

Advantages of coincident XPS-Raman in the analysis of mineral oxides species

Key words: XPS, Raman spectroscopy, material characterisation, surface analysis, minerals, multitechnique, Nexsa, iXR

Abstract

X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are two popular analytical techniques due to their flexibility, ease of use, and the wealth of information they provide. Until recently analysis of a material with both of these techniques required the use of two different instruments, however the development of coincident XPS-Raman allows for straightforward and quick utilisation of both techniques opening up new exciting materials characterisation opportunities.

Introduction

XPS is an extremely versatile technique that has found widespread use in a myriad of application areas, from contact lenses to aerospace materials. XPS is unique in that it can quantify the elemental and chemical composition of a material's surface with extreme selectivity; the typical information depth of XPS being less than 10 nanometres.

Raman spectroscopy is utilised in many similar application areas as it requires little sample preparation, is non-destructive, provides information on molecular structure, and enables users to identify materials quickly, thanks to extensive spectral libraries.

The implementation of XPS and Raman with other analysis techniques is well established; XPS has a long history of complementary use with related UHV analysis techniques, such as UV photoelectron spectroscopy, Auger electron spectroscopy and ion scattering spectroscopy. In these cases, additional equipment is added to the spectrometer to give co-incident, complementary information.



Figure 1: Thermo Scientific iXR Raman Spectrometer coupled to a Thermo Scientific Nexsa XPS System.

Raman spectroscopy is also frequently used in conjunction with other analytical techniques to provide information on molecular structure and chemical environment. However, coincident XPS and Raman spectroscopy has not been possible. Instead samples have had to be transferred between instruments; which not only increases the amount of time required to acquire data, but also adds a degree of uncertainty as to whether the analysis has been collected from the same region of the sample.

To overcome these problems, the Thermo Scientific™ Nexsa™ spectrometer has been integrated with the Thermo Scientific™ iXR™ Raman Spectrometer (figure 1) to provide a multi-modal analysis platform. The system aligns the XPS analysis position exactly with the Raman analysis position, ensuring that the data is collected from the same position.

The coincident XPS-Raman removes any requirement to transfer the sample from one instrument to the next between analyses, which minimizes additional sample handling and exposure to different conditions which can lead to sample contamination or degradation.

Analysis of calcium carbonate (CaCO_3) and titanium dioxide (TiO_2) polymorphs serve as excellent examples of the powerful information that can be gleaned from performing XPS and Raman spectroscopy concurrently. Both compounds occur in multiple crystalline forms, which can be distinguished using Raman but not easily by XPS. However, determining the quantity and type of contamination present in naturally occurring mineral samples is difficult using Raman in isolation, as is identifying compounds that are not contained within a spectral library.

Calcium carbonate occurs naturally in three different polymorphs: Calcite, Aragonite and Vaterite, with Calcite and Aragonite being the two most abundant. Calcite possesses a trigonal crystal structure and is the most thermodynamically stable form of calcium carbonate. Aragonite possesses an orthorhombic crystal structure, is less thermodynamically stable, slowly changing to Calcite under ambient conditions, and forms, geologically, at high temperature and pressure. The differences in crystal structure lead to variation in the physical properties of the different polymorphs, such as solubility. Establishing the causes behind these differences is not only important to understanding geological formations, but it also important in a diverse range of applications areas, such as industrial scale formation, pancreatic calcification¹ and biomineralisation². Mixtures of Calcite and Aragonite occur naturally in marine molluscs and the water temperature, pressure and salinity all strongly influence the proportion of each polymorph found in the shells of different species.

Titanium dioxide is one of the most studied materials in surface science, due to its availability, low toxicity and widespread range of applications, such as photovoltaics, catalysis and self-cleaning windows. As a result of this prevalence throughout the field, it is often referred as the prototypical metal oxide surface. Whilst many polymorphs of TiO_2 are known to exist, only two occur naturally in abundance: Rutile and Anatase. Rutile- TiO_2 is the more thermodynamically stable form however Anatase- TiO_2 is more energetically favourable when forming nanoparticles at atmospheric temperature and

pressure, conditions which are utilised when growing films by solution based processes in devices such as solar cells. Additionally Anatase- TiO_2 has previously been recognised as more photocatalytically active than Rutile- TiO_2 , however recent research indicates that the greatest photovoltaic efficiencies are achieved in devices that contain a mixture of both polymorphs.

Experiment and results

XPS spectra across a wide range of binding energies, known as survey spectra, were acquired from natural crystals of Aragonite and Calcite (see figure 2) to determine the elemental composition, as expected for naturally occurring crystals, surface contamination was observed in the form of silicon and sodium. High resolution spectra of each photoemission peak were then acquired to allow determination of chemical states present at the surface; the C 1s photoemission peak shows the presence of aliphatic carbon contamination in addition to the carbonate peak. Repeated cycles of sputtering with Ar1000+ clusters at 6kV generated by the Thermo Scientific™ MAGCIS™ (Monatomic and Gas Cluster Ion Source) removed aliphatic carbon contamination from the surface (figure 3), and reacquisition of the survey spectra confirms the removal of silicon and sodium contamination, leaving stoichiometric CaCO_3 .



Figure 2: Photographic image of aragonite (right) and calcite (left) crystals.

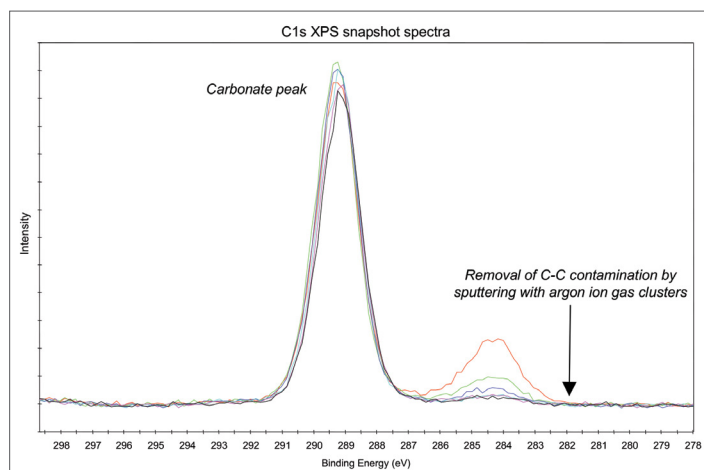


Figure 3: Removal of surface contamination on CaCO_3 crystals with argon ion gas clusters.

As can be seen from the overlay of the survey and valence band spectra acquired from the cluster-cleaned aragonite and calcite crystals (figure 4), it is not possible to distinguish between the two different polymorphs of CaCO_3 using XPS. Nevertheless the combination of XPS and cleaning with argon ion gas clusters does determine that the surface possesses the correct stoichiometry and is free of contamination, thereby allowing Raman spectra to be acquired with absolute confidence in the elemental and chemical composition of the region of interest.

Figure 5 shows the Raman spectra obtained from the two different crystalline forms of CaCO_3 . The higher shifted peaks correspond to what are referred to as internal modes associated with the carbonate anion. While a slight shift can be observed in some of these peaks they are similar in both polymorphs. The peaks in the lower shifted region are due to lattice modes and depend on the way the carbonate anions are arranged in relationship to each other in the crystal structures. The lower symmetry in the Aragonite structure leads to many more peaks in this region of the Raman spectrum. The exact assignments of these different vibrational modes have been addressed elsewhere.³

It is also possible to determine the ratio of polymorphs in mixed samples using Raman spectroscopy. By using polymorphically pure samples, of titanium dioxide (TiO_2), as references it is possible to develop a method for determining the percentage of each polymorph present. A total of five powders were analysed using coincident XPS-Raman: Pure Anatase- TiO_2 , pure Rutile- TiO_2 and 3 mixed powders.

Survey spectra, high resolution C 1s, O 1s, Ti 2p and valence band photoemission spectra were repeatedly acquired from all the TiO_2 powders whilst performing cleaning cycles with Ar_{2000}^+ gas clusters at 4kV to remove surface carbon contamination. The use of argon ion gas clusters allows surface contamination to be removed without damaging the chemistry of the underlying substrate, as evidenced by the lack of a metallised titanium peak at 455eV, this emerges when etching with monatomic argon due to the preferential sputtering of oxygen, forming sub-stoichiometric TiO_{2-x} .

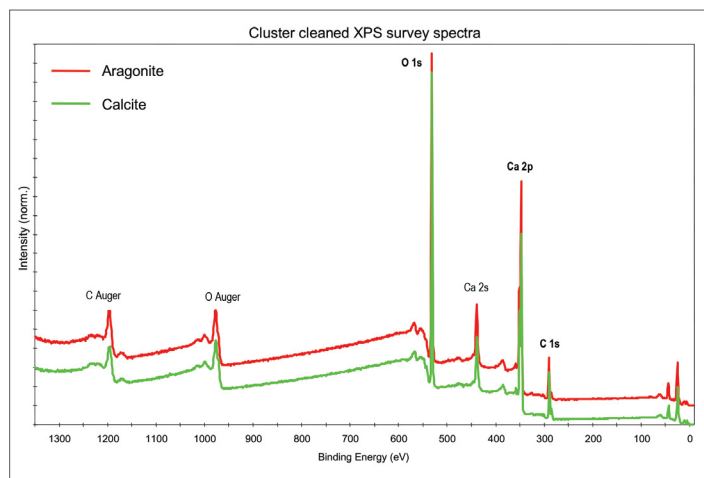


Figure 4: XPS spectral overlay (cluster-cleaned)

Emission peak	Aragonite as received	Calcite as received	Aragonite cluster cleaned	Calcite cluster cleaned
C 1s	46.1	54.2	19.5	23.2
Ca 2p	10.1	10.2	21.2	19.3
Na 1s	0.7	0.4	n/a	n/a
O 1s	40.5	34.6	59.3	57.5
Si 2p	2.6	0.6	n/a	n/a

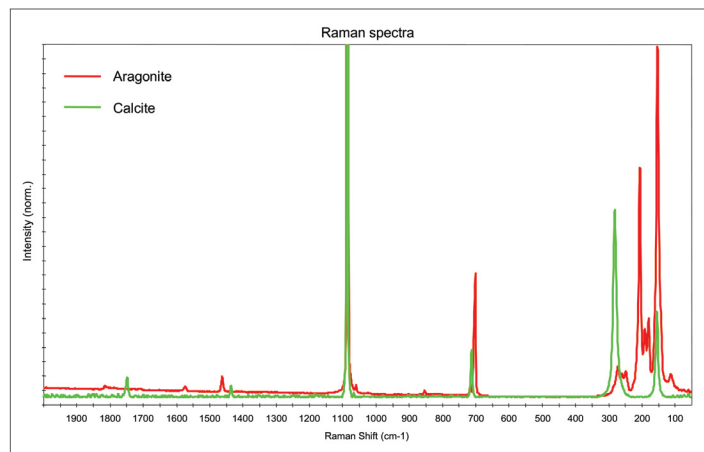
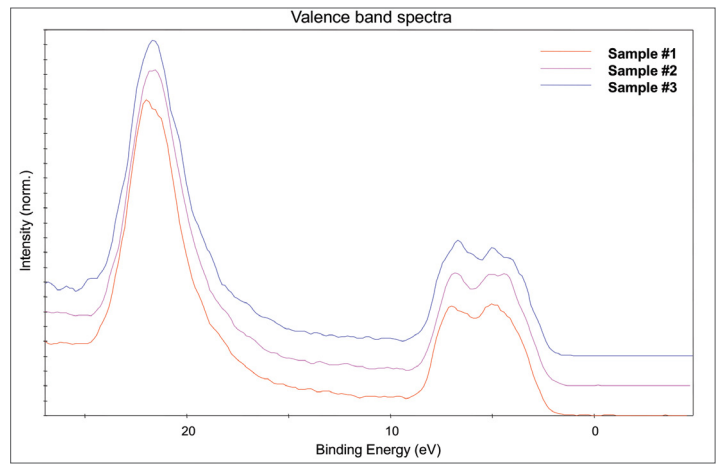


Figure 5: Overlay of the Raman spectra obtained from the CaCO_3 crystals.

Slight differences can be observed in the valence band spectral shapes acquired from the pure Anatase-TiO₂ and Rutile-TiO₂ powders using XPS (figure 6), however the differences are subtle, making determination of the relative proportion of each polymorph difficult (figure 7). However, the markedly different Raman shift peak positions observed in the pure Anatase-TiO₂ and Rutile-TiO₂ powder spectra allow easily distinguishing between the Anatase and Rutile polymorphs (Figure 8). Furthermore the spectral profiles can be used as references for non-linear least squares fitting of the Raman spectra acquired from the mixed powders (figure 9), enabling quick and straightforward determination of the Anatase:Rutile ratio of the three mixed powder samples. It is also possible to use the 142 cm⁻¹ peak in the Raman spectrum of Anatase as the basis of a quantitative method for determining the percentage of Anatase in a mixture of Anatase and Rutile. The Thermo Scientific™ TQ Analyst™ software provides a convenient way to develop these types of quantitative methods.



Sample	Anatase : Rutile Ratio
1	9:91
2	49:51
2	71:29

Figure 7: XPS valence band comparison – Mixed TiO₂ powders

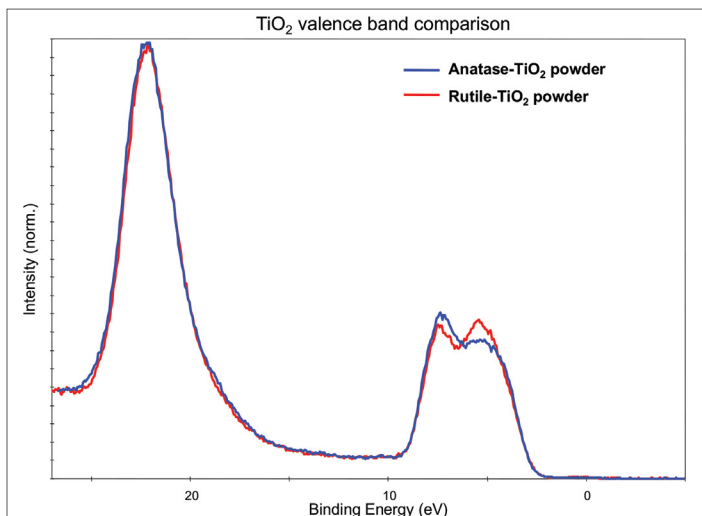


Figure 6: XPS valence band comparison – Pure TiO₂ powders.

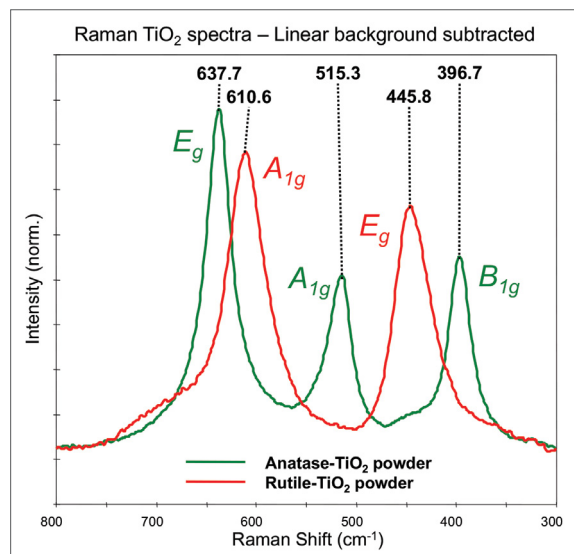


Figure 8: Comparison of the Raman spectra of the pure TiO₂ powders.

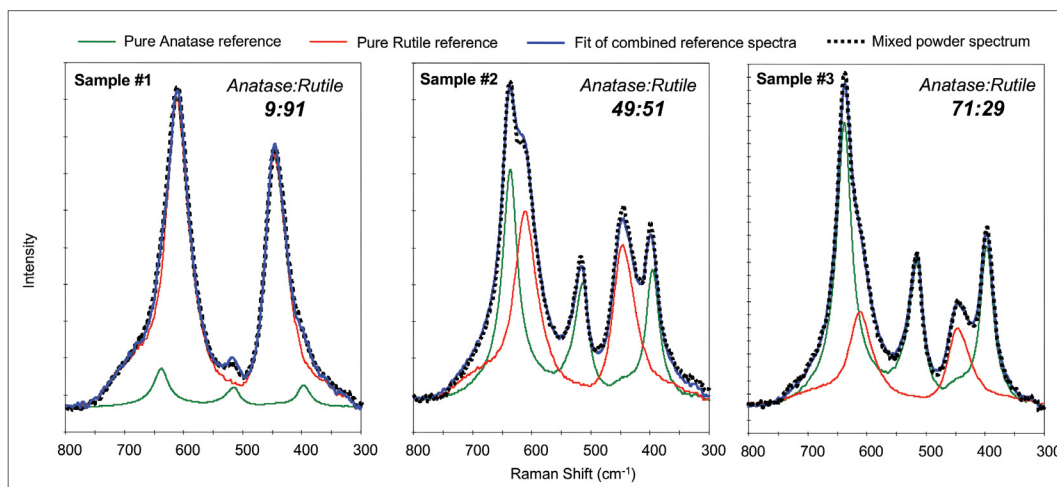


Figure 9: Comparison of the Raman spectra of the mixed TiO₂ powders

Summary

In conclusion, XPS is used for quantitative determination of both elemental and chemical composition for any solid material compatible with ultra-high vacuum. Whereas Raman spectroscopy is used for identification of referenced compounds by careful spectral matching employing searching algorithms and spectral databases. The combination of XPS and Raman on a single instrument, Nexsa and iXR, allows more powerful analysis of a material than either technique in isolation, with the cleanliness, purity and stoichiometry of a sample determined using XPS, and identification and quantification of molecular structures to be determined using Raman spectroscopy. As both techniques are aligned to the same position within the vacuum system all the time consuming aspects of locating the same analysis point when transferring between instruments is removed, giving absolutely certainty that the information acquired has all come from the same region of sample, which is particularly useful when studying non-uniform samples.

References

1. Christos G. Kontoyannis and Nikos V. Vagenas, *Calcium carbonate phase analysis using XRD and FT-Raman spectroscopy*, *Analyst*, 2000, **125**, 251-255.
2. Lia Addadi, Derk Joester, Fabio Nudelman, and Steve Weiner, Mollusk Shell Formation: A Source of New Concepts for Understanding Biomineralization Processes, *Chem. Eur. J.* 2006, 12, 980-987
3. W.B. White, *The carbonate minerals*. Chap. 12, In: V.C. Farmer (ed.), *The Infrared Spectra of Minerals*, Mineralogical Society of London, 1974, p. 227-284.

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