Supplementary Data

Magnetic shepherding of nanocatalysts through hierarchically-assembled Fe-filled CNTs hybrids

Michele Melchionna,[a] Alessandro Beltram,[a] Antoine Stopin,[b] Tiziano Montini,[a,c] Rhys W. Lodge,[d] Andrei N. Khlobystov,[d] Davide Bonifazi,[*b] Maurizio Prato[*a,e,f] and Paolo Fornasiero[*a,c]

[a] Dr. M. Melchionna, Dr A. Beltram, Dr. T. Montini, Prof. Dr. P. Fornasiero, Prof. Dr. M. Prato
Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy. Emails: prato@units.it, pfornasiero@units.it
[b] Dr. A. Stopin, Prof. Dr. D. Bonifazi
School of Chemistry, Cardiff University, Park Place, Main Building, CF10 3AT, Cardiff, United Kingdom. Email: bonifazid@cardiff.ac.uk
[c] Prof. Dr. P. Fornasiero, Dr T. Montini
ICCOM-CNR, University of Trieste, Via L. Giorgieri 1, 34127 Trieste, Italy
[d] R.W. Lodge, Prof. Dr. A.N. Khlobystov, School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom.
[e] Prof. Dr. M. Prato
Carbon Nanobiotechnology Laboratory, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia-San Sebastian (Spain).
[f] Prof Dr. M. Prato
Ikerbasque, Basque Foundation for Science, 48013 Bilbao (Spain).

Figures and tables

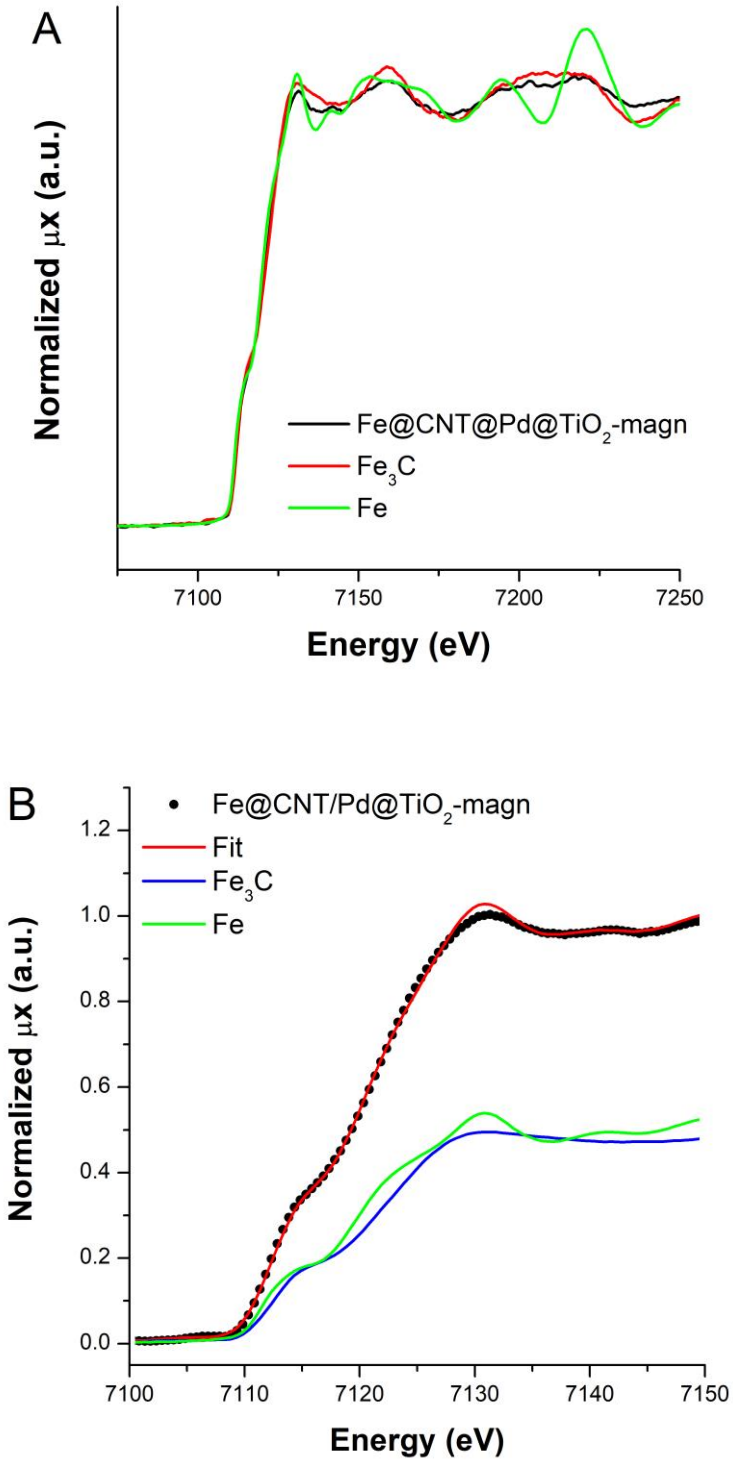


Figure S1: (A) Comparison of the XANES spectra of Fe@CNT@Pd@TiO_2-magn after treatment in H_2/Ar at 450 °C with those of the standard Fe_3C and metallic Fe; (B) Results from linear combination fitting of the XANES spectrum of Fe@CNT@Pd@TiO_2-magn after treatment in H_2/Ar at 450 °C.

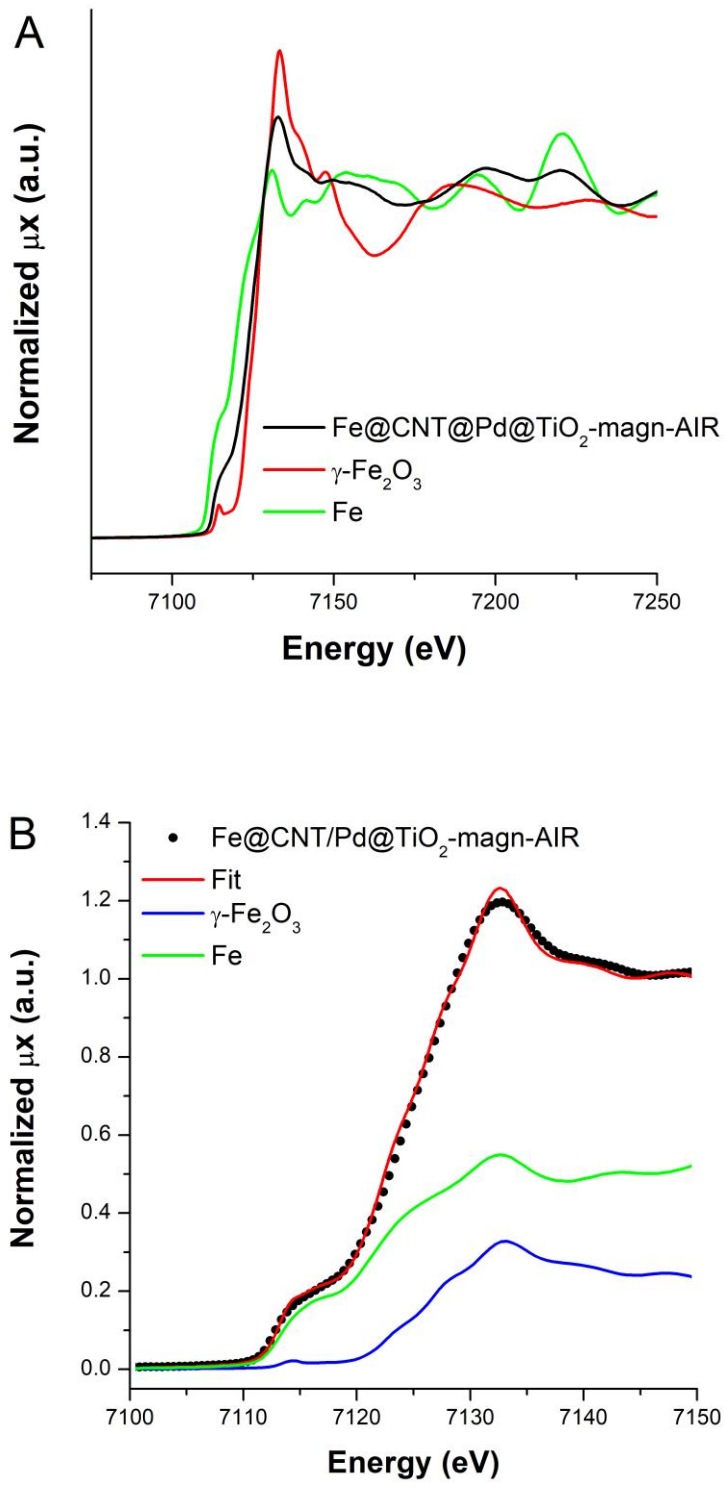


Figure S2: (A) Comparison of the XANES spectra of Fe@CNT@Pd@TiO_2-magn after treatment in air at 450 °C with those of the standard Fe_3C and metallic Fe; (B) Results from linear combination fitting of the XANES spectrum of Fe@CNT@Pd@TiO_2-magn after treatment in air at 450 °C.

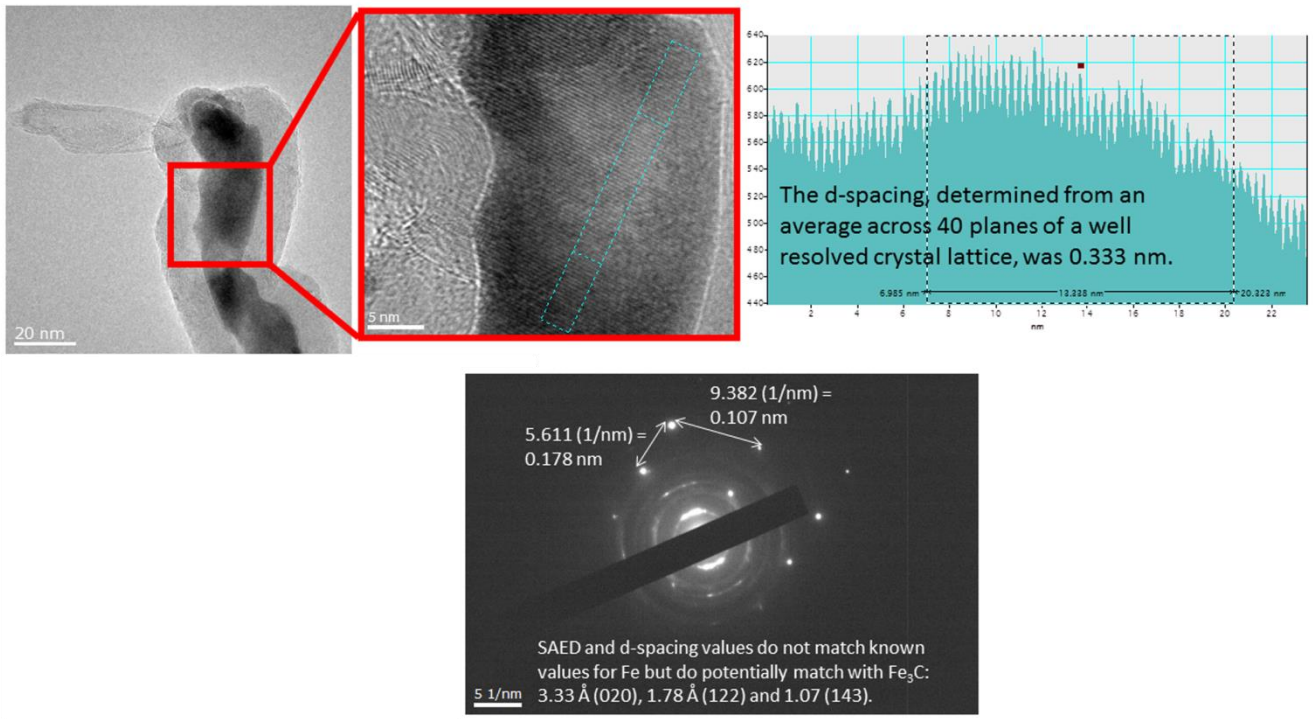


Figure S3: HR-TEM and SAED analysis of the Fe@CNTs precursor evidencing the presence of Fe_3C as main component.

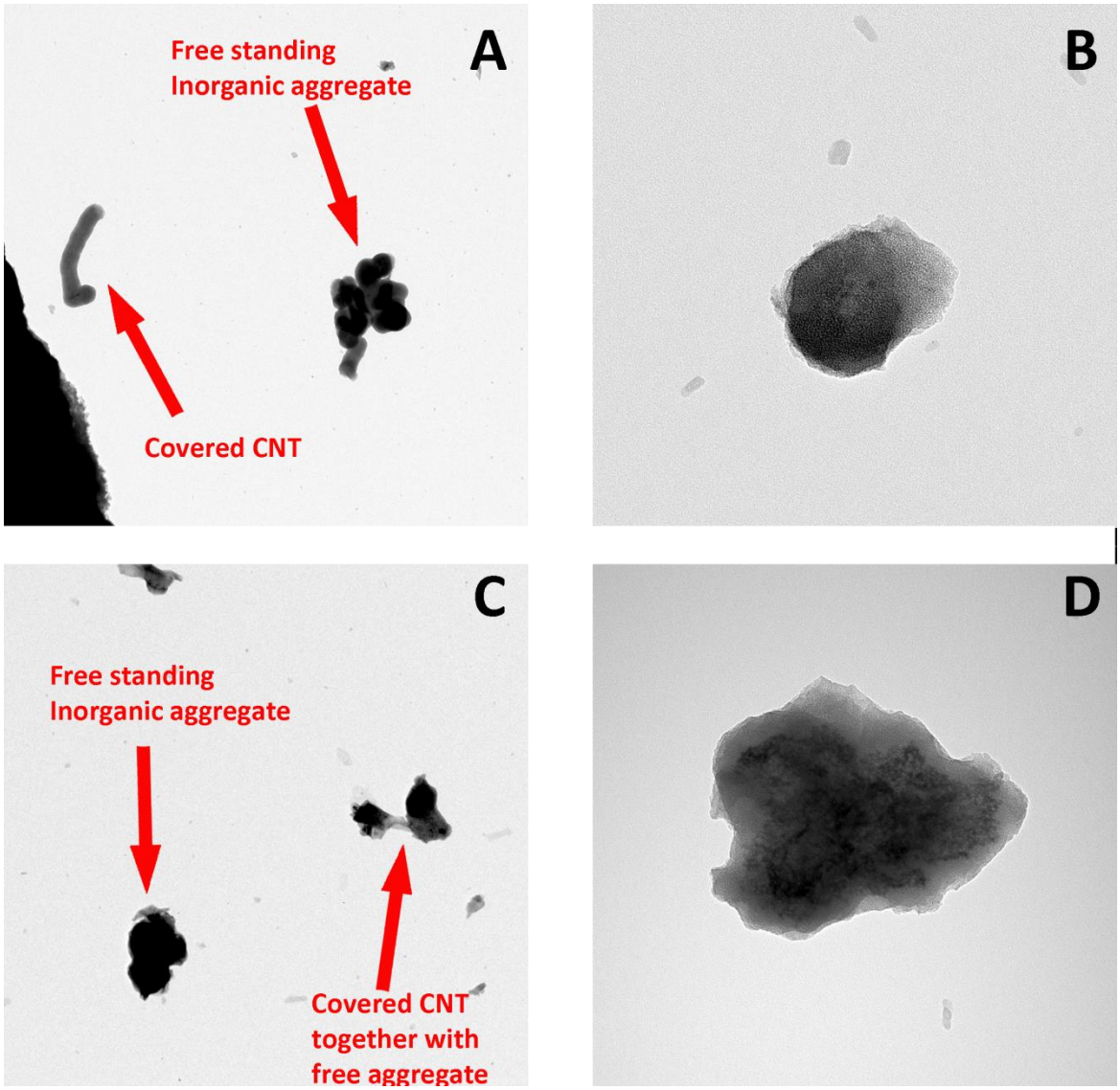


Figure S4: A) and C) Representative TEM images of Fe@CNTs/Pd@TiO_2-filtr as prepared showing both the covered CNTs and free standing aggregates made of Pd@TiO_2. B) and D) Typical higher magnification of free standing aggregates clearly indicating absence of the CNT core.

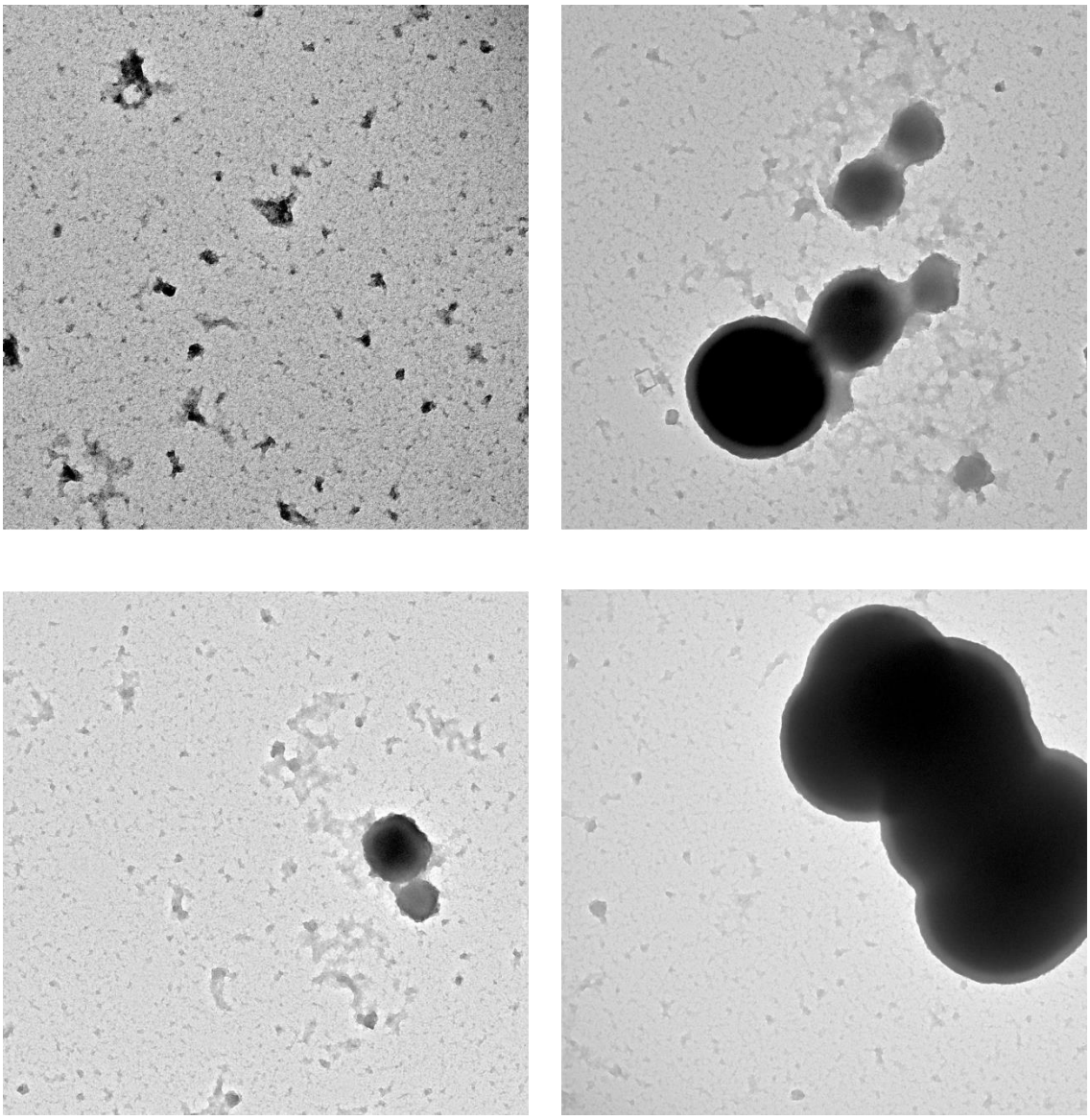


Figure S5: Representative TEM images of the magnetically separated liquid phase of Fe@CNTs/Pd@TiO_2-filt at different magnifications, showing a large population of free standing aggregates of titania.

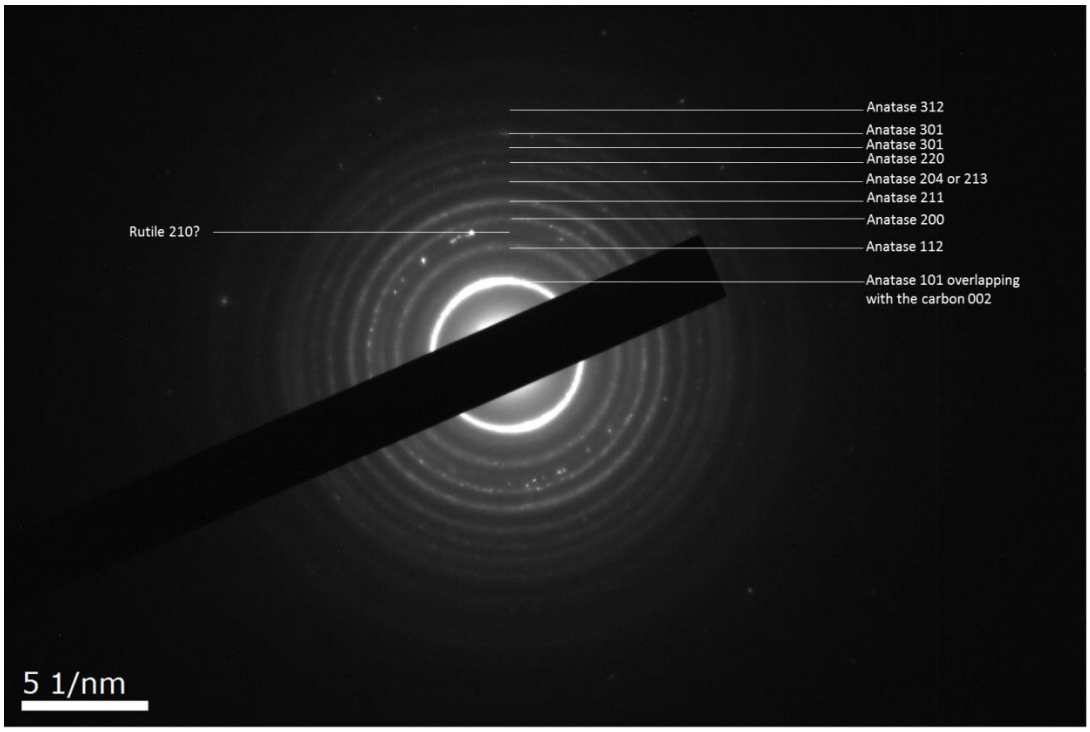
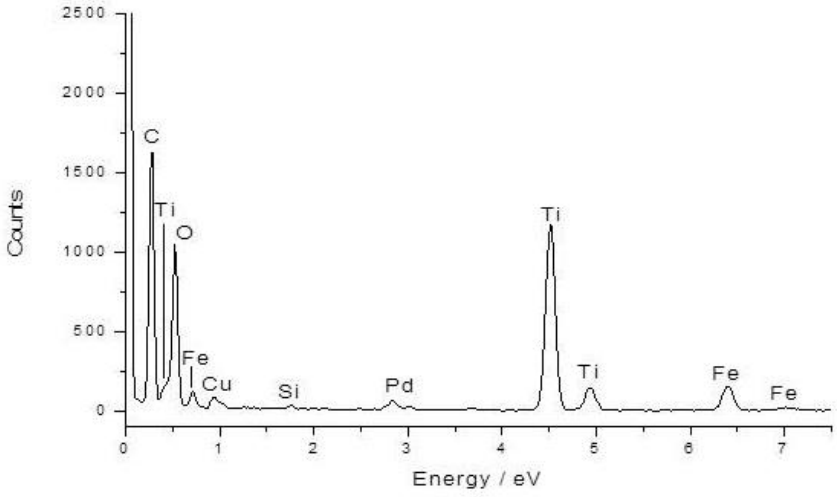


Figure S6: Fast Fourier Transform of Fe@CNTs/Pd/TiO_2-magn after thermal treatment indicating that the titania is mostly in the anatase phase.



Element	Atomic %
C	51.72
Ti	11.51
O	24.90
Pd	0.48
Fe	1.60
Cu	9.57
Si	0.22

Figure S7: EDX spectrum of Fe@CNTs/Pd/TiO_2-magn after thermal treatment and corresponding table with atomic %. The Cu and Si signals are contributions from the TEM grid.

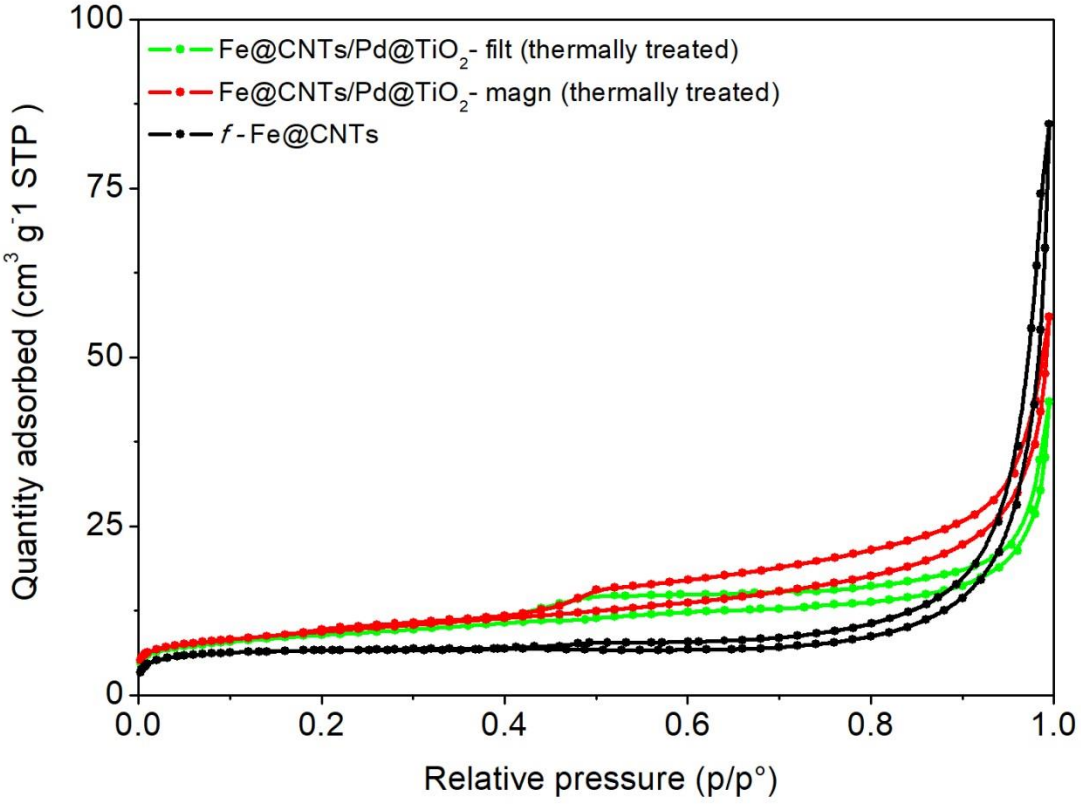


Figure S8: N_2 physisorption isotherms of Fe@CNTs/Pd@TiO_2-filt and Fe@CNTs/Pd@TiO_2-magn thermally treated and *f*-Fe@CNTs

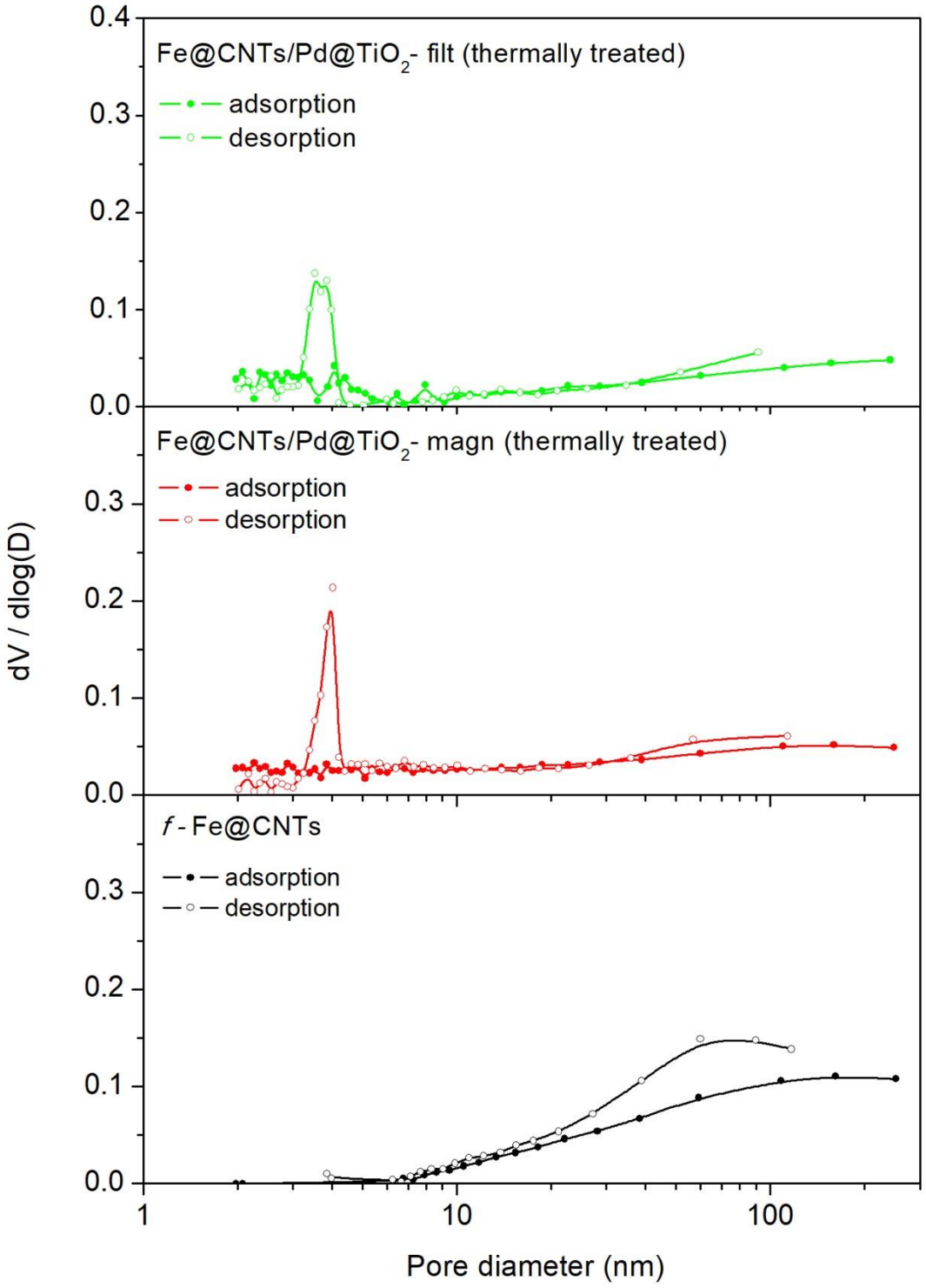


Figure S9: Pore size distribution of Fe@CNTs/Pd@TiO_2-filt and Fe@CNTs/Pd@TiO_2-magn thermally treated and *f*-Fe@CNTs.

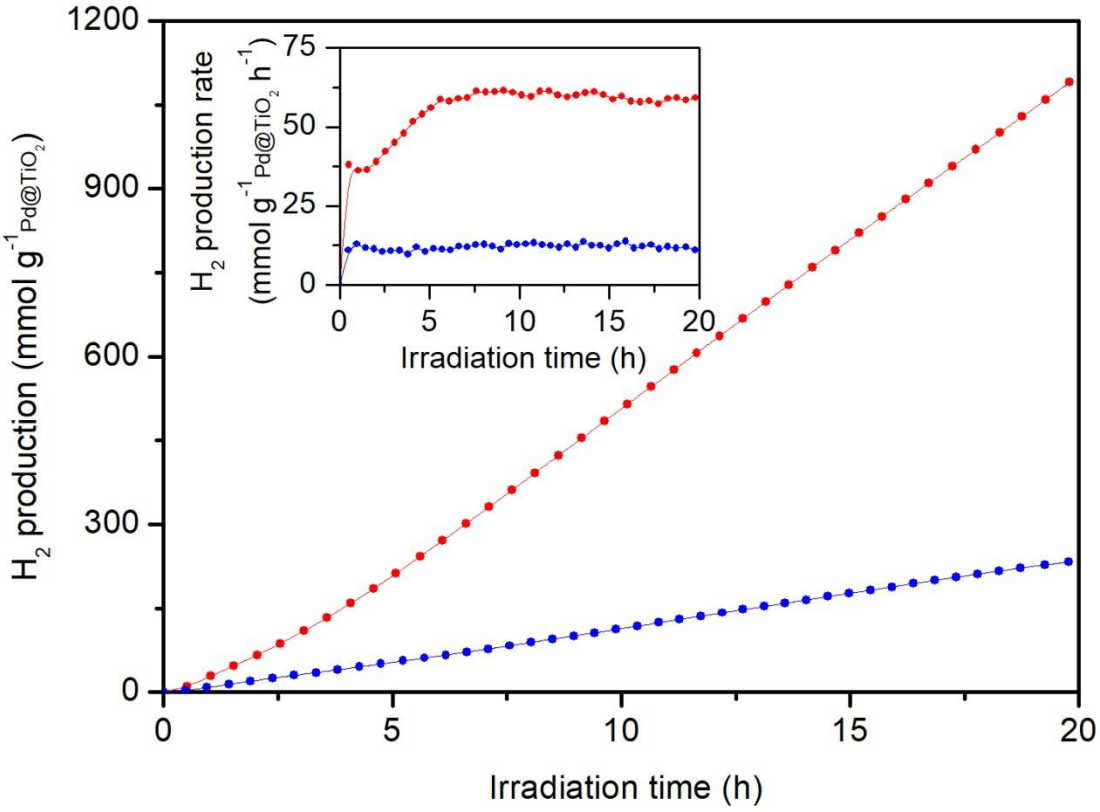


Figure S10: Fe@CNTs/Pd@TiO_2-magn as prepared (blue) and thermally treated (red) photocatalytic hydrogen production from ethanol/water solutions under UV irradiation. Activities are normalized by g of Pd@TiO_2. Inset: H_2 evolution rates.

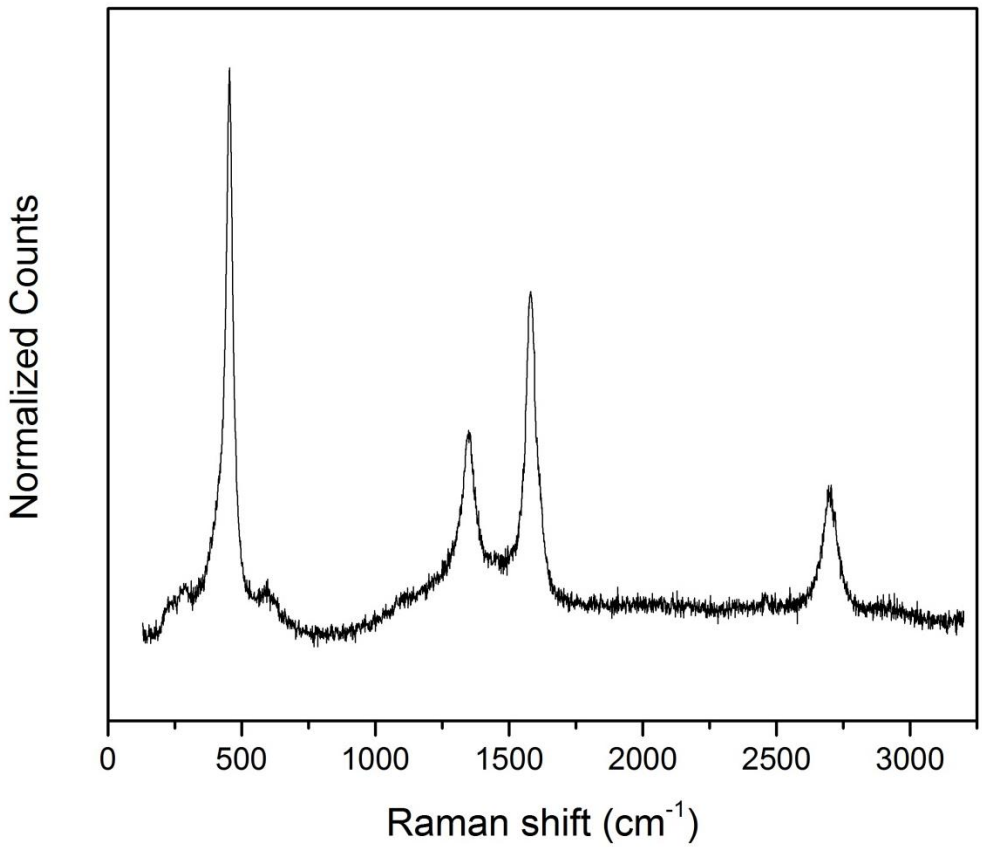


Figure S11: Raman spectrum of Fe@CNTs/Pd@CeO_2-magn after thermal treatment.