Journal Name

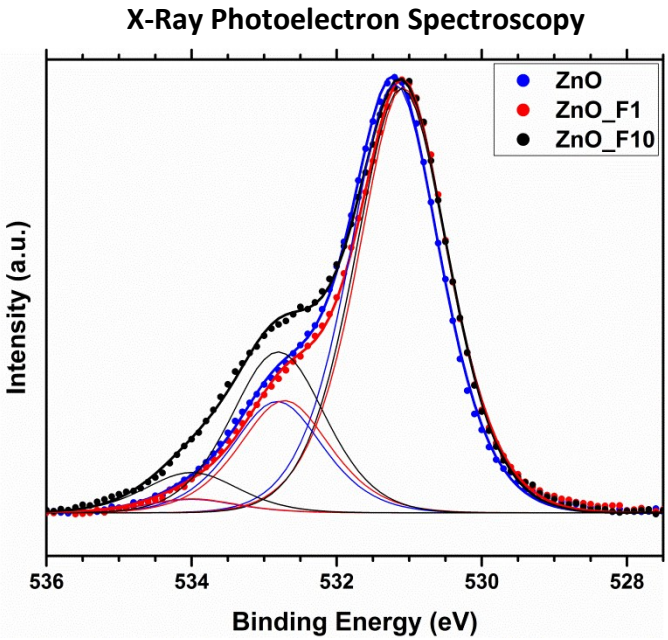
ARTICLE

F-doping of nanostructured ZnO: A way to modify structural, electronic, and surface properties

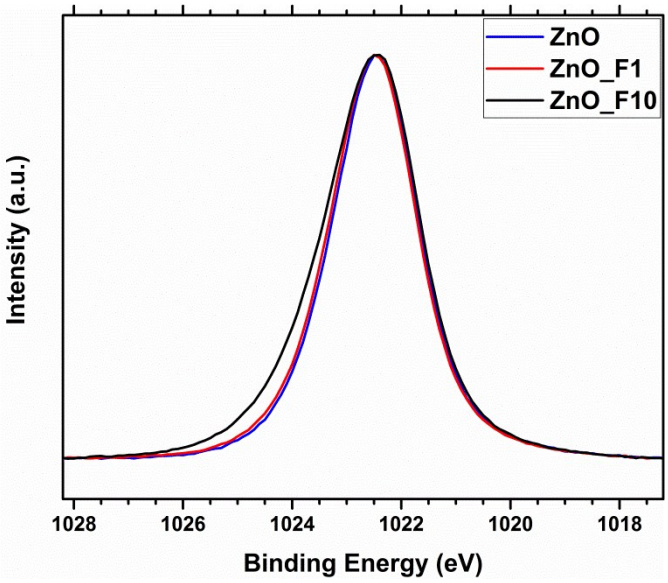
Elisabeth Hannah Wolf,[a] Marie-Mathilde Millet,[a] Friedrich Seitz,[a] Frenio A. Redeker,[b] Wiebke Riedel,[b] Gudrun Scholz,[c] Walid Hetaba,[a,d] Detre Teschner,[a,d] Sabine Wrabetz,[a] Frank Girgsdies,[a] Alexander Klyushin,[a] Thomas Risse,[b] Sebastian Riedel,[b] and Elias Frei*[a]

Supporting Information

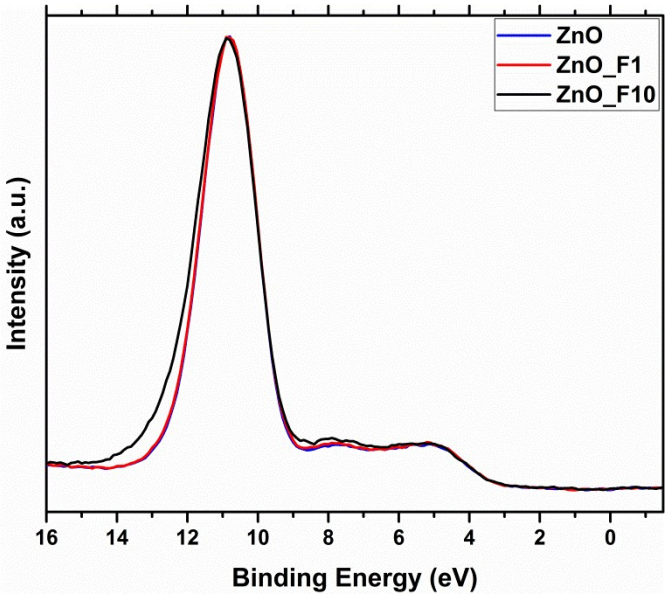
Table of content



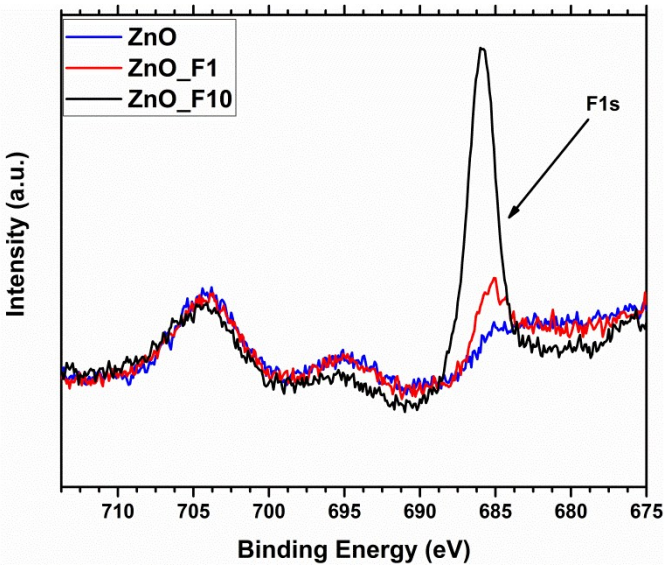
SI 1: XPS O1s spectra of ZnO, ZnO_F1 and ZnO_F10.



SI 2: XPS Zn2p(3/2) spectra of ZnO, ZnO_F1 and ZnO_F10.



SI 3: XPS Zn 3d and valence band spectra of ZnO, ZnO_F1 and ZnO_F10.



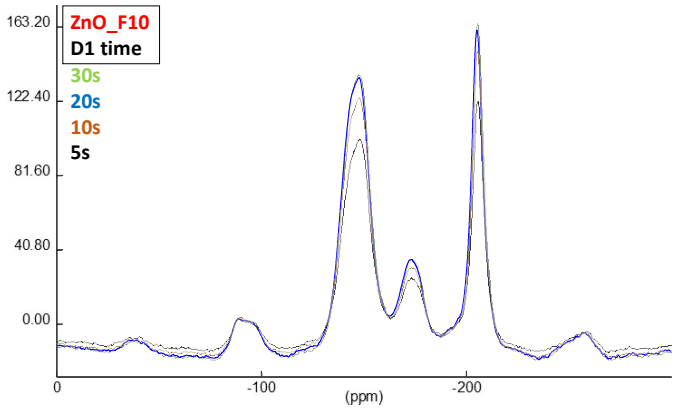
SI 4: XPS F1s spectra of ZnO, ZnO_F1 and ZnO_F10.

1. HRTEM

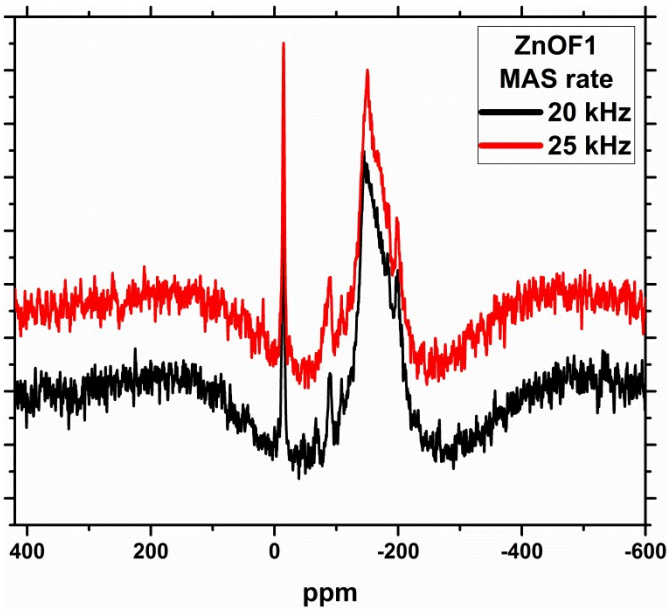
Phase	Reflection [hkl]	Distance [nm]
ZnO	2-1-1	0.137
ZnF_2	210	0.210
ZnF_2	200	0.235
ZnO	10-1/1-1-1	0.247
ZnO	002	0.259
ZnF_2	101	0.261
ZnO	010/100	0.281

SI 5: Table of selected distances of reflections associated with ZnO and ZnF_2.

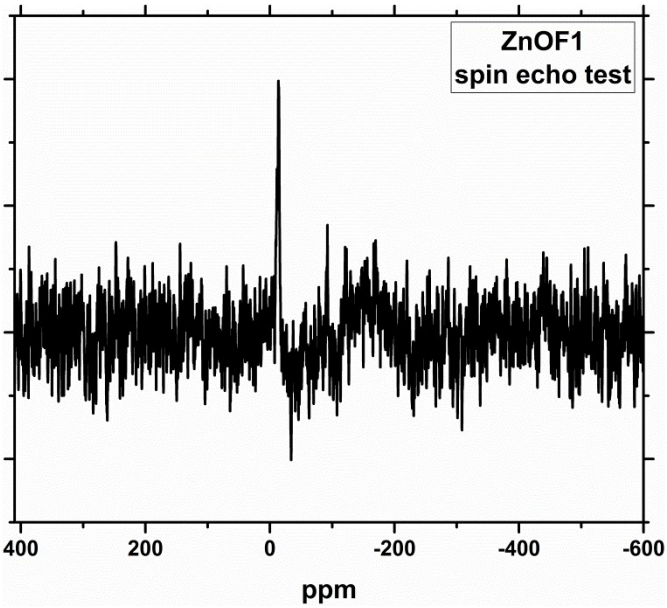
Nuclear Magnetic Resonance



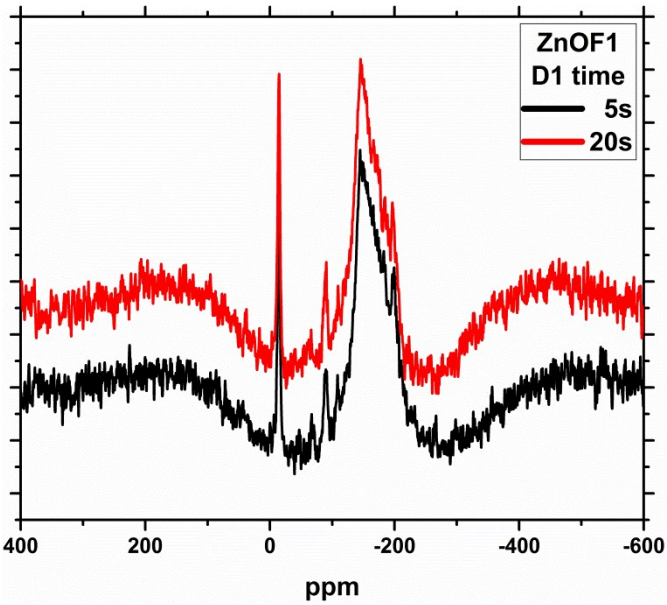
SI 6: D1 time variation for ZnO_F10



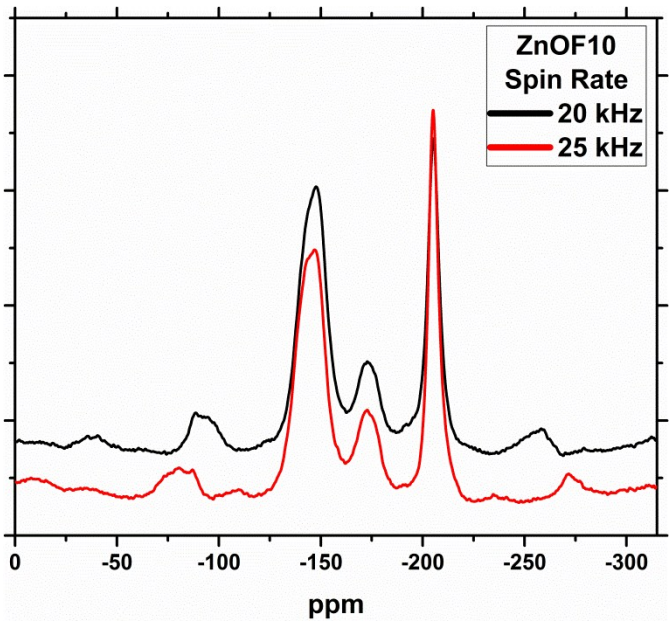
SI 7: MAS frequency variation for ZnO_F1



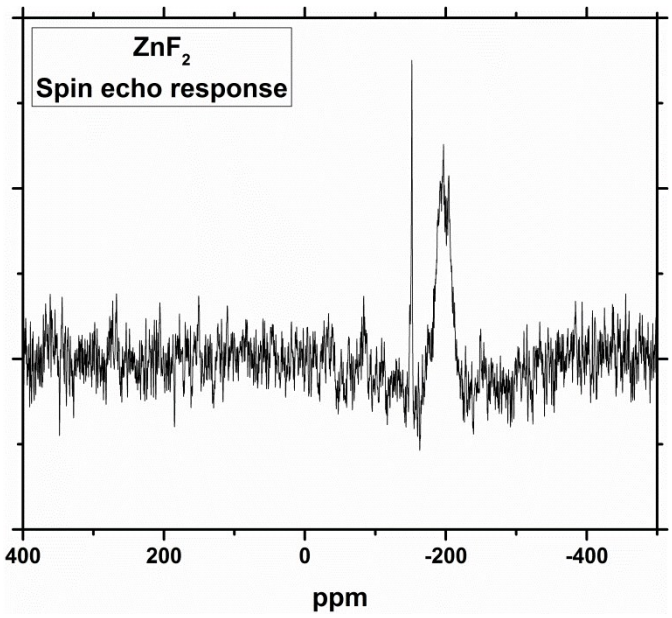
SI 8: Rotor-synchronised spin-echo MAS NMR spectrum of ZnO_F1, taken with a dipolar evolution time of 0.5 ms (ns = 256)



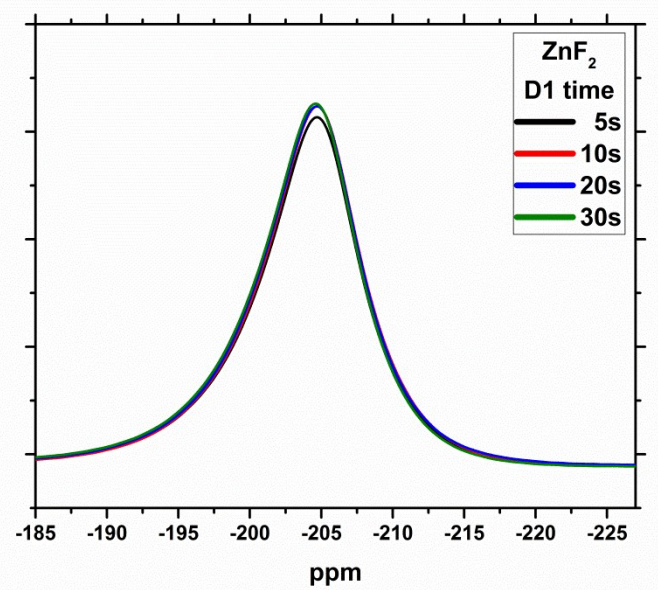
SI 9: D1 time variation ZnO_F1



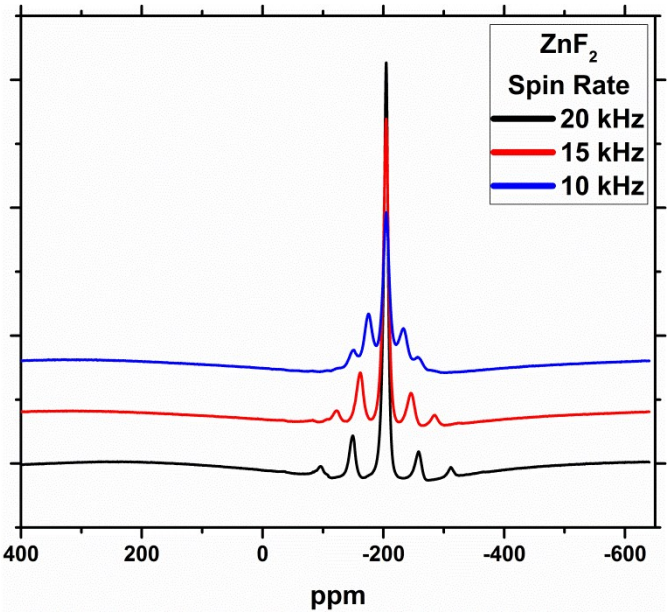
SI 10: MAS frequency variation for ZnO_F10.



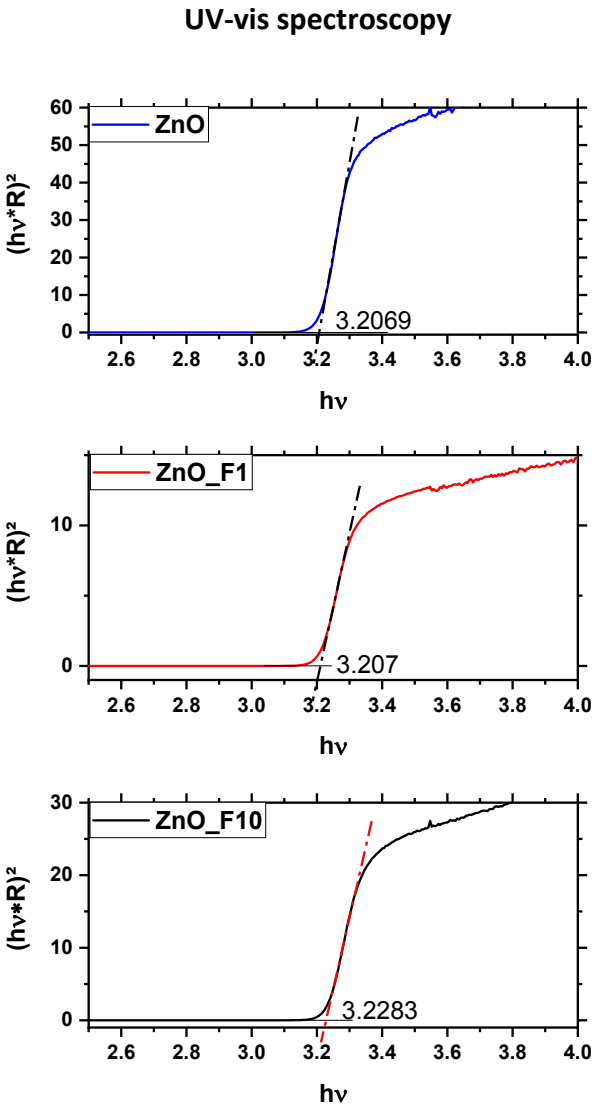
SI 11: Rotor-synchronised spin-echo MAS NMR spectrum of ZnF_2, taken with a dipolar evolution time of 0.5 ms (ns = 256).



SI 12: D1 time variation for ZnF_2

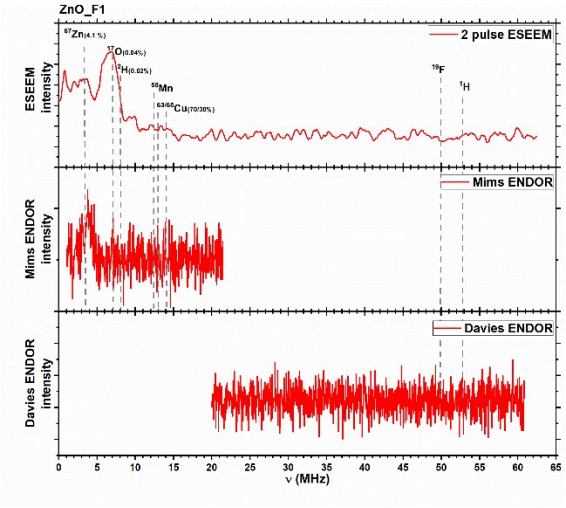


SI 13: MAS frequency variation of ZnF_2.



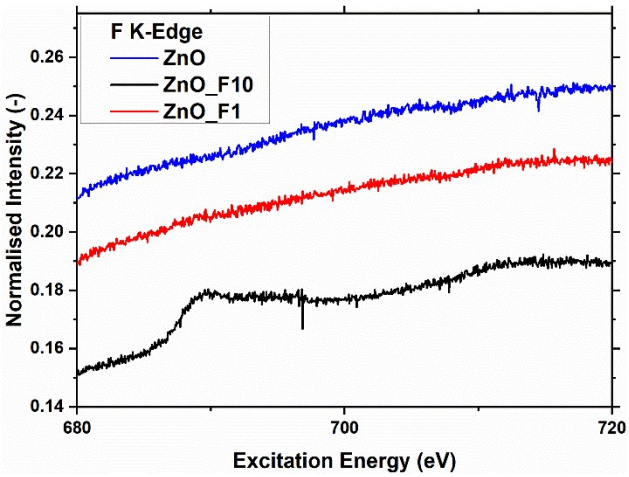
SI 14: Tauc plot of ZnO, ZnO_F1 and ZnO_F10

EPR



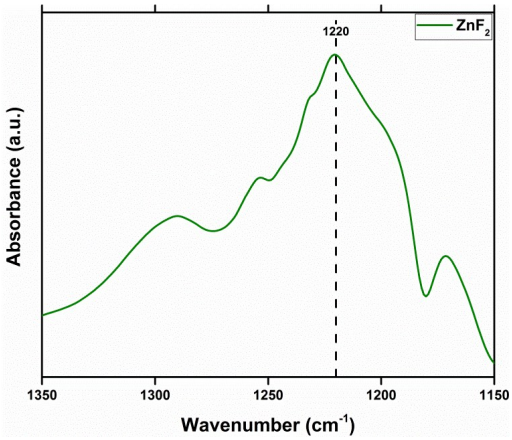
SI 15: ESEEM and ENDOR (Mims / Davies) EPR measurements of ZnO_F1. Pulsed EPR measurements at Q-band frequencies were conducted on a Bruker ElexSys 580 setup with a home-built cavity (F. Lendtzian, TU Berlin. ENDOR (Electron Nuclear Double Resonance) spectra were measured at 10 K applying both Mims and Davies sequences (π/2 pulse length of 20 ns, delay time τ of 300 ns and rf-pulse length of 40 µs) sequences as well as ESEEM (Electron Spin Echo Envelope Modulation) spectra were aquired using both 2-pulse and 3-pulse sequences (π/2 pulse length of 20 ns, delay time τ of 200 ns) to test for potential coupling of EPR active species to fluorine or other nuclei.

NEXAFS



SI 16: NEXAFS F K-Edge spectrum of fluorinated and untreated ZnO. The presence of ZnF_2 in ZnO_F10 is visible (reference: T. Yamamoto, T. Mizoguchi, K. Tatsumi, I. Tanaka, H. Adachi, Y. Muramatsu, E. M. Gullikson and R. C. C. Perera, *Mater. Trans.*, 2004, **45**, 1991–1993.)

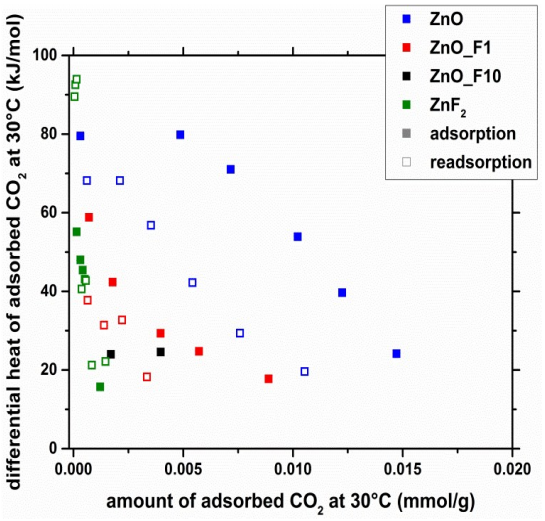
IR spectroscopy



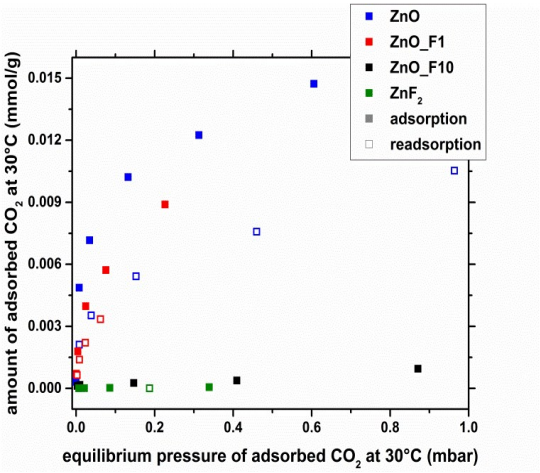
SI 17: IR spectrum of ZnF_2 after NH_3 adsorption.

Microcalorimetry

(a)

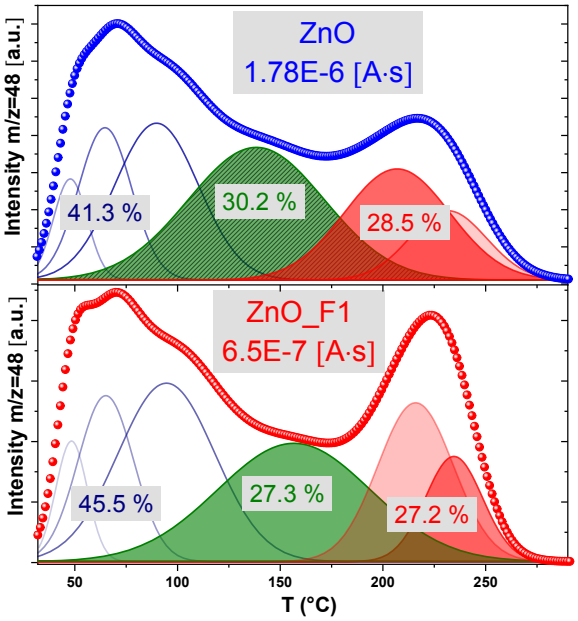


(b)



SI 18: Amount of CO2 adsorbed on the sample surfaces determined by microcalorimetry and the corresponding differential heats of adsorption

TDS



SI 19: TDS desorption signal m/z = 48.