COMMENT

Reply to the 'Comment on "Crystal growth and aggregation in suspensions of δ-MnO₂ nanoparticles: implications for surface reactivity"' by A. Manceau, *Environ. Sci.: Nano*, 2018, 5, DOI: 10.1039/C8EN00126J

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In his comment on our initial article (Marafatto *et al.*, *Environ. Sci. Nano*, 2018, **5**, 497), Manceau challenges the approach used to model the X-ray diffraction (XRD) patterns and the actual coherent scattering domain size values derived using this approach (Manceau, *Environ. Sci.: Nano*, 2018, DOI: 10.1039/C8EN00126J). The present reply clarifies the conservative assumptions underlying the XRD modeling performed in the initial article. These assumptions aimed (i) at providing apparent particle sizes consistent with the objectives of the initial article and (ii) at not over-parameterizing the model in the absence of quantitative experimental constraints.

In Marafatto *et al.* (2018),[1] we investigated the synthesis, structure, and microstructure of nanocrystalline δ-MnO₂ and found significant variations in average particle size, as probed by X-ray diffraction (XRD), dynamic light scattering, and BET specific surface area (SSA) measurements. Both the coherent scattering domain (CSD) size in the *ab* (layer) plane and the wet-aggregate size of synthesized nanocrystalline δ-MnO₂ decreased with increasing suspension pH and Na content. However, these two estimates of average particle size showed non-linear scaling, which we interpreted in terms of aggregation/agglomeration. In addition, we found that SSA was inversely correlated with suspension pH and Na : Mn ratio. Furthermore, the SSA values could be reversed upon acidification or basification of the parent suspensions, whereas CSD size only increased upon acidification. These observations provide evidence for the highly dynamic nature of δ-MnO₂ nanoparticles.

In Marafatto *et al.* (2018),[1] the CSD size was assessed in two ways: (i) from the profile of the 20,11 band, which was fitted by refining structural and microstructural parameters including average CSD size, and (ii) indirectly from the full width at half maximum intensity (FWHM) of the 02,31 band, which has a profile that is weakly influenced by the layer structure. In his comment, Manceau challenges the approach used to model the XRD patterns and the actual CSD size values derived using this approach.[2] Specifically, two main is-

sues are raised in the comment: (i) CSD sizes obtained by modeling the 20,11 band are not fully consistent with the FWHM of the 02,31 band, (ii) the "Bragg-rod" modeling approach is unable to fit the entire XRD pattern under the assumption of a unique CSD size and size distribution for the different bands because additional broadening is expected from strain in the *ab* plane.[2]

The first issue raised by Manceau derives from his stated assumption that the hydrodynamic radius should scale in a similar manner (*i.e.* with the same power law) to the FWHM of the 02,31 band and to the CSD size derived from the modeling of the 20,11 band.[2] This assumption relies on two implicit hypotheses, however. The first one is that the FWHM of the 02,31 band is inversely proportional to the CSD size (as in the Scherrer equation),[3] with no other significant source of line broadening. This first hypothesis is challenged by Manceau in his own comment in which strain is proposed as a source of additional broadening of the 02,31 band.[2] If indeed strain contributes significantly to the broadening of the 02,31 band, there is no direct and easy relation between the breadth of this band and the actual size of CSDs. The known limitations of the Scherrer equation logically imply that there is no physical basis for which the hydrodynamic radius should scale identically to the FWHM of the 02,31 band and to the CSD size derived from the modeling of the 20,11 band. The second implicit hypothesis is the isotropy of δ-MnO₂ CSDs whereas anisotropic CSD shapes could contribute further to the discrepancy between CSD sizes obtained from the two bands, which have different *hk* indices. In the absence of direct experimental evidence in favor of or in contradiction to this

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Table 1 Microstructure parameters used to fit XRD patterns of synthesized δ-MnO₂ samples

Sample name	CSD[a] (ab plane) from 20,11 modeling [nm]	α and β² parameters[b] of the lognormal CSD size distribution (20,11 modeling)	CSD[a] (ab plane) from 02,31 modeling [nm]	α and β² parameters[b] of the lognormal CSD size distribution (02,31 modeling)
δ-MnO₂_A3	7.2 ± 0.5	4.0394/0.4745	3.0	3.2090/0.3843
δ-MnO₂_B2	3.8 ± 0.5	3.4333/0.4087	2.0	2.8245/0.3426
δ-MnO₂_C2	2.8 ± 0.5	3.1436/0.3772	1.5	2.5516/0.3129

[a] CSD sizes were determined as the radius of disks within the *ab* plane. [b] α and β^2 were calculated as: $\alpha = 0.9485\ln(<D>) - 0.017$ and $\beta^2 = 0.103\ln(<D>) + 0.034$.[4]

second hypothesis, our modeling of *hk* bands assumed disk-like shaped CSDs in the *ab* plane.

We agree with Manceau,[2] however, that the correlated influence of both the average CSD size ($<D>$) and the CSD size distribution on the 20,11 band profile may lead to a bias in the determination of the average CSD size. To minimize possible bias, all calculations of the *hk* bands reported in our initial article were performed using a constant reduced lognormal CSD size distribution, characterized by α and β^2 parameters which correspond to the mean value and variance of $\ln(D)$, as reported by Drits *et al.* for nanocrystalline phyllosilicates.[4] In the absence of supporting experimental data, the relations between α and β^2 parameters of these reduced distributions and $<\ln(D)>$ determined by these authors were used in the calculations reported in our initial article. The linear relationship between the variance of $\ln(D)$ (the β^2 parameter) and $<D>$ was supported by direct TEM observation of phyllosilicate crystal sizes,[4] in contradiction to Manceau's hypothesis of an increased variance with decreasing CSD size.[2] In the absence of experimental data supporting (i) the actual shape of CSDs, (ii) a specific CSD size distribution, and/or (iii) the presence, absence, density, extent, or anisotropy of strains related to layer bending or to other structure defects, the assumptions used for the XRD modeling reported in our initial article are thus conservative ones and serve to minimize the number of refined parameters that we could not constrain experimentally. Therefore, CSD sizes derived from XRD whole pattern modeling must be considered qualitatively as apparent sizes in the absence of further experimental constraints, as discussed by Scardi *et al.*[5] These authors made these recommendations based on diffraction patterns whose *hkl* reflections were resolved thus providing additional constraints to the refined parameters compared to current XRD patterns of δ-MnO₂ that exhibit only unresolved *hk* bands typical of turbostratic disorder.

The second issue raised by Manceau is the inability of the "Bragg-rod" approach to fit the angular range considered using a single set of structural and microstructural (including CSD size) parameters.[2] In our initial article, 20,11 and 02,31 bands were calculated indeed assuming different average size of CSDs (Table 1). The relative scaling of the two bands is not based on the band integral width as erroneously stated in Manceau's comment,[2] but rather on the band integrated intensity that is not affected by size broadening. A similar decrease of CSD size with increasing *hk* indices of the diffraction bands has been reported recently for halloysite, a

phyllosilicate tubular in shape.[6] From the diffraction point of view, our approach is equivalent to the introduction of strain proposed by Manceau in his comment, with the exception that in our modeling the two CSD sizes are not linked by an additional "dimensionless parameter (δ) describing strain". The addition of this strain parameter is hypothesized by Manceau from the bending of δ-MnO₂ nanoparticles observed with transmission electron microscopy.[2,7] In the absence of more comprehensive and quantitative experimental constraints, this strain parameter must be considered qualitatively as an apparent strain parameter.[5] Furthermore, when used to fit a larger angular range (Manceau *et al.* 2013 – Fig. 8),[7] this parameter induces an unrealistic broadening and dampening of the *hk* bands occurring at higher angles, whereas considering a broad angular range encompassing a large number of reflections is key to a reliable separation and quantification of size and strain broadening effects.[8] The intrinsic high background and low scattering power of highly defective materials, like δ-MnO₂, is expected to hamper further a reliable size-strain separation.[8]

Based on a number of independent data, our initial article showed how crystallite size and particle aggregation/agglomeration of δ-MnO₂ nanoparticles depend on solution chemistry and surface charge.[1] These processes have direct implications on the reactivity of the reaction products, as probed by measured SSA. The importance of aggregation/agglomeration raises important questions regarding particle size and the methods used to assess this quantity as quantitative estimates of the different size parameters are needed to unravel their mechanistic impact on reactivity. Direct statistical observations of nanocrystalline samples (particle size and shape, distribution of these parameters, density, extent, or anisotropy of strains) appear as the sole way to provide realistic constraints on the quantitative assessment of these parameters.

Conflicts of interest

There are no conflicts of interest to declare.

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