

A combination of EPR, microscopy,
electrophoresis and theory to elucidate the
chemistry of W and N doped TiO₂
nanoparticle/water interfaces
SUPPORTING INFORMATION

Sam Gorman^a, Kirstie Rickaby^a, Li Lu^b,
Christopher J. Kiely^b, Donald E. Macphee^a and Andrea Folli^{*c}

October 27, 2021

Contents

^{*} *Corresponding Author; Tel.: +44.(0)29208-74780; E-mail: folli@cardiff.ac.uk.*

^a Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, AB24 3UE, Aberdeen, UK.

^b Department of Materials Science and Engineering, Lehigh University, Whitaker Laboratory, 5 East Packer Ave, Bethlehem, Pennsylvania 18015, United States.

^c School of Chemistry, Cardiff University, Main Building, Park Place, CF10 3AT, Cardiff, UK.

1 Mass titrations

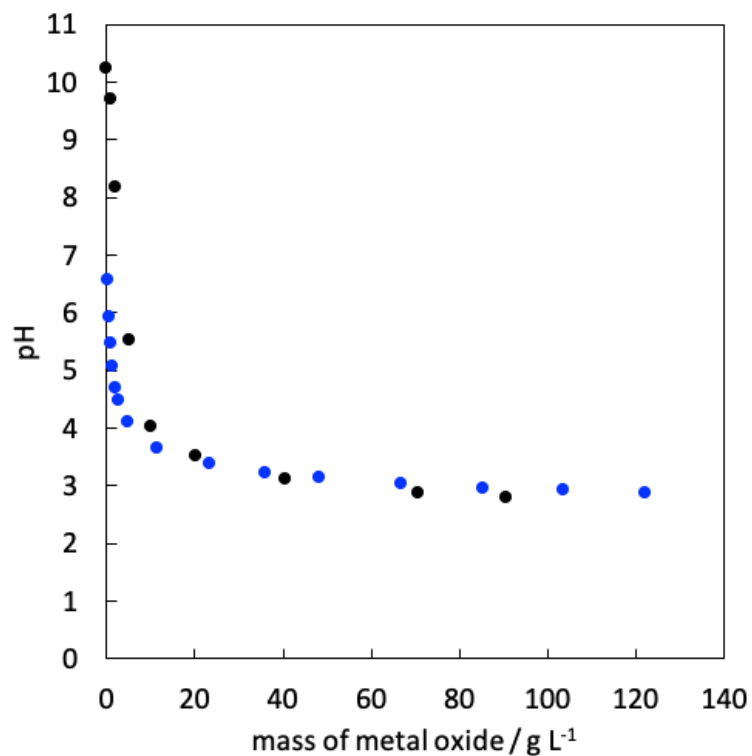


Figure S1: Mass titration of $\text{Ti}_{0.909}\text{W}_{0.091}\text{O}_2\text{N}_x$ in deionised water and NaNO_3 as a supporting electrolyte to adjust the ionic strength at the constant value of $I = 10^{-2} \text{ mol L}^{-1}$. Two titrations (alkaline runs) were performed starting at a pH farer (black markers) and closer (blue markers) to the expected pH of zero charge pH_{pzc} . The starting pH was obtained adding a 0.1 mol L^{-1} solution of NaOH.

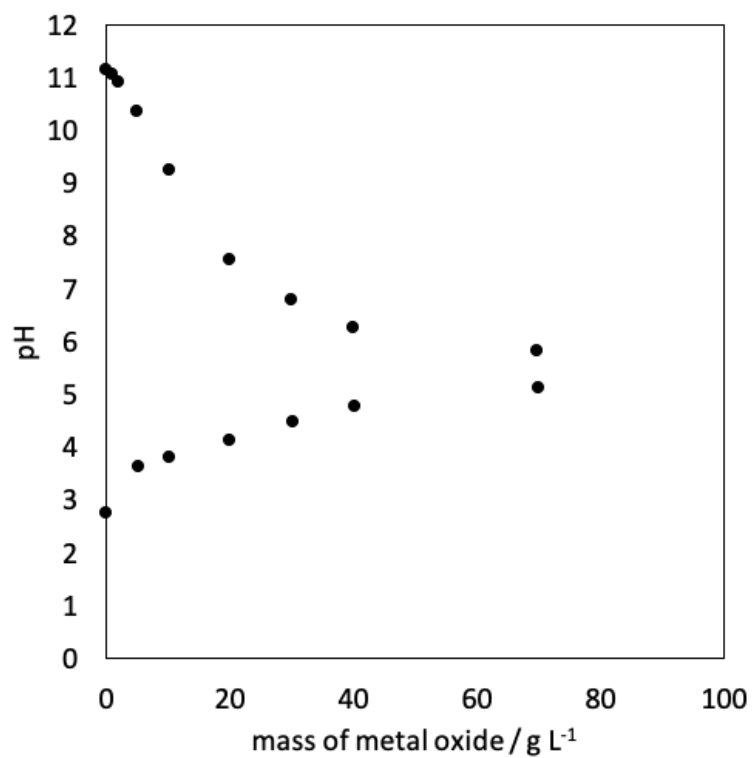


Figure S2: Mass titration of undoped anatase TiO_2 in deionised water and NaNO_3 as a supporting electrolyte to adjust the ionic strength at the constant value of $I = 10^{-2} \text{ mol L}^{-1}$. The decaying curve represents the alkaline run (starting pH obtained adding a 0.1 mol L^{-1} solution of NaOH) whilst the growing curve represents the acidic run (starting pH obtained adding a 0.1 mol L^{-1} solution of HNO_3).

2 Degree of contamination titration

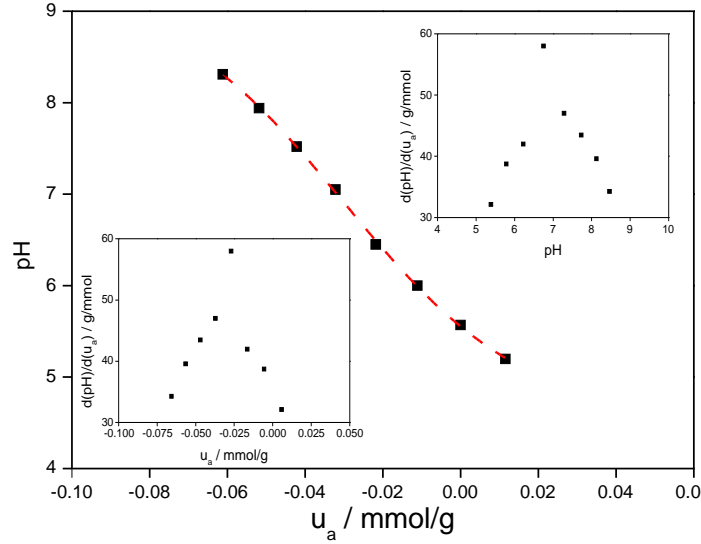


Figure S3: Titration for the determination of the degree of contamination u for the undoped anatase TiO_2 used in this work.

3 Notes on symmetric/asymmetric association of counterions for undoped anatase TiO_2

It is worth noting though that whilst Piasecki et al.[?] reported a symmetric association of counterions for undoped TiO_2 water suspensions in the presence of the indifferent electrolyte NaCl, very similar to what we are proposing here, Preočanin and Kallay[?] proposed a preferential association of anions. Experimentally, the electroneutrality condition can only be achieved in the presence of solely indifferent electrolytes (i.e. no specific adsorption of ions, hence the use of NaNO_3 or NaCl as supporting electrolytes) and at low concentrations to guarantee either symmetrical or absence of association. In fact, the affinities of binding cations and anions are not necessarily the same and the shift of pH_{pzc} , pH_{pzp} , pH_{iep} with respect to pH_{eln} are usually expected at higher electrolyte concentrations.[?] In this context, it is worth noting that the Preočanin and Kallay's investigation involved different (and also higher than $10^{-2} \text{ mol l}^{-1}$) ionic strengths, which allowed them to rule in favour of a asymmetric association. It is possible that if we were to investigate the effect of different ionic strengths, we might come to the same conclusion. However, this would go be-

yond the scope of the present work, which is to compare undoped and doped TiO_2 , in the same electrolyte and ionic strength conditions.

References

Piasecki, W.; Rudzinski, W.; Charmas, R. 1-p K and 2-p K Protonation Models in the Theoretical Description of Simple Ion Adsorption at the Oxide/Electrolyte Interface: A Comparative Study of the Behavior of the Surface Charge, the Individual Isotherms of Ions, and the Accompanying Electrokinetic. *J. Phys. Chem. B* **2001**, *105*, 9755–9771.

Preocanin, T.; Kallay, N. Point of zero charge and surface charge density of TiO₂ in aqueous electrolyte solution as obtained by potentiometric mass titration. *Croat. Chem. Acta* **2006**, *79*, 95–106.

Sonnefeld, J. On the influence of background electrolyte concentration on the position of the isoelectric point and the point of zero charge. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2001**, *190*, 179–183.