

X-Ray Excited Optical Luminescence Studies of Calcium Carbonate

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Introduction

Polymers can control mineralization and affect the structure and properties of the materials formed. Synthetic acrylamide-based polyelectrolytes have been studied as templates or promoters for *in vitro* mineralization of calcium carbonate [1]. The fact that biological systems are able to perform synthesis of highly ordered materials with excellent mechanical properties under ambient condition is a great inspiration for researchers, who often use methods involving high temperature and pressure [2]. Calcium carbonate is also known to interact with polymers, which is detected by blue-emission when excited by an appropriate energy source [3]. However, the detailed

picture about how polymer gels affect the mineralization of calcium carbonate (CaCO_3) is still unclear. The initial stages of biomineralization are rapid and are difficult to observe *in situ*. However, carefully designed experiments allow for synthesis of interesting materials and reveal details such as nucleation, growth and aggregation. We believe that advanced X-ray spectroscopy may reveal additional features of these solids. Here we present preliminary results and discussions of X-ray Absorption Near-Edge Structure (XANES) spectroscopy and X-ray Excited Optical Luminescence (XEOL) of synthetic calcite samples under controlled conditions.

Science

All samples were prepared by precipitation. Four different samples were studied, labelled as: DP0, DP1, DP2 and DP3. DP0 and DP1 contain no polymer attachment. DP2 and DP3 contained significant additions of polymers, consisting of polyelectrolyte attachments having acid and sulphate groups, respectively. All XANES and XEOL measurements were performed on the SGM beamline 11ID-1. XEOL spectra were collected using QE6500 Scientific-grade Spectrometer (Ocean Optics, Dunedin, FL), and a network CCD camera (Axis 2120). Each sample was freshly prepared by spreading the powder on a piece of double-sided conducting carbon tape on a steel disk (diameter $\sim 1\text{cm}$), which was mounted onto a sample holder.

Discussion

XANES spectra in TEY mode of the four calcite samples, and a standard CaCO_3 powder are shown in Figure 1. All spectra have been normalized to incoming photon flux. All spectra have main peaks at 350.7 eV and 354.1 eV, as well as shoulder peaks at 349.5 eV and 352.8 eV that precede the main peaks. The peaks are due to excitation from core $2p^63d^0$ to $2p^53d^1$ or $2p^54s^1$ (dipole allowed). The position of the peaks can be correlated to site symmetry around the Ca^{2+} ion and crystal-field splitting. The spectra of the DP0, DP1, DP2 and DP3 have similar spectral features to that of the CaCO_3 standard with a substantial broadening, line indicating either a chemical inhomogeneity or more extensive interactions within the samples. Details of the interactions await further study.

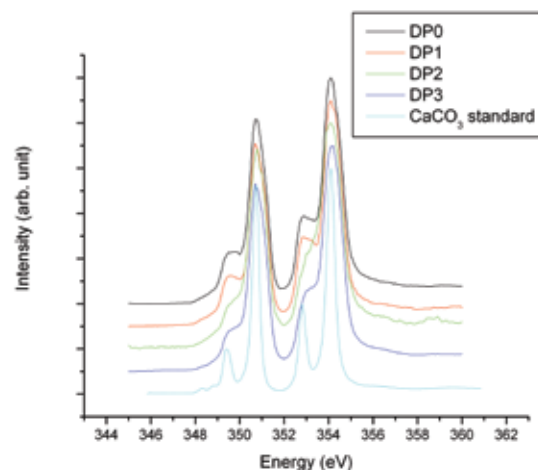


Figure 1: $\text{Ca } L_{3,2}$ -edge XANES spectra of the synthetic calcite samples (DP0, DP1, DP2, and DP3), and standard CaCO_3 powder

Figure 2 shows XEOL spectra of the samples that were excited above the $\text{Ca } L_{3,2}$ -edge (360 eV). Four second integration time was used in all spectra, and each was averaged over four trials. Luminescence is weak in all cases. DP0 and DP1, even though they were made via a different synthetic route, have a similar broad, asymmetric UV peak centred around 385 nm and a visible peak at 605 nm, the former being more intense. The spectra of DP2 and DP3 are distinctly different, not only from the spectra of DP0 and DP1, but also from each other. For DP2, there is a weak, broad emission peak centred on 520 nm, whereas for DP3, two peaks are distinct at 386 nm and 618 nm, the latter being more intense. The longer wavelength emission is likely due to defects; the origins for the peaks are still under investigation.

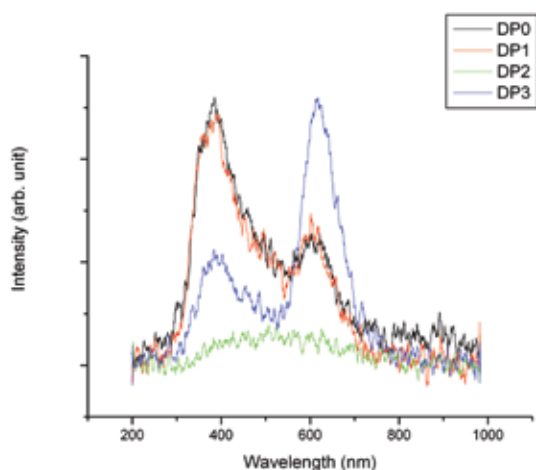


Figure 2: XEOL spectra of the synthetic calcite samples. All samples were excited at 360 eV

Figure 3 shows XEOL spectra of each sample excited below the Ca $L_{3,2}$ -edge (345 eV), at the Ca $L_{3,2}$ -edge (350 eV, 355 eV), and above it (360 eV). With the exception of the series DP3 spectra, relative intensity of the peaks present at all excitation energies is similar. With DP3, we observe that at an excitation energy at 345 eV, the relative intensity of the visible peak at 618 nm is intensified. The origin of this phenomenon is still under investigation.

Conclusion

In summary, the synthetic calcite samples have chemical properties that are closely related to the standard CaCO_3 , but

there is evidence of chemical inhomogeneity, as well as other interactions that are not present in the standard CaCO_3 . From XEOL studies, the calcite samples without polymer attachment have similar luminescent properties, whereas the samples with polymer attachments have a drastically different emission profile depending on what kind of group the attached polymers belong to, a very interesting preliminary observation. Further studies will be done to investigate chemical compositions, as well as chemical interactions within the samples.

References

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Acknowledgements

Research at the University of Western Ontario is supported by Natural Sciences and Engineering Research Council of Canada, Canada Foundation for Innovation, Ontario Innovation Trust, and Canada Research Chairs program. Authors would like to thank Tom Regier and Robert Blyth for their technical assistance with the experiments at CLS.

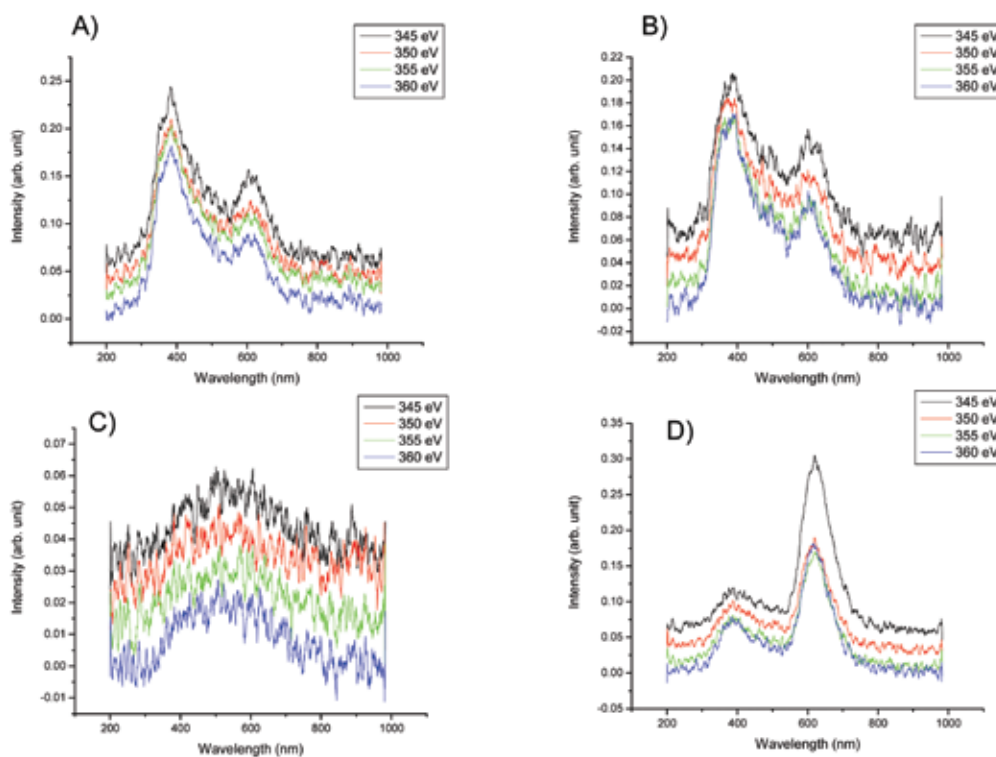


Figure 3: XEOL spectra at various excitation energies of the synthetic calcite samples A) DP0, B) DP1, C) DP2, D) DP3