Supplementary Information for

Evidence for Covalent Bonding of Aryl Groups to MnO$_2$ Nanorods from Diazonium-Based Grafting

K. J. Bell, P. A. Brooksby, M. I. J. Polson and A. J. Downard[a]

Experimental

Materials and Reagents

Millipore Milli-Q water (resistivity > 18 MΩ cm) was used in all aqueous solutions and cleaning steps. Fluoroboric acid (50% in water, Sigma Aldrich), 4-nitroaniline (Sigma-Aldrich), NaNO$_2$ (Sharlau Chemie, Spain), acetonitrile (reagent grade), diethyl ether (reagent grade),KMnO$_4$ (reagent grade), MnSO$_4$ (Sigma-Aldrich), H$_2$SO$_4$ (99%), (NH$_4$)$_2$Fe(SO$_4$)$_2$ (Sharlau Chemie, Spain) and Na$_4$P$_2$O$_7$ (BDH Chemicals) were used as received.

Synthesis

Synthesis of 4-nitrobenzenediazonium tetrafluoroborate was based on a standard procedure: [1] 4 mL of (25%) fluoroboric acid was added slowly with stirring to 5 mmol of 4-nitroaniline in an ice bath. A cold solution of 5 mmol of NaNO$_2$ dissolved in water was then added dropwise with stirring to the amine solution in the ice bath. The collected product was then recrystallised from acetonitrile and diethyl ether, dried and stored in a desiccator.

Synthesis of manganese dioxide nanorods: 20 mmol of KMnO$_4$ and 30 mmol of MnSO$_4$ were separately dissolved in 1 M H$_2$SO$_4$ (75 mL and 150 mL respectively) and purged with nitrogen. The KMnO$_4$ solution was then added to the MnSO$_4$ solution with vigorous stirring under nitrogen. The volume of the resulting solution was adjusted to 250 mL and aged in a 60°C oven for a week. The nanorods were then washed by repeated cycles (minimum of 5) of sonication and centrifugation in ultrapure water.

Modification of MnO$_2$ nanorods with nitrophenyl and aminophenyl groups to give NP- MnO$_2$ and AP-MnO$_2$, respectively, is described in the accompanying communication.

Characterisation

Electrochemistry:

All electrochemical measurements were performed using an Eco Chemie Autolab PGSTAT302 potentiostat/galvanostat. Glassy carbon (GC) disk working electrodes (3 mm diameter) were

polished with 1 μm alumina powder. The auxiliary electrode was platinum mesh and the reference electrode was KCl-saturated calomel (SCE). Unless stated otherwise, all cyclic voltammograms were obtained in deoxygenated solutions with scan rate = 50 mV s^{-1}.

X-ray Photoelectron Spectroscopy (XPS):

XPS data were obtained using a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Kα source operating at 100-150 W. Wide scans were recorded with a step size of 1 eV and pass energy of 160 eV; for narrow scans the corresponding parameters were 0.1 and 20 eV, respectively. Samples were mounted by pressing the MnO_2 powder into indium.

Scanning Electron Microscopy (SEM):

SEM images were obtained using a Raith 150 e-beam lithography system operating with a 10 keV acceleration voltage. MnO_2 nanorods were prepared for imaging by drop-casting onto planar conducting carbon substrates.

X-ray Powder Diffraction (XRD):

Samples were ground in a small amount of perfluoronated oil to make a paste and mounted on a glass fibre. Data were collected on a SuperNova, Dual, Cu at zero, Atlas single crystal diffractometer. The samples were kept at 298.0 K during data collection. Data were integrated at 2θ = 0.05° intervals, and corrected for scan speed and baseline corrected.

Average Oxidation State (AOS):

The AOS of MnO_2 samples was measured either directly by potentiometric titration, or, for NP-MnO2 and AP-MnO_2 that were poorly soluble in the titration conditions, by using a correlation between the AOS and the multiplet splitting of the Mn 3s core level XPS spectra.[2]

Potentiometric Titration: Average oxidation state was determined by potentiometric titration using the method described in Dose and Donne:[3] 0.1 g of MnO_2 sample was dissolved in 25 mL of 0.25 M acidifed $(NH_4)_2Fe(SO_4)_2$ solution. This was then titrated against standardised 0.2 M $KMnO_4$ solution (oxalate method[4]) with the volume of $KMnO_4$ for this titration denoted V_1. The volume for this titration without any sample, V_0, was also determined. An excess (approximately 15 g) of $Na_4P_2O_7$ was added to the solution from the first titration to stabilise the Mn (III) complex formed in the subsequent titration. The pH of this solution was then adjusted to 6-7 by addition of H_2SO_4. A second titration was then performed using the same $KMnO_4$ solution as previous, giving the volume V_2. The value of x in MnO_x was then calculated by:

$$x = 1 + \frac{5(V_0 - V_1)}{2(V_2 - V_1)}$$

Correlation with XPS Data: A correlation curve (Figure S4) was derived using AOS values obtained from potentiometric titrations of as-prepared and blank MnO_2 samples, and the Mn 3s multiplet splitting values for the same samples from XPS measurements, and literature values for other MnO_2 compounds.[5] From this plot and the Mn 3s multiplet splitting values for NP-MnO_2 and AP-MnO_2, the corresponding AOS values were determined.
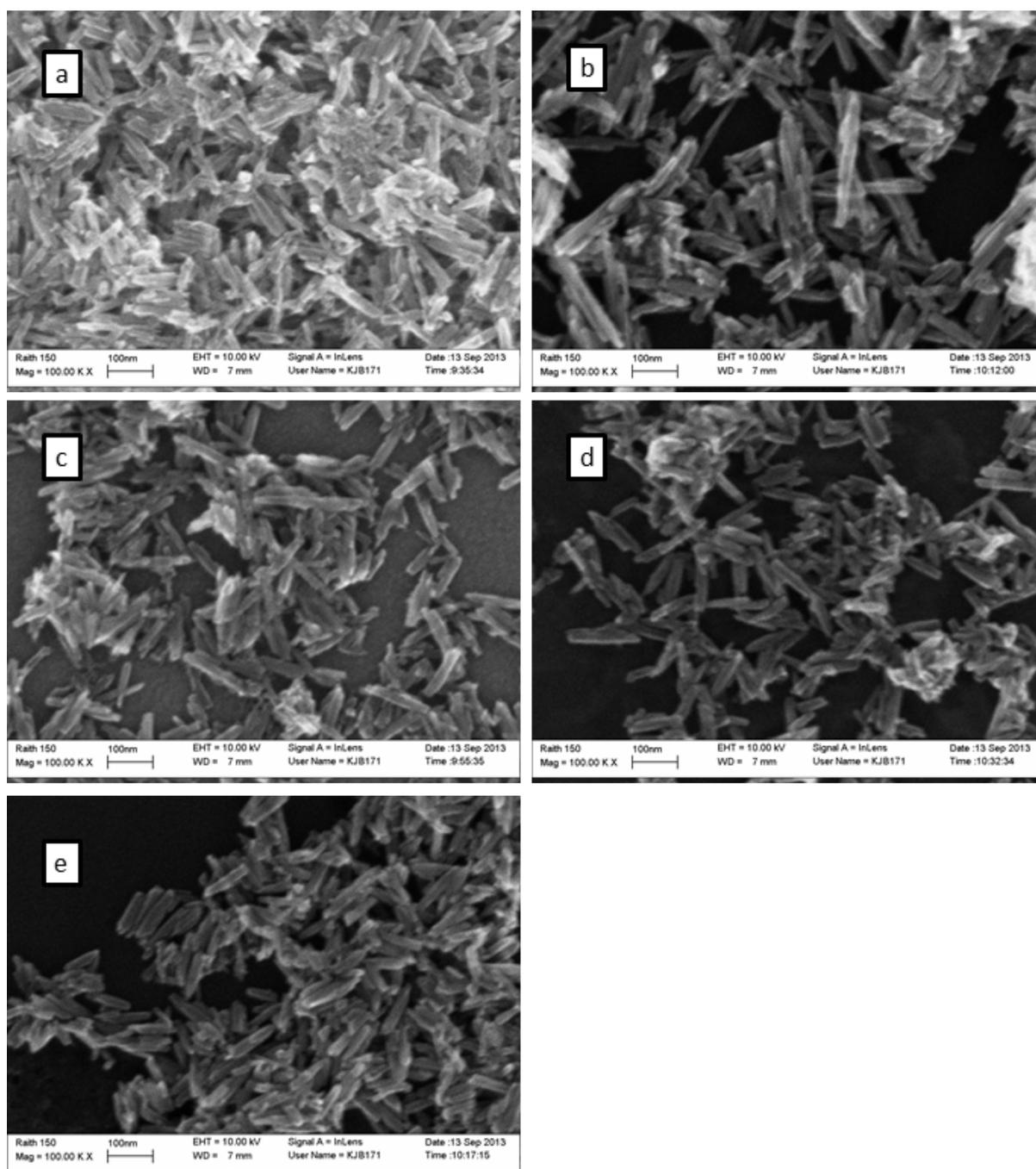
Figures

Figure S1: SEM images of MnO_2 a) unmodified, b) NP- MnO_2, c) after treatment in NaOH (NaOH blank), d) AP- MnO_2 and (e) after treatment in acetonitrile (ACN blank).
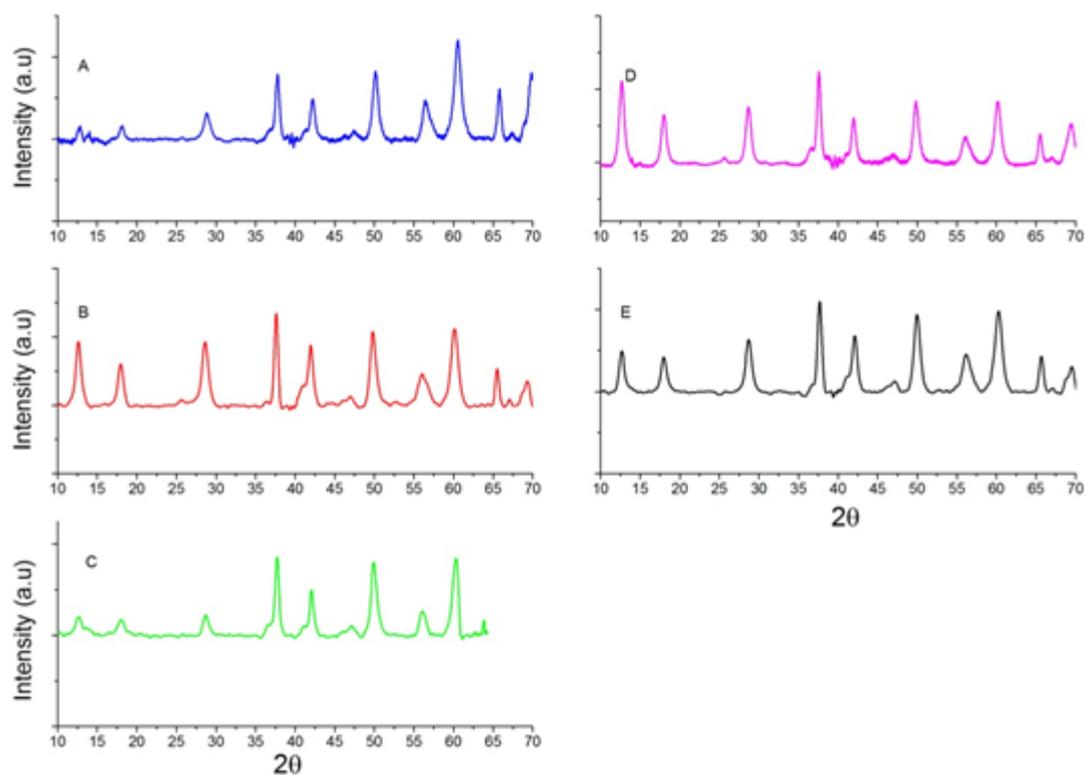
Figure S2: XRD of MnO$_2$ nanorods A) unmodified, B) NP- MnO$_2$, C) NaOH blank, D) AP- MnO$_2$ and E) ACN blank
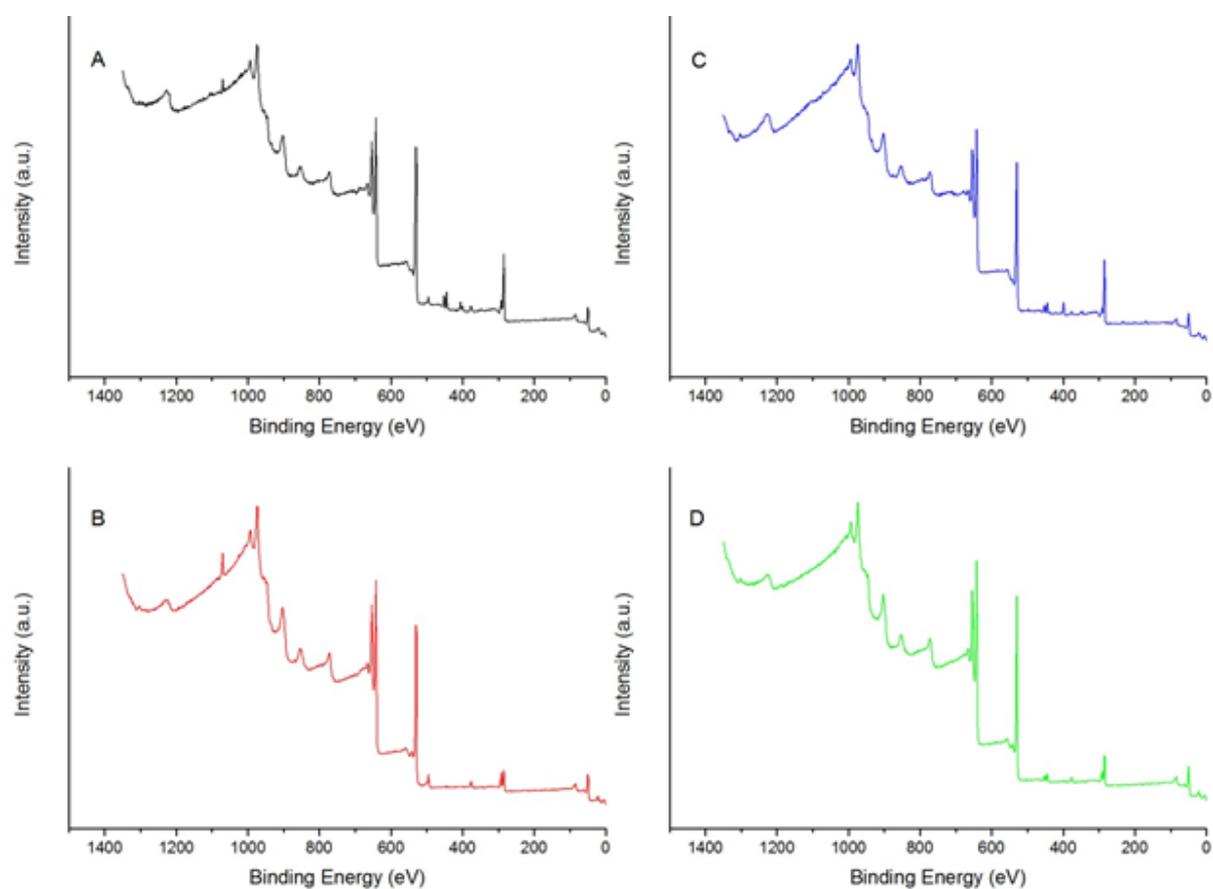

Figure S3: XPS Survey scans A) NP- MnO$_2$, B) NaOH blank, C) AP- MnO$_2$, D) ACN Blank.
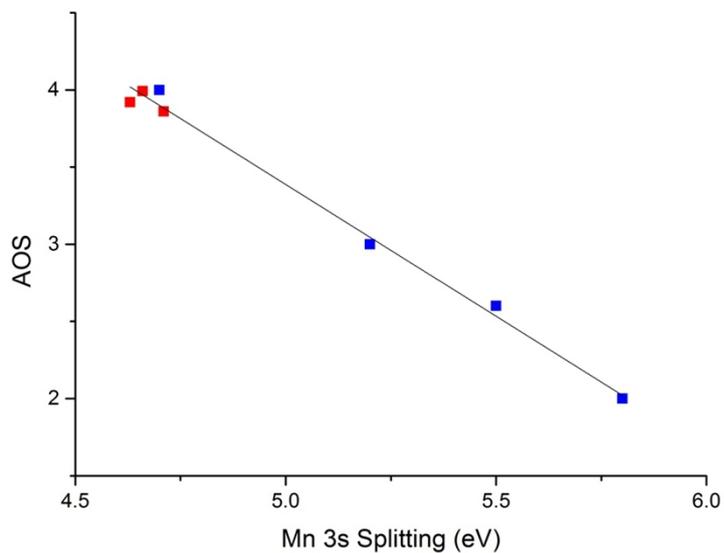
Figure S4: correlation plot for average oxidation state (AOS) of MnO_2 nanorods. (Blue – literature data,[5] Red – this work). Line equation: $AOS = -1.68 \times Splitting + 11.8$
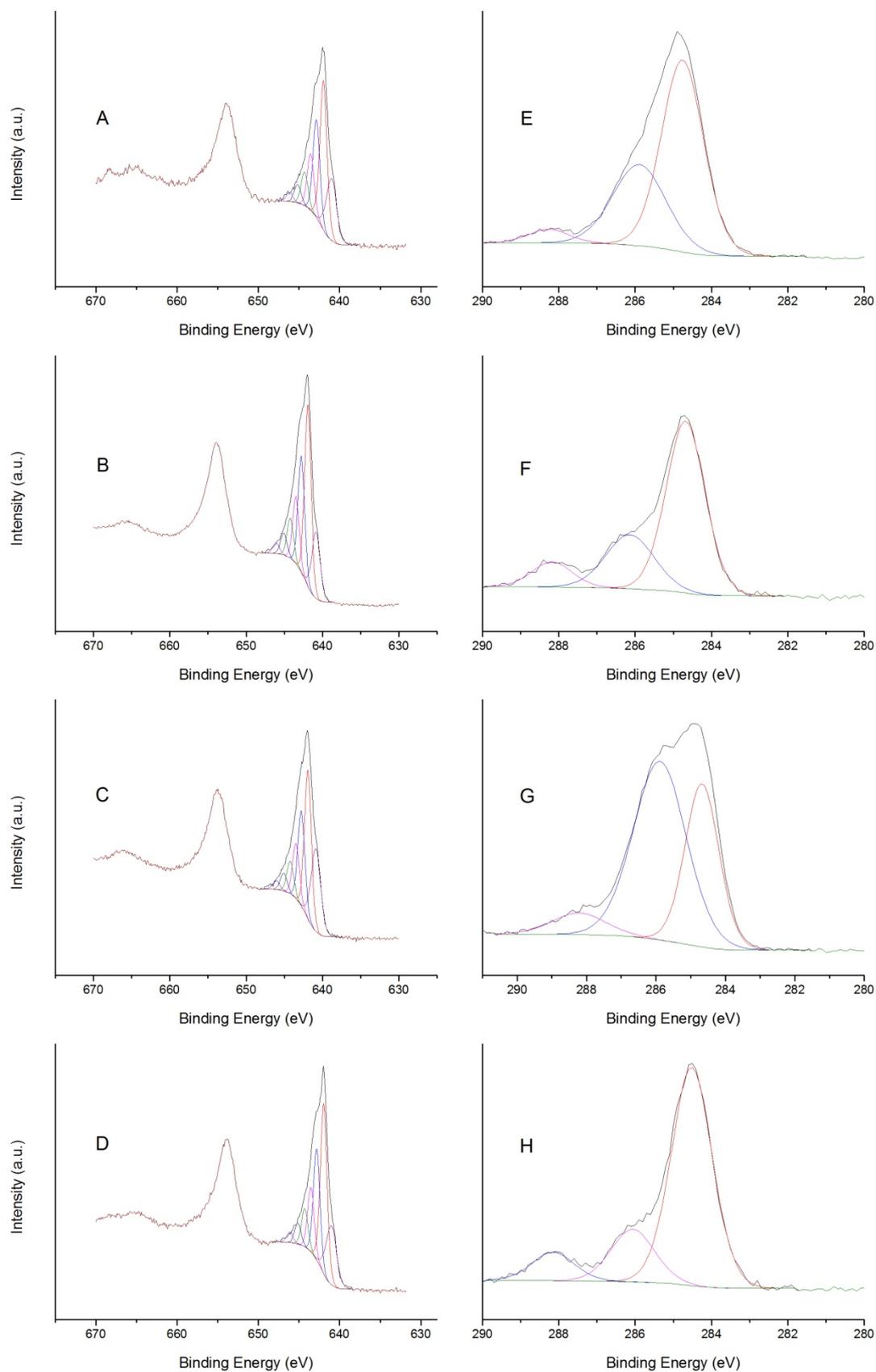
Figure S5: XPS narrow scans of MnO$_2$ nanorods: A-D) Mn 2p for A) NP- MnO$_2$, B) NaOH Blank, C) AP-MnO$_2$, D) ACN blank and E-H) C 1s for E) NP- MnO$_2$, F) NaOH blank, G) AP- MnO$_2$, H) ACN blank. Peak fitting for Mn 2p based on Nesbitt and Banerjee. [6]

References:

1   K. H. A. R. L. M. Saunders, *Aromatic diazo compounds*, Edward Arnold, London; Baltimore, 1985.

2   M. Toupin, T. Brousse and D. Bélanger, *Chem. Mater.*, 2002, **14**, 3946.

3   W. M. Dose and S. W. Donne, *Mater. Sci. Eng., B*, 2011, **176**, 1169.

4   A. I. Vogel and G. H. Jeffery, *Vogel's Textbook of Quantitative Chemical Analysis*, Longman Scientific & Technical, Harlow, Essex, England, 1989.

5   M. Oku, K. Hirokawa and S. Ikeda, *J. Electron. Spectrosc. Relat. Phenom.*, 1975, **7**, 465.

6   H. W. Nesbitt and D. Banerjee, *Am. Mineral.*, 1998, **83**, 305.