



## Ultra-High Field NMR for Assessing the Stability of the Organic-Inorganic Interfaces of Metal Oxide Nanocrystals

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### Introduction

Nanoparticulate metal oxides are a major research area in materials chemistry. In particular, zinc oxide (ZnO) is of long-standing interest due to its versatility and unique catalytic and electro-optical characteristics. The nature of the nanoparticle-ligand interface plays a large role in determining the inherent physicochemical properties of ZnO nanoparticles (NPs), so an atomic-scale understanding of this interface is of large interest. In this work, we move past the ligand and study the environment of the surface atoms from the inorganic core with  $^{17}\text{O}$  and  $^{67}\text{Zn}$  NMR. The quadrupolar nature of these nuclei necessitates the use of the highest magnetic fields to discriminate similar environments.

### Experimental

$^{17}\text{O}$  and  $^{67}\text{Zn}$  NMR spectra were acquired at CEA Grenoble using a 9.4 T Bruker Avance III NMR spectrometer, equipped with a Bruker 3.2 mm low-temperature magic angle spinning (MAS) probe and at the NHMFL with the SCH, a 1.5 GHz Bruker Avance NEO NMR console and a 3.2 mm MAS probe developed at the NHMFL. The measurements were recorded with a MAS frequency of 11.111 kHz using a sample temperature of  $\sim 105$  K at 9.4 T and with a MAS frequency of 16 kHz using ambient sample temperature at 35 T.

### Results and Discussion

**Fig. 1** shows a comparison between two different types of  $^{17}\text{O}$ -enriched ZnO NPs, one capped with hexanamide and the other synthesized in the absence of capping ligand (i.e. "bare"). **Fig. 1** also shows a comparison between  $^{17}\text{O}$  and  $^{67}\text{Zn}$  NMR spectra recorded at 9.4 T and using the SCH at 35 T. It is clear that  $^{17}\text{O}$  NMR spectroscopy at much lower magnetic field is not able to resolve different surface oxygen sites (cf. **Fig. 1a** and **Fig. 1b** at  $\{^{17}\text{O}\} = -19$  and  $-26$  ppm for the bare ZnO NPs). Moreover, the ultra-high-field measurements have revealed differences between the surface oxygen environments of ligand-capped and bare ZnO NPs (cf. spectra in **Fig. 1b** in orange and blue).  $^{17}\text{O}$  2D triple-quantum MAS spectra (not shown) provide further resolution improvements and facilitate the extraction of exact quadrupolar parameters. This work gives insight into the structural changes occurring at O-rich surfaces as a result of ligand coordination.

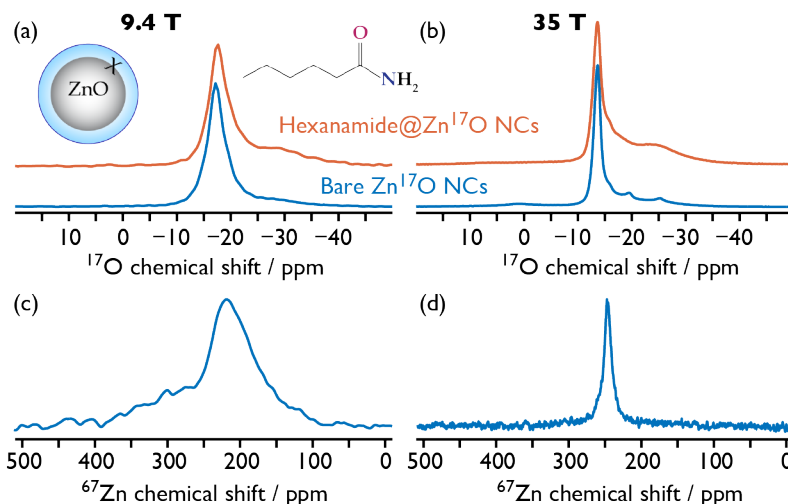
Complementary  $^{67}\text{Zn}$  NMR spectroscopy was performed to study Zn-rich surfaces of the ZnO NPs. Owing to the poorer sensitivity of natural isotopic abundance  $^{67}\text{Zn}$  NMR relative to  $^{17}\text{O}$  NMR of the  $^{17}\text{O}$ -enriched ZnO NPs,  $^{67}\text{Zn}$  2D TQMAS spectra were not able to be acquired in a reasonable experimental time. Nevertheless, 1D  $^{67}\text{Zn}$  NMR spectra show substantial line narrowing at 35 T compared to 9.4 T (cf. **Fig. 1c** and **Fig. 1d**) and analysis of these two spectra allows the extraction of quadrupolar parameters.

### Conclusions

Performing  $^{17}\text{O}$  and  $^{67}\text{Zn}$  NMR spectroscopy at the highest magnetic fields has allowed the inorganic interface to be resolved in ZnO NPs, opening the possibility of an in-depth study of this crucial zone at an atomic level.

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**Fig. 1** Direct excitation  $^{17}\text{O}$  (a) and (b) and  $^{67}\text{Zn}$  (c) and (d) MAS NMR of bare (blue) and ligand-capped (orange) zinc oxide nanoparticles, recorded at 9.4 T (a) and (c) and 35 T (b) and (d).