Phase Quantification by X-ray Photoemission Valence Band Analysis Applied To Mixed Phase TiO₂ Powders

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Abstract

A method of quantitative phase analysis using valence band X-ray photoelectron spectra is presented and applied to the analysis of TiO_2 anatase-rutile mixtures. The valence band spectra of pure TiO_2 polymorphs were measured, and these spectral shapes used to fit valence band spectra from mixed phase samples. Given the surface sensitive nature of the technique, this yields a surface phase fraction. Mixed phase samples were prepared from high and low surface area anatase and rutile powders. In the samples studied here, the surface phase fraction of anatase was found to be linearly correlated with photocatalytic activity of the mixed phase samples, even for samples with very different anatase and rutile surface areas. We apply this method to determine the surface phase fraction of P25 powder. This method may be applied to other systems where a surface phase fraction is an important characteristic.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is an analysis technique rooted in surface science but increasingly applied to materials science and solid-state chemistry. XPS using Al Kα incident radiation (E = 1486.6 eV) as is typical in a laboratory setting, is capable of ejecting electrons from the core atomic orbitals of all elements that possess them, and as such is a highly versatile technique for elemental quantification.[1-2] Due to the relatively low kinetic energy of electrons ejected with Al Kα, and therefore small inelastic mean free path in a condensed phase, XPS interrogates only the near surface region of the sample.

Core line XP spectroscopy can thus give surface specific information on composition, chemical state, as well as in some cases other properties such as plasma energy,[3] plasmon resonance,[4] and heterojunction band offsets.[5-6] However, the energy of core orbitals usually cannot be interpreted in terms of the local and long range structure; core level XPS cannot usually be used to distinguish different structures of the same composition, for example crystalline polymorphs,[7] or amorphous vs crystalline phases, unless, as is the case for diamond and graphite, or carbon based polymers, differences in bonding leads to distinctive energy loss features around the core lines.[8-10] In contrast, the valence electrons strongly interact with the neighbouring atoms, and their energy distribution will be influenced by the geometrical surroundings of each atom. Valence band spectra have been widely interpreted in terms of chemical modification of semiconductors,[11-13] for example, doping may introduce new filled electronic states at or around the valence band maximum (VBM) which can be detected by XPS or UPS. Alternatively, the offset between the VBM and the Fermi Level, referenced at the zero point on the binding energy scale can be measured to determine changes in n/p type doping or to establish the workfunction of the surface.[14] The spectral shape of the valence band is a reflection of the energy distribution of the density of filled states, which itself is dependent on the atomic structure. Hence valence band shapes can be calculated from a theoretical partial density of states.[3, 15-16] While the valence band spectral shape thus contains phase information, this has so far not been exploited in quantitative phase analysis.

For heterogeneous catalysts or photocatalysts an important concept is the surface phase, *i.e.* the phase of material present at the surface of the solid catalyst directly in contact with the reactants.[17-20] Titanium dioxide is the preferred material for photocatalysis due to its low cost, and high activity.[21-22] It is the basis for many applications such as solar cells[23-24] and environmental purification.[25-26] The two main TiO_2 crystalline phases that are used in photocatalytic reactions are anatase (a-TiO_2) and rutile (r-TiO_2).

We show here that valence band spectra can be used to quantitatively determine the phase composition of a rutile-anatase TiO_2 mixture. The phase information we obtain in this way is, as expected from XPS, surface limited, and significant differences are seen when anatase and rutile samples with different relative surface areas are used. We demonstrate that the surface phase determined by XPS valence band analysis linearly correlates with photocatalytic activity of the material for organic dye degradation.

2. Method

TiO_2 powders were purchased from Sigma Aldrich and used as received. Both rutile (r-TiO_2) and anatase (a-TiO_2) phases were obtained in different particle sizes: 325 mesh anatase powder, approximately equal to 45 micron particles (referred to as *bulk anatase*), 25 nm particle diameter anatase powder (*nano anatase*), 100 nm diameter rutile powder (*nano rutile*) and rutile powder with no specified particle size (*bulk rutile*). Details of the characterisation of the as received samples can be found in the Supporting Information.

Mixed phase samples were produced by mixing the desired weight ratio of the commercial powders, followed by thorough mixing by agitation of the powders.

XPS was carried with a two chamber Thermo K-alpha spectrometer using a monochromated Al K-alpha X-ray source (1486.6 eV) in constant analyser energy mode. X-rays were focused to a 400 micron spot at the sample surface, which defined the analysis area. Sample charging was prevented by use of a dual beam flood gun. High resolution valence band spectra, were recorded at 50 eV pass energy, and survey spectra were recorded at 200 eV pass energy. Samples were prepared by placing

into a copper well plate holder. Spectra were carefully examined to ensure no signal from the copper holder was seen in the survey spectra.

BET surface area measurements of the powders were carried out on a Micromeretics ASAP 2420 Accelerated Surface Area and Porosimetry System.

Photocatalytic degradation of 7×10^{-5} M aqueous methyl orange (MO) was performed in a UVA light box (365 nm, 0.428 mW/cm^2). For each sample, 0.05 g of the powder was added to 12 mL of MO solution. The powders were left to adsorb the solution overnight, then the UV-vis spectrum of the solution was recorded. The powder with solution was then magnetically stirred under UVA irradiation for 1 hour, and the UV-vis spectra recorded again.

3. Results

The VB spectra of bulk r-TiO$_2$ and bulk a-TiO$_2$ are shown in Figure 1. A Shirley background, defined between binding energies of 0 and 12.0 eV has been subtracted for all spectra presented henceforth. The VB spectra from the two TiO$_2$ polymorphs have distinctive shapes.[27] In each case the valence band spectrum consists of two distinct maxima separated in binding energy by approximately 2.5 eV. However, in r-TiO$_2$, the lower binding energy spectral maximum is greater in height, whereas in a-TiO$_2$ the higher binding energy spectral maximum is considerably greater in height.

The spectral shapes of bulk r-TiO$_2$ and bulk a-TiO$_2$ were modelled by fitting with three Gaussian-Lorentzian convolved peaks, the parameters for which are shown in the Supporting Information. No physical meaning is attached to the modelled components, they merely reproduce the VB spectral shape for use in the analysis presented below. The VB spectra from the nano powders were also taken and there was no discernible difference between the models, indicating that for these compounds and for the particle sizes studied, the VB spectral shape is not strongly influenced by the particle size.

Having obtained the VB spectral shapes for the pure phase compounds, the VB shapes for a-TiO$_2$ and r-TiO$_2$ were then used to fit the experimental VB spectra taken from mixed phase TiO$_2$ samples. Mixed phase samples were produced by combining the phase pure TiO$_2$ powders together in the desired mass ratio, followed by agitation to ensure a homogeneous mixture. Three series of mixed

phase TiO_2 samples were produced: bulk a-TiO_2 mixed with bulk r-TiO_2, nano a-TiO_2 mixed with bulk r-TiO_2 and bulk a-TiO_2 mixed with nano r-TiO_2. Whenever powders of differing particle sizes are mixed, there is the risk of a granular convection effect occurring whereby the distinct particle populations separate.[28-29] To ensure that a portion taken from the mixed powders was representative of the nominal phase ratio, XRD analysis was used to quantify the mass ratio of the phases (Figure S2, supporting information).[30]

Figure 2 shows the VB spectra taken from the mixed phase TiO_2 bulk powders. Visually, the height ratio between the two maxima of the VB spectral shape can be seen to change monotonically between the end members. The spectra were fitted with a linear combination of the a-TiO_2 and r-TiO_2 VB spectral shapes determined from the pure compounds. For all fittings, the shape of the two models were constrained, only the relative positions and intensities were allowed to change. A similar treatment was also carried out for mixed phase nano and bulk powders (see supporting information). In each case a good agreement between model and experimental data was found.

Sample preparation is important for obtaining repeatable results; since every material will have electron density in the low binding energy region, it is essential for accurate analysis that only signal from the sample is recorded. We found that use of a well plate, where care is taken to ensure that no signal is recorded from the holder, is the preferable method for studying powders. Sticking the powders to carbon tape or pressing into indium foil were much less successful techniques, as even small contributions from the underlying material can influence the valence band spectrum. Additionally, carbon contamination is present for most samples studied by XPS. We took no special measures to clean the samples before measurement, and in the work reported here, no interference in the results due to carbon contamination could be detected. However, the cleanliness of the samples may become an important consideration for other suites of samples, and protocols such as plasma cleaning may be necessary.

The intensity of a photemission peak is proportional to the concentration of the emitting species, the attenuation of the photoelectron due to the depth of the emitting species, and the photoionisation cross section, itself a function of the orbital and the photon energy. Hence the intensity of a valence band

spectrum will depend upon its orbital makeup. Since the TiO_2 phases have the same chemical composition it is assumed here that the valence band spectrum has essentially the same orbital make-up (in this case consisting primarily of O 2p with some Ti 3d contribution) and thus the same overall photoionisation cross section. Therefore we relate the intensity of the fitted anatase component of a VB spectrum to the amount of anatase present within the sampling depth of the measurement. In this way we propose that the XPS VB can be used to extract quantitative phase information.

The amount of anatase determined by fitting the XPS VB spectrum described above was compared with the nominal mass percentage of anatase in the mixed powders (Figure 3). As can be seen, each of the three series presents a different relationship between XPS VB quantified anatase proportion and the nominal proportion. For the sample series containing nano-scale rutile, *i.e.* with a high surface area of rutile particles, the amount of anatase derived from the XPS VB is lower than the nominal amount. For the other two series, i.e. bulk a-TiO_2/bulk r-TiO_2 and nano a-TiO_2/bulk r-TiO_2, the proportion of anatase determined by XPS VB is above the nominal amount. It is noteworthy that for a particular nominal mass ratio, the XPS derived anatase fraction increases with the increasing relative BET surface area of the anatase phase (Table S1, Supporting Information). For example, for samples with a nominal mass ratio of 40% anatase, in the series with nanoscale anatase and bulk rutile, XPS measures 63% anatase. In the series with bulk anatase and bulk rutile, XPS measures 52% anatase, and in the series with bulk anatase and nano rutile, XPS measures only 10% anatase. The remainder of all three series follow the same pattern. These results suggest that XPS VB spectroscopy affords a phase measurement weighted by surface area in this TiO_2 system. XPS is known to be a surface sensitive technique, and using Al Kα radiation the sampling depth is typically 5-10 nm. Therefore it is to be expected that the phase fraction determined from XPS VBs will be representative of surface phase rather than the overall or bulk phase which is typically determined by standard XRD geometries. That is, XPS phase quantification will be scaled by the fraction of a phase at the surface of the sample, just as XPS elemental composition is scaled by the proportion of an element at the surface of the sample.

To assess whether the surface phase determined by XPS VB analysis is related to functional properties of the materials, photocatalysis experiments were conducted using the mixed phase powders described above. The initial rate of aqueous methyl orange degradation under UV light and in the presence of the catalyst in suspension was measured. The spectra of the dye solutions before and after degradation can be seen in the SI, Figures S4-S6. Anatase is known to be the more photoactive phase, and for each series of mixtures, the pure anatase sample gave the greatest photocatalytic activity. It is known that mixed phase anatase-rutile systems can show enhanced photoactivity over either of the end members. This was not observed here, but such enhancement is thought to require chemically bonded rutile-anatase heterojunctions rather than physical mixtures of distinct populations of phase pure particles.[31-32] The photocatalytic rate for the remainder of the series were normalised to the value for pure anatase. The results plotted against the nominal phase composition are shown in the SI, Figure S7. There was a significant difference between the photocatalytic activities of the three different series at a given composition. However, the photocatalytic activity has a linear relationship (R^2=0.97) with the surface anatase phase, determined from XPS VB analysis (Figure 4). This suggests that in these mixed samples, the overall photocatalytic rate is simply a sum of the photocatalytic contributions from each phase, a-TiO_2 and r-TiO_2, i.e. the two phases do not interact.

In addition we have applied this analytical technique to a commercial sample of mixed Degussa P25, a mixture of a-TiO_2 and r-TiO_2 which is a widely used photocatalysis standard. Measurement of the VB spectrum yielded a a-TiO_2:r-TiO_2 ratio of 85:15 (Figure S12, SI), whilst XRD analysis showed a a-TiO_2:r-TiO_2 ratio of 90:10. These results suggest that the rutile phase may have a slightly larger surface area in P25.

4. Conclusion

We have shown a method to quantitatively determine surface phase composition by valence band XPS analysis. For the TiO_2 rutile/anatase system, the measured surface phase correlates linearly to photocatalytic performance, whereas XRD phase quantification does not, since XRD measures the

bulk or total phase composition rather than the surface phase. This method has the potential to work with many mixed or multi-phase systems.

Acknowledgements

References

[1] T.L. Barr, RECENT ADVANCES IN X-RAY PHOTOELECTRON-SPECTROSCOPY STUDIES OF OXIDES, Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films, 9 (1991) 1793-1805.

[2] C.S. Fadley, X-ray photoelectron spectroscopy: Progress and perspectives, Journal of Electron Spectroscopy and Related Phenomena, 178 (2010) 2-32.

[3] J.M. Kahk, C.G. Poll, F.E. Oropeza, J.M. Ablett, D. Geolin, J.P. Rueff, S. Agrestini, Y. Utsumi, K.D. Tsuei, Y.F. Liao, F. Borgatti, G. Panaccione, A. Regoutz, R.G. Egdell, B.J. Morgan, D.O. Scanlon, D.J. Payne, Understanding the Electronic Structure of IrO2 Using Hard-X-ray Photoelectron Spectroscopy and Density-Functional Theory, Physical Review Letters, 112 (2014).

[4] S. Hufner, G.K. Wertheim, J.H. Wernick, XPS CORE LINE ASYMMETRIES IN METALS, Solid State Communications, 17 (1975) 417-422.

[5] H.C.L. Tsui, L.E. Goff, R.G. Palgrave, H.E. Beere, I. Farrer, D.A. Ritchie, M.A. Moram, Valence band offsets of ScxGa1-xN/AlN and ScxGa1-xN/GaN heterojunctions, Journal of Physics D-Applied Physics, 49 (2016).

[6] P.D.C. King, T.D. Veal, C.E. Kendrick, L.R. Bailey, S.M. Durbin, C.F. McConville, InN/GaN valence band offset: High-resolution x-ray photoemission spectroscopy measurements, Physical Review B, 78 (2008).

[7] C. Wan, Y.N. Regmi, B.M. Leonard, Multiple Phases of Molybdenum Carbide as Electrocatalysts for the Hydrogen Evolution Reaction, Angewandte Chemie-International Edition, 53 (2014) 6407-6410.

[8] J. Diaz, G. Paolicelli, S. Ferrer, F. Comin, Separation of the sp(3) and sp(2) components in the C1s photoemission spectra of amorphous carbon films, Physical Review B, 54 (1996) 8064-8069.

[9] S.T. Jackson, R.G. Nuzzo, DETERMINING HYBRIDIZATION DIFFERENCES FOR AMORPHOUS-CARBON FROM THE XPS C-1S ENVELOPE, Applied Surface Science, 90 (1995) 195-203.

[10] J.C. Lascovich, R. Giorgi, S. Scaglione, EVALUATION OF THE SP2/SP3 RATIO IN AMORPHOUS-CARBON STRUCTURE BY XPS AND XAES, Applied Surface Science, 47 (1991) 17-21.

[11] Y. Cong, J.L. Zhang, F. Chen, M. Anpo, D.N. He, Preparation, photocatalytic activity, and mechanism of Nano-TiO2 co-doped with nitrogen and iron (III), Journal of Physical Chemistry C, 111 (2007) 10618-10623.

[12] V. Etacheri, M.K. Seery, S.J. Hinder, S.C. Pillai, Oxygen Rich Titania: A Dopant Free, High Temperature Stable, and Visible-Light Active Anatase Photocatalyst, Advanced Functional Materials, 21 (2011) 3744-3752.

[13] I. Takahashi, D.J. Payne, R.G. Palgrave, R.G. Egdell, High resolution X-ray photoemission study of nitrogen doped TiO2 rutile single crystals, Chemical Physics Letters, 454 (2008) 314-317.

[14] E.N.K. Glover, S.G. Ellington, G. Sankar, R.G. Palgrave, The nature and effects of rhodium and antimony dopants on the electronic structure of TiO2: towards design of Z-scheme photocatalysts, Journal of Materials Chemistry A, 4 (2016) 6946-6954.

[15] L. Asbrink, C. Fridh, E. Lindholm, HAM-3, A SEMIEMPIRICAL MO THEORY .2. PHOTOELECTRON-SPECTRA, Chemical Physics Letters, 52 (1977) 69-71.

[16] K.G. Godinho, G.W. Watson, A. Walsh, A.J.H. Green, D.J. Payne, J. Harmer, R.G. Egdell, A comparative study of the electronic structures of SrCu(2)O(2) and PbCu(2)O(2) by density functional theory, high resolution X-ray photoemission and electron paramagnetic resonance spectroscopy, Journal of Materials Chemistry, 18 (2008) 2798-2806.

[17] J. Zhang, M. Li, Z. Feng, J. Chen, C. Li, UV Raman Spectroscopic Study on TiO2. I. Phase Transformation at the Surface and in the Bulk, The Journal of Physical Chemistry B, 110 (2006) 927-935.

[18] J. Zhang, Q. Xu, Z. Feng, M. Li, C. Li, Importance of the relationship between surface phases and photocatalytic activity of TiO2, Angewandte Chemie-International Edition, 47 (2008) 1766-1769.

[19] G. Liu, J.C. Yu, G.Q. Lu, H.M. Cheng, Crystal facet engineering of semiconductor photocatalysts: motivations, advances and unique properties, Chemical Communications, 47 (2011) 6763-6783.

[20] M.A. Henderson, A surface science perspective on TiO2 photocatalysis, Surface Science Reports, 66 (2011) 185-297.

[21] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results, Chemical Reviews, 95 (1995) 735-758.

[22] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental Applications of Semiconductor Photocatalysis, Chemical Reviews, 95 (1995) 69-96.

[23] U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Gratzel, Solid-state dye-sensitized mesoporous TiO2 solar cells with high photon-to-electron conversion efficiencies, Nature, 395 (1998) 583-585.

[24] B. Oregan, M. Gratzel, A LOW-COST, HIGH-EFFICIENCY SOLAR-CELL BASED ON DYE-SENSITIZED COLLOIDAL TIO2 FILMS, Nature, 353 (1991) 737-740.

[25] A. Fujishima, X.T. Zhang, D.A. Tryk, TiO2 photocatalysis and related surface phenomena, Surface Science Reports, 63 (2008) 515-582.

[26] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, ENVIRONMENTAL APPLICATIONS OF SEMICONDUCTOR PHOTOCATALYSIS, Chemical Reviews, 95 (1995) 69-96.

[27] A.C. Breeson, G. Sankar, G.K.L. Goh, R.G. Palgrave, Rutile to anatase phase transition induced by N doping in highly oriented TiO2 films, Physical Chemistry Chemical Physics, 18 (2016) 24722-24728.

[28] H.M. Jaeger, S.R. Nagel, R.P. Behringer, The physics of granular materials, Physics Today, 49 (1996) 32-38.

[29] J.B. Knight, H.M. Jaeger, S.R. Nagel, VIBRATION-INDUCED SIZE SEPARATION IN GRANULAR MEDIA - THE CONVECTION CONNECTION, Physical Review Letters, 70 (1993) 3728-3731.

[30] R.A. Spurr, H. Myers, Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer, Analytical Chemistry, 29 (1957) 760-762.

[31] G.H. Li, L. Chen, M.E. Graham, K.A. Gray, A comparison of mixed phase titania photocatalysts prepared by physical and chemical methods: The importance of the solid-solid interface, Journal of Molecular Catalysis a-Chemical, 275 (2007) 30-35.

[32] C.Y. Wu, Y.H. Yue, X.Y. Deng, W.M. Hua, Z. Gao, Investigation on the synergetic effect between anatase and rutile nanoparticles in gas-phase photocatalytic oxidations, Catalysis Today, 93-5 (2004) 863-869.