In-Situ Photon-in/Photon-out Soft-X-Ray Spectroscopy in Interface and Nanoscience

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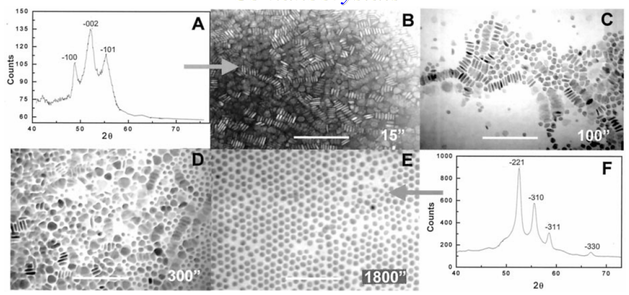
Introduction

A fundamental understanding of the growth and properties of the nanocrystals would greatly benefit from a detailed information of their electronic structure as a function of size and of the presence and nature of the molecules bound to their surface. Because the Co nanocrystals are extremely reactive and oxidize easily, it is important to use techniques that can interrogate the particles in their growth environment so that their electronic and chemical structure can be followed during growth and during catalytic reactions.

Advances in the synthesis of particles of nanometer dimensions, narrow size distribution, and controlled shape have generated interest because of the potential to create novel materials with tailored physical and chemical properties. [Somorjai & Borodko, *Catal. Lett.* ***76****, 1 (2001); Konya et al., Catal. Lett.* ***81****, 137 (2002)*]. New properties arise from quantum confinement effects and from the increasing fraction of surface atoms with unique bonding and geometrical configurations.

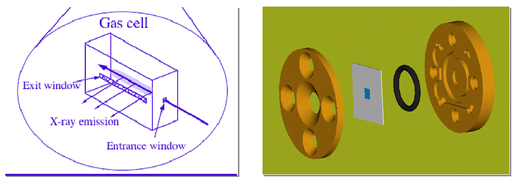
Co nanocrystals



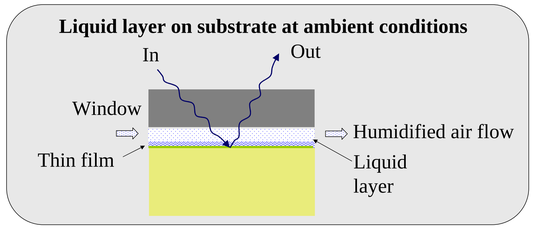
Co nanocrystals display a wealth of size-dependent structural, magnetic, electronic, and catalytic properties. The challenges in making isolated Co nanocrystals are to overcome the large attractive forces between the nanoparticles, due to surface tension and van der Waals interactions that tend to aggregate them [*Puntes et al., Science* ***291****, 2115 (2001); Natural Materials* ***3****, 263 (2004)*].

Experimental Setup

Soft x-rays require a vacuum environment in the beamline and fluorescence spectrometer. Thus, the gaseous and liquid phase samples will be maintained in cells inside the vacuum chamber with windows to allow the penetration of soft x-rays.



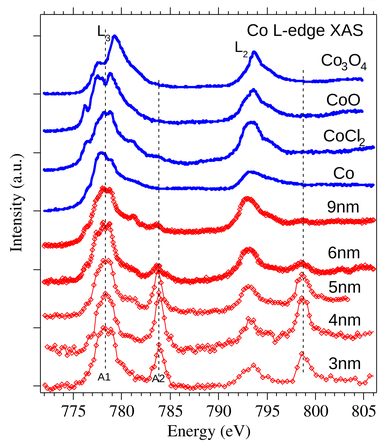
Guo et al., PRL **89**, 137402 (2002); Guo et al., PRL **91**, 157401 (2003).

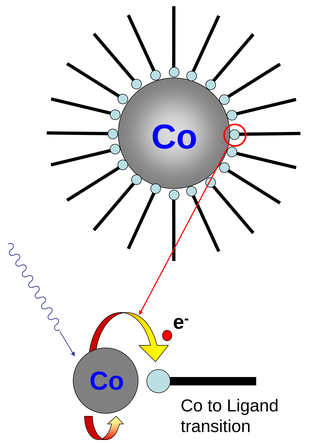


Fordberg et al., Rev. Sci. Instrum. 78, 083110 (2007)

XAS of Co nanocrystal suspension:

- **Surfactant:** *Oleic Acid, $C_{18}H_{34}O_2$ [$CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H$]*
- **Solvent:** *Dichlorobenzene, $C_6H_4Cl_2$*

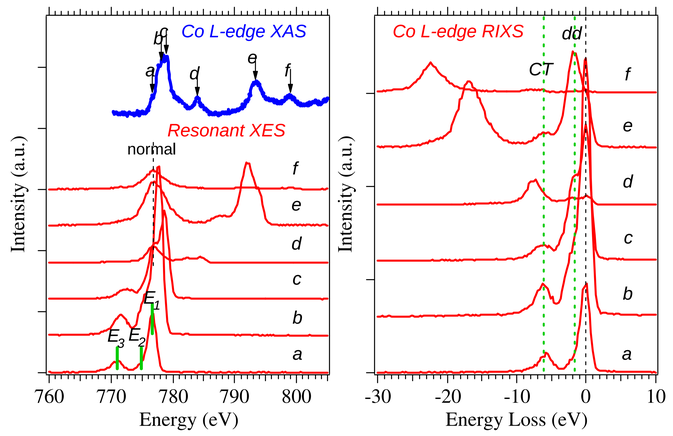




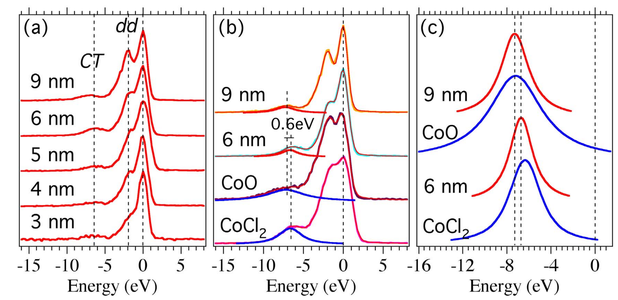
The most notable feature in the spectra of the Co nanocrystals is the new absorption peak at 6 eV above the main absorption edge that is absent in the Co metal, CoO, Co_3O_4, and $CoCl_2$. This satellite peak is assigned as MLCT transitions between Co and the oleic acid or 1,2-dichlorobezene.

In Co metal, the ground state is $4s^23d^7$, while for CoO, one uses the ground state configuration [$3d^7 + 3d^8L^{-1}$] (L^{-1}denotes a hole in the ligand level). Although this explained the CoO spectrum quite well, the [$3d^7 + 3d^8L^{-1}$] never yielded a significant satellite contribution, as seen in Co nanocrystals. The only known octahedral systems with large satellites are cyanide complexes, where large satellites are caused by π back-bonding, i.e., [$3d^7 + 3d^6L$]. The main structure is a [$2p^53d^8 + 2p^53d^7L$] bonding combination and the satellite is the antibonding part. It is worth noticing that the MLCT acts mainly on the t_{2g} electrons.

In-situ RIXS of Co nanocrystal suspension:



Strong resonance effects are observed in the scattering intensity as incident energy changes from a to f. The same data are plotted on an energy-loss scale.



(a) Raman features of Co L_3-edge RIXS for Co nanocrystals of different diameters. (b) RIXS spectra of CoO and $CoCl_2$ compared with nanocrystals of 6 and 9 nm. The spectra are fitted by a sum of Voigt function. (c) The charge-transfer peaks, at -7.3 eV for the 9 nm and -6.7 eV for the 6 nm nanocrystals, respectively, coincide in position with those of CoO and $CoCl_2$.

Conclusions

1. XAS, XES, and RIXS were used to study Co nanocrystals.
2. Nanocrystals interact more strongly with solvent molecules in the initial stages of growth, while at a later stage, the interaction is dominated by the oleic acid surfactant.
3. The interaction between Co nanocrystals and surfactant and solvent molecules can be measured by in situ techniques, opening the way for in situ studies of nanostructure growth and reactivity.

Citations

1. "Electronic Structure of Cobalt Nanocrystals Suspended in Liquid", Hongjian Liu, Jinghua Guo, Yadong Yin, Andreas Augustsson, Chungli Dong, Joseph Nordgren, Chinglin Chang, Paul Alivisatos, Geoff Thornton, D. Frank Ogletree, Felix G. Requejo, Frank de Groot, and Miquel Salmeron, Nano Lett. **7**, 1919 (2007).
2. "Direct Contact vs. Solvent-shared Ion Pairs in $NiCl_2$ Electrolytes Monitored by Multiplet Effects at the Ni(II) L-edge X-Ray Absorption", Emad F. Aziz, Stefan Eisebitt, Frank de Groot, Jau W. Chiou, Chungi Dong, and Jinghua Guo, Wolfgang Eberhardt, J. Phys. Chem. B **111**, 4440 (2007).
3. "One-Step Synthesis of Highly Water-Soluble Magnetite Colloidal Nanosrystals", Jianping Ge, Yongxing Hu, Maurizio Biasini, Chungli Dong, Jinghua Guo, Ward P. Beyermann, and Yadong Yin, Chem. Eur. J. **13**, 7153 (2007).
4. "Soft-x-ray Spectroscopy Experiment of Liquids", Jinghua Guo, Tyler Tong, Lukas Svec, John Go, Chungli Dong, and Jau-Wern Chiou, JVST A **25**, 1231 (2007).

Acknowledgments

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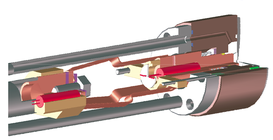
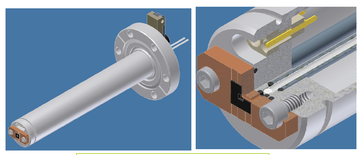
Further information

Chemical cells under development:



Temperature: 80 - 550 K



Electrochemical, Flow Liquid Cell

Please contact *jguo@lbl.gov*. More information on this and related projects can be obtained at http://ssg.als.lbl.gov/ssgdirectory/guo/jguo_Co-nanos.pdf

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