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

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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 utilization of both techniques to open up new exciting materials characterization 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, since the typical information depth of XPS being less than 10 nanometers.

Raman spectroscopy is utilized in many similar application areas as it requires little sample preparation, is nondestructive, 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 ultra-high vacuum (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 coincident, complementary information.

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Raman spectroscopy is also frequently used in conjugation with other analytical techniques to provide information on molecular structure and chemical environment. However, the usage of 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 was collected from the same region of the sample.

To overcome these problems, the Thermo Scientific™ Theta Probe Angle-Resolved X-ray Photoelectron Spectrometer (ARXPS) System has been integrated with the Thermo Scientific iXR™ DXR3 Flex Raman Spectrometer to provide a multimodal 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, minimizing additional sample handling and exposure to different conditions that can lead to sample contamination or degradation.

Analysis of calcium carbonate (CaCO3) and titanium dioxide (TiO_2) polymorphs provides 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 with XPS. However, Raman spectroscopy in isolation has difficulty in determining the quantity and type of contamination present in naturally occurring mineral samples, as well as in 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 $CaCO_3$. Aragonite possesses an orthorhombic crystal structure and 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 is also important in a diverse range of applications, such as industrial scale formation, pancreatic calcification,[1] and biomineralization. Mixtures of calcite and aragonite occur naturally in marine molluscs; 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 to as the prototypical metal oxide surface. While 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 favorable when forming nanoparticles at atmospheric temperature and pressure, conditions which are utilized when growing films by solution-based processes in devices such as solar cells. Additionally anatase-TiO_2 had been recognized 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 $Ar_{1000}+$ clusters at 6 kV generated by the Thermo Scientific MAGCIS (Monatomic and Gas Cluster Ion Source) removed aliphatic carbon contamination from the surface (Figure 3). Reacquisition of the survey spectra confirms the removal of silicon and sodium contamination, leaving stoichiometric $CaCO_3$.
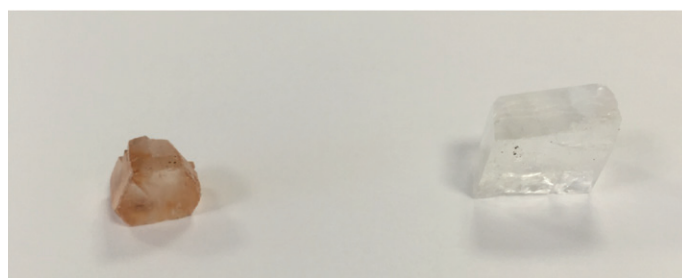

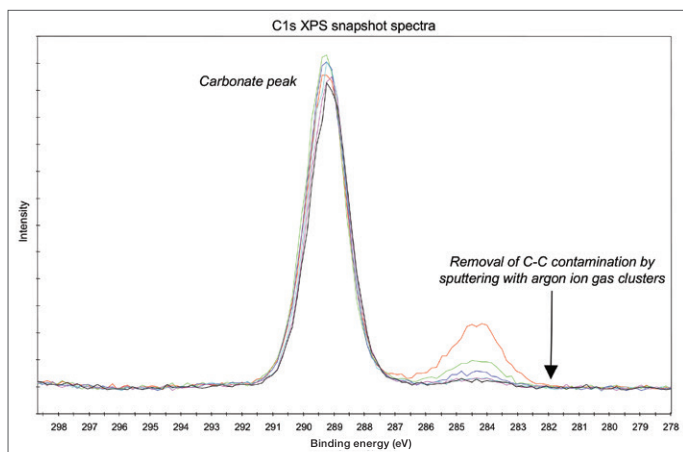**Figure 1. Photographic image of (right) aragonite and (left) calcite crystals.**

Figure 2. Removal of surface contamination on CaCO₃ crystals with argon ion gas clusters.

Figure 3. Cluster-cleaned XPS spectral overlay.

As can be seen from the overlay of the survey and valence band spectra acquired from the cluster-cleaned aragonite and calcite crystals (Figure 3), it is not possible to distinguish between the two different polymorphs of CaCO3 using XPS. Nevertheless, the combination of XPS and cleaning with argon ion gas clusters ensures 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 4 shows the Raman spectra obtained from the two different crystalline forms of CaCO₃. 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 arrangement of the carbonate anions 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 analyzed using coincident XPS-Raman: pure anatase-TiO_2, pure rutile-TiO_2, and three mixtures of the two powders at different ratios.

Survey spectra, high resolution C 1s, O 1s, Ti 2p, and valence band photoemission spectra were repeatedly acquired from all the TiO_2 powders while performing cleaning cycles with $Ar_{2000}+$ gas clusters at 4 kV to remove surface carbon contamination. The use of argon ion gas clusters allows the removal of surface contamination without damaging the chemistry of the underlying substrate, as evidenced by the lack of a metallized titanium peak at 455 eV. This peak emerges when etching with monatomic argon due to the preferential sputtering of oxygen, forming sub-stoichiometric TiO_2-x.
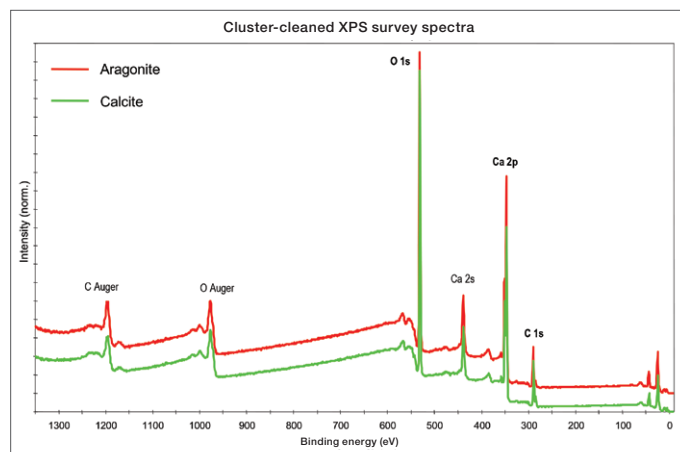
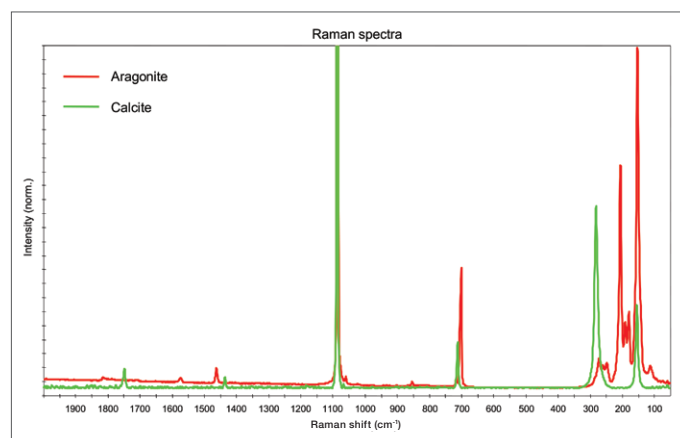| Emission peak	Aragonite as received	Calcite as received	Aragonite cluster cleaned	Calcite cluster cleaned
C 1s	46.1	54.2	19.5	23.2
Ca 2p	10.1	10.2	21.2	19.3
Na 1s	0.7	0.4	n/a	n/a
Oa 1s	40.5	34.6	59.3	57.5
Si 2p	2.6	0.6	n/a	n/a

Figure 4. Overlay of the Raman spectra obtained from the CaCO₃ crystals.

Slight differences can be observed in the valence band spectral shapes acquired from the pure anatase-TiO_2 and rutile-TiO_2 powders using XPS (Figure 5); however, the differences are subtle, making determination of the relative proportion of each polymorph difficult (Figure 6). However, the markedly different Raman shift peak positions observed in the pure anatase-TiO_2 and rutile-TiO_2 powder spectra allow easy distinguishing between the anatase and rutile polymorphs (Figure 7). Furthermore, the spectral profiles can be used as references for nonlinear least squares fitting of the Raman spectra acquired from the mixed powders (figure 8), 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.
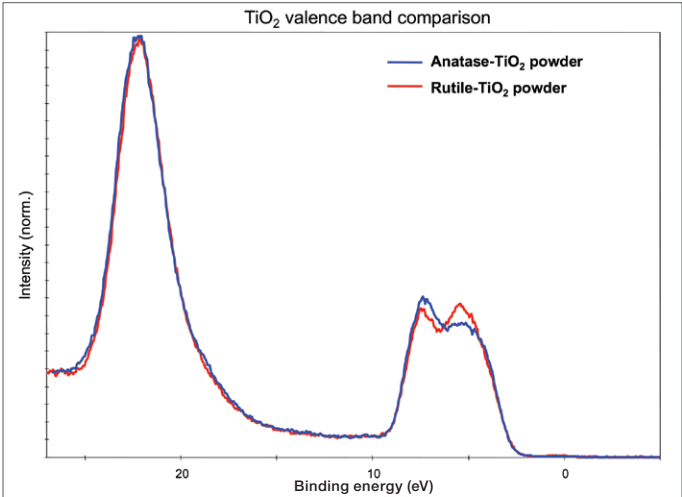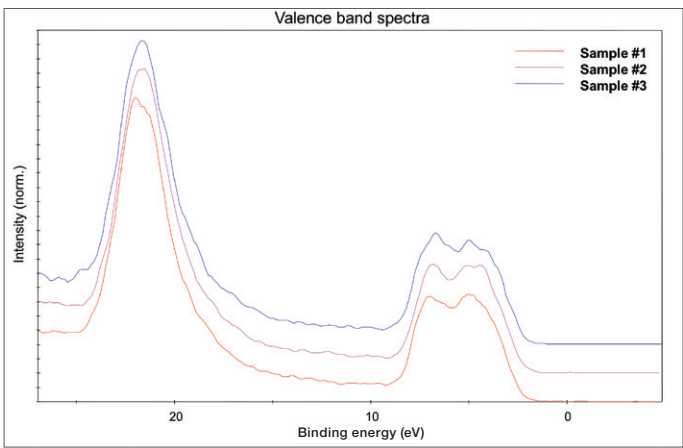

Sample	Aragonite:rutile ratio
1	9;91
2	49.51
2	71:29

Figure 6: XPS valence band comparison—Mixed TiO_2 powders

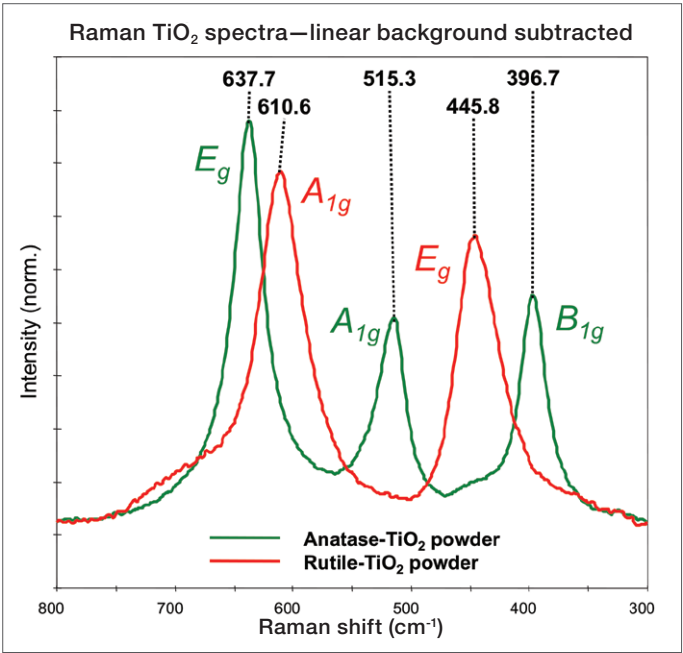Figure 5: XPS valence band comparison—Pure TiO2 powders.

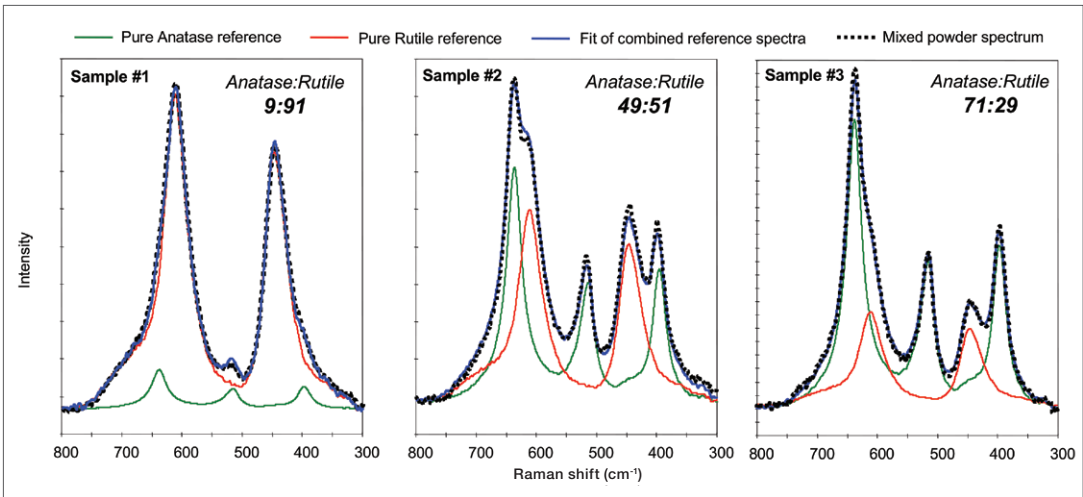Figure 7: Comparison of the Raman spectra of the pure TiO_2 powders.

Figure 8: Comparison of the Raman spectra of the mixed TiO_2 powders.

Summary

In conclusion, XPS is used for quantitative determination of both elemental and chemical composition for any solid material compatible with UHV analysis, whereas Raman spectroscopy is used for identification of referenced compounds by careful spectral matching that searches algorithms and spectral databases. The combination of XPS and Raman spectroscopy on the DXR3 Flex Raman Spectrometer integrated with the Theta Probe ARXPS System, 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 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 all the information acquired has come from the same region of sample, which is particularly useful when studying nonuniform samples.

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