged from 81 ± 10 to 105 ± 12 μg L^{-1}. Intraday precision (RSD, n = 9) ranged from 1.91 to 9.01 %, whereas inter day precision (RSD, n = 9) ranged from 7.02 to 17.9 %.

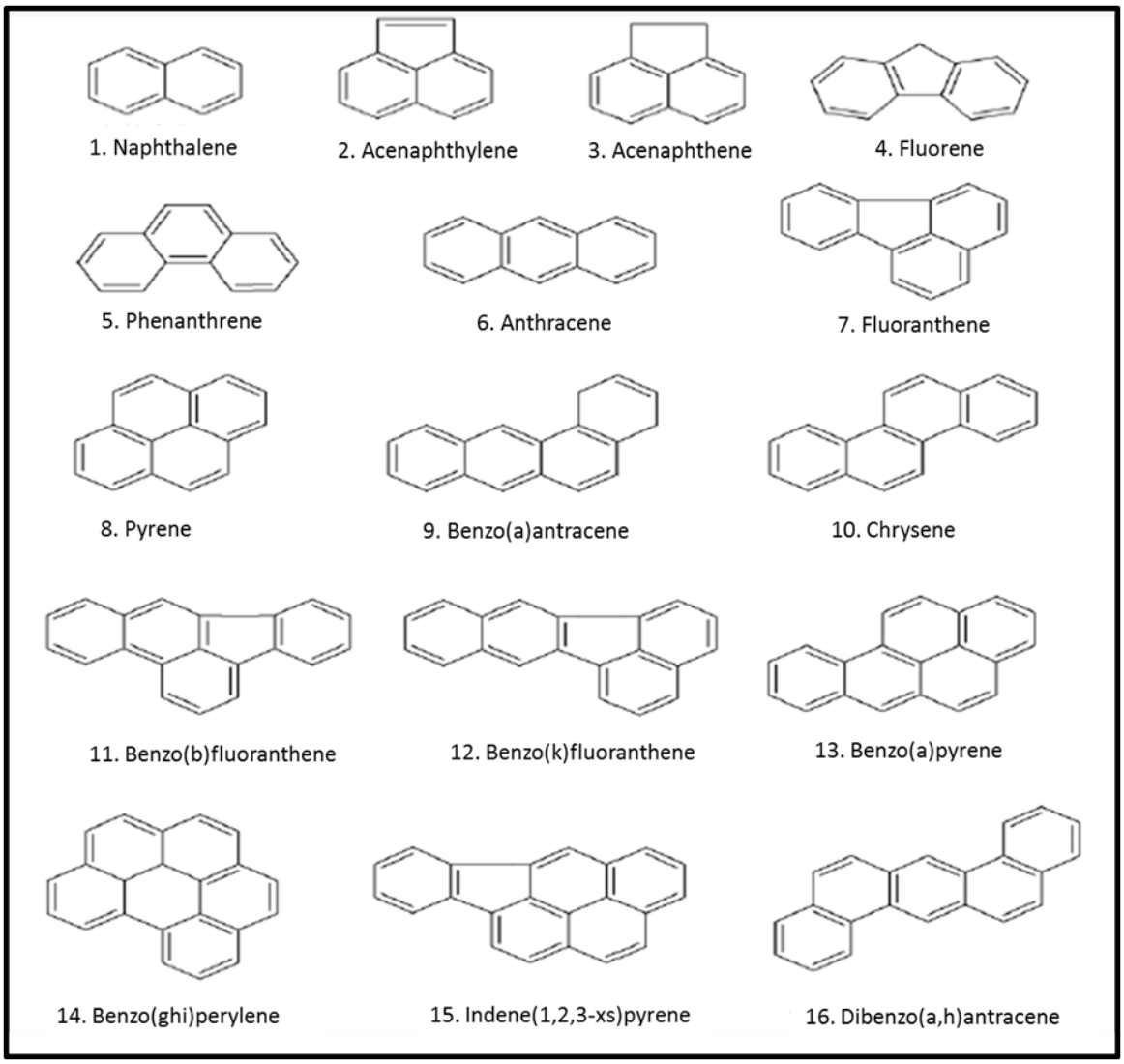


Figure S9. Chemical structures of 16 PAHs considered priority pollutants by the U.S. Environmental Protection Agency.

S10. Analytical Evaluation

After assessing the sorption capacity of PAH by CNT, and under the optimal extraction conditions, the factors that affect the analytical performance, such as linearity (R^2), linear range, limit of detection (LOD), limit of quantification (LOQ), recovery, and precision were carefully investigated. The experimental results are presented in Table S2. A linear range of 0.18 μg L^{-1} to 80 μg L^{-1} was used in the investigation. The linearity was assessed by determination coefficient (R^2) and was in the range 0.9810 to 0.9914. The LOD and LOQ were calculated from the mean and standard deviation of 10 blank measurements with 95% confidence, according to Eurachem guidelines. The LOD ranged from 0.05 μg L^{-1} to 0.42 μg L^{-1}, and LOQ ranged from 0.18 μg L^{-1} to 1.40 μg L^{-1}. The recovery study was performed in triplicate for each three concentrations 20 μg L^{-1}, 40 μg L^{-1} and 80 μg L^{-1}. Recovery (n = 9) ranged from 81 ± 10 μg L^{-1} to 105 ± 12 μg L^{-1}. Intraday and interday precision were performed in triplicate for each three concentrations 20 μg L^{-1}, 40 μg L^{-1} and 80 μg L^{-1}. Intraday precision (RSD, n = 9) ranged from 1.91 % to 9.01 %, whereas interday precision (RSD, n = 9) ranged from 7.02 % to 17.9 %. The merit parameters obtained in this study are similar to the results obtained in other studies assessing PAH in water.

Table S1. Analytical performance of method using CNTs for the extraction of PAH and analysis by GC/MS.

PAH [a]	Identification Ions (m/z)	Quantitation Ions (m/z)	Linearity (R^2)	Linear Range (μg L^{-1})	Recovery [b] (%)	LOD (μg L^{-1})	LOQ (μg L^{-1})	Precision (%RSD) [c]	
								Intra day	Inter day
Naphthalene	128, 129, 127	128	0.9904	1.40 – 80.00	104.5 ± 11	0.42	1.40	3.40	16.50
Acenaphthylene	151, 152, 153	152	0.9810	0.24 – 80.00	105.0 ± 14	0.07	0.24	3.60	17.65
Acenaphthene	152, 153, 154	153	0.9911	0.32 – 80.00	98.2 ± 13	0.10	0.32	7.12	11.40
Fluorene	165, 166, 167	166	0.9901	0.96 – 80.00	94.8 ± 15	0.29	0.96	9.01	17.91
Phenanthrene	176, 178, 179	178	0.9910	0.55 – 80.00	80.5 ± 10	0.17	0.55	4.70	13.20
Anthracene	176, 178, 179	179	0.9914	0.18 – 80.00	97.4 ± 5	0.05	0.18	1.91	7.02
Fluoranthene	200, 202, 203	202	0.9903	0.54 – 80.00	110.2 ± 9	0.16	0.54	7.95	12.31
Pyrene	200, 202, 203	203	0.9902	0.26 – 80.00	104.9 ± 14	0.08	0.26	6.75	15.12
Benzo[*a*]anthracene	226, 228, 229	228	0.9912	1.19 – 80.00	81.1 ± 11	0.36	1.19	4.93	17.94
Chrysene	203, 228, 226	228	0.9911	1.01 – 80.00	105.4 ± 12	0.30	1.01	11.4	13.4

[a] Compounds are listed in sequence of elution.

[b] Recoveries of PAH spiked into water samples at three different concentrations all analyzed in triplicate. Recoveries are given as average values ± standard deviations (n=9).

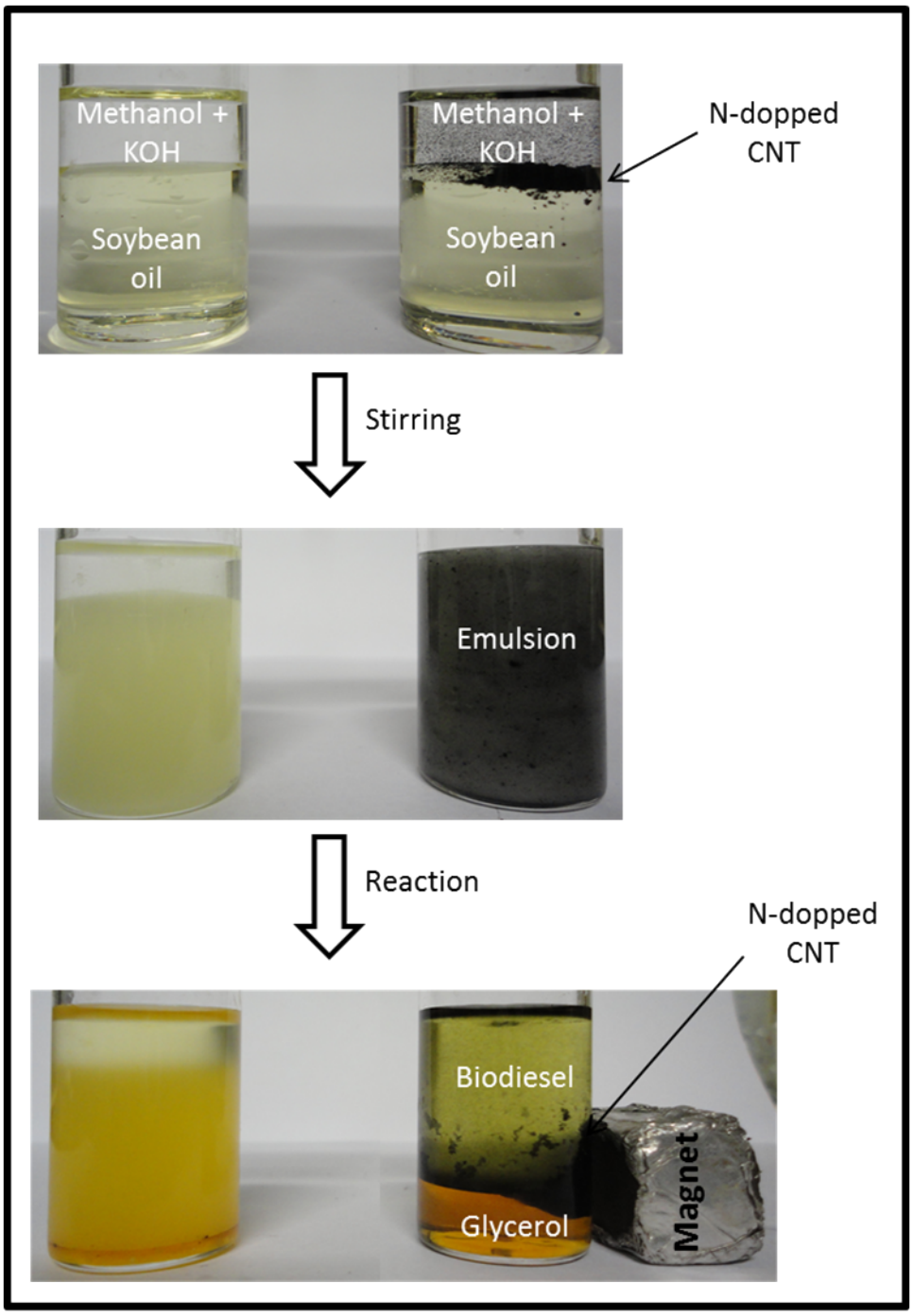


Figure S11. Photograph of biodiesel synthesis, in the absence and in the presence of the sample A10E20.

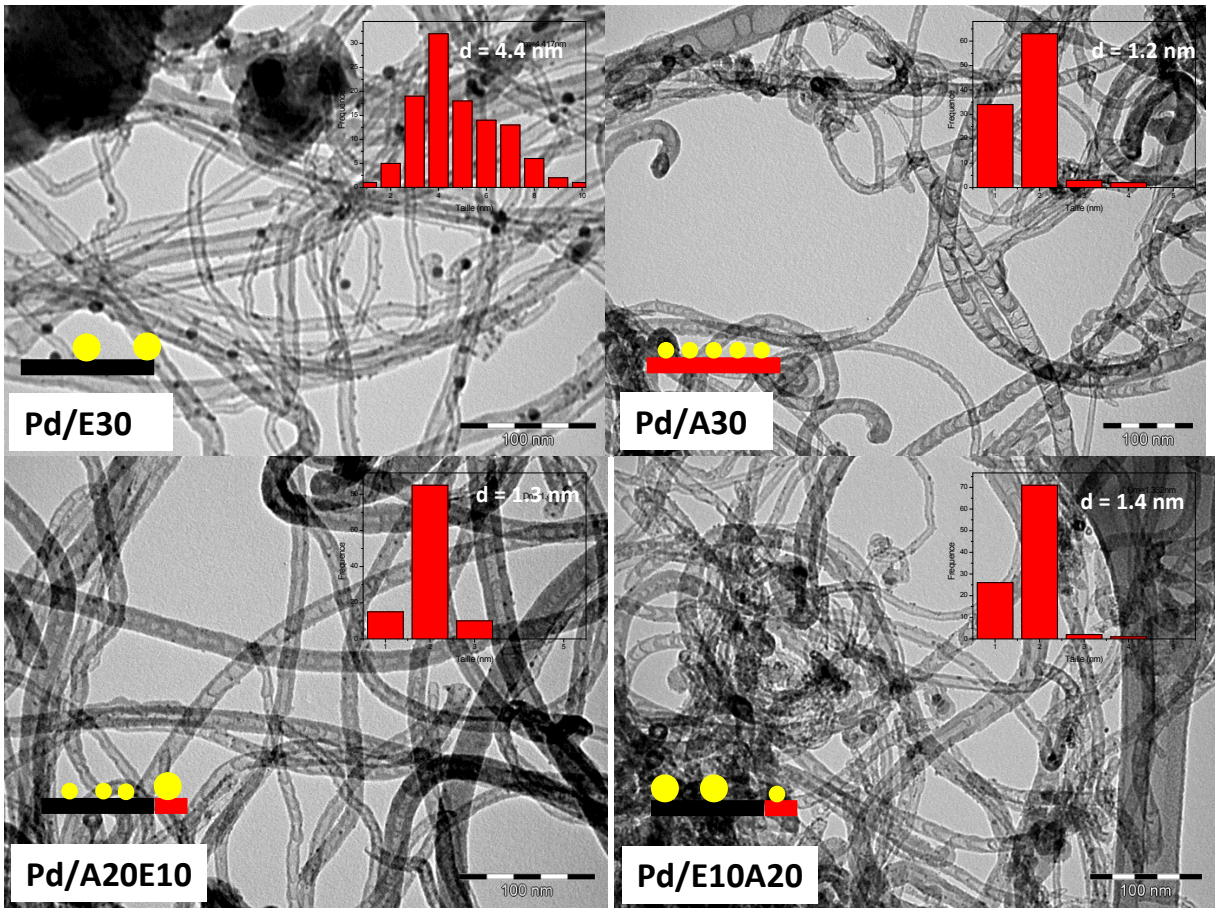


Figure S12. TEM micrographs and Ru particle size distribution of the 2 wt.% Pd catalysts.