

Atomic-Scale Reversible Opto-Structural Switching of Few Atom Luminescent Silver Clusters in LTA Zeolites Unraveled By a Combination of XAFS and Optical Spectroscopies

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Introduction

Highly luminescent few-atom silver clusters (AgCLs) confined within LTA and FAU zeolites feature large Stokes shifts and broad emission colors spanning over the whole visible range with promising applications in bio-imaging, sensing and photonics.¹ The zeolite topology, the AgCLs charge, the type of extra framework cations and the hydration level are all well-known tunable parameters for tailoring and stabilizing molecular AgCLs in zeolites.¹⁻³ However, the detailed correlations between the structures at the atomic level of AgCLs and their optical properties is still debated. In particular, the detailed understanding of the dynamic interaction of AgCLs with the zeolite framework oxygen atoms (O_F) and/or extra-framework water ligands and its role on the cluster formation, structure and optical properties has not been fully achieved. Herein, we report a reversible water-tunable on-off optical and structural switch of luminescent AgCLs into their non-luminescent (dark) counterparts in partially Ag exchanged Ag_3Na_9LTA zeolite. We have applied a combination of XAFS, UV-Vis-NIR and PL spectroscopies to unravel the dynamical structural changes at the atomic scale responsible for switching AgCLs optical properties.

Experimental methods

Partially Ag exchanged Na-LTA zeolite (Ag_3Na_9LTA) in their hydrated and dehydrated states were investigated with XAFS in transmission mode at the Ag K-edge at ROBL (BM20) and DUBBLE (BM26A) Beamlines of The European Synchrotron (ESRF). Emission and excitation spectra were recorded using an Edinburgh Instruments FLS 980 spectrometer. An UV-Visible-NIR Lambda 950 Perkin Elmer spectrometer equipped with a 150 mm diameter integrating sphere coated with Spectralon was used to record the DRS spectra from 200 to 2500 nm.

Results and discussion

Combined XAFS and optical spectroscopies show that the hydration and rehydration of the $\text{Ag}_3\text{Na}_9\text{LTA}$ sample produce a material with green-yellowish luminescence that originates from Ag_4 clusters coordinated to 4 extra-framework water molecules located in the center of the sodalite cages and surrounded by Na and Ag cations positioned along the axis of the sodalite six-membered rings. Upon dehydration, the luminescent $\text{Ag}_4(\text{H}_2\text{O})_4$ clusters are entirely converted into octahedral Ag_6 clusters that directly interact with the O_F of the sodalite four-membered rings. The new $\text{Ag}_6(\text{O}_F)_{14}$ clusters are non-luminescent, while the zeolite color changes from pale yellow to brick-red. XAFS results clearly demonstrate that besides the well documented size and quantum confinement effect,^{2, 3} water and framework oxygen ligands play a crucial role in the opto-structural switch highlighting the high sensitivity of few atoms clusters functional properties towards atomic scale structural changes.

Conclusion

Hydration - dehydration of partially Ag exchanged LTA zeolites ($\text{Ag}_3\text{Na}_9\text{LTA}$) induce a remarkable reversible optical switch that is closely associated with the atomic scale structural dynamics of AgCLs confined in the sodalite cages of LTA zeolites. This reversible high-contrast opto-structural switching of AgCLs in LTA zeolites is a unique and responsive model system that has multiple potential applications as sensor, erasable memory and molecular probes.

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References

1. O. Fenwick, E. Coutino-Gonzalez, D. Grandjean, W. Baekelant, F. Richard, S. Bonacchi, D. De Vos, P. Lievens, M. Roeffaers, J. Hofkens and P. Samori, *Nat Mater*, 2016, 15, 1017-1022.
2. G. De Cremer, E. Coutino-Gonzalez, M. B. Roeffaers, B. Moens, J. Ollevier, M. Van der Auweraer, R. Schoonheydt, P. A. Jacobs, F. C. De Schryver, J. Hofkens, D. E. De Vos, B. F. Sels and T. Vosch, *J Am Chem Soc*, 2009, 131, 3049-3056.
3. E. Coutino-Gonzalez, W. Baekelant, J. A. Steele, C. W. Kim, M. B. J. Roeffaers and J. Hofkens, *Accounts Chem Res*, 2017, 50, 2353-2361.