Characterization of Photoluminescence and Crystal Structure of Luminescent Silver nanoclusters Confined Zeolite X

Cheol Woong Kim¹, Wouter Baekelant¹, Maarten B. J. Roeffaers², Johan Hofkens^{1,*}

¹Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium ²Center for Surface Chemistry and Catalysis, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

E-mail: cheolwoong.kim@kuleuven.be

Luminescent silver nanoclusters confined inside large single crystals of Ag-exchanged zeolite X have been synthesized and their photoluminescence and crystal structure were characterized. Large colorless single crystals up to 120 μ m of Na-X zeolite (FAU, Si/Al = 1.4) were synthesized from gels of composition 2SiO₂ : Na₂O : Al₂O₃ : xH2O : TEA (tetraethylammonium) at 353 K for 28 days^[1] (Fig. 1a)). After calcination at 723 K for 2 days, removing the remaining structure directing agents (SDAs), Ag⁺-exchanged zeolites were prepared by ion-exchange method with an aqueous AgNO₃ solution and then the crystals were activated by heat-treatment at 723 K in air to achieve the formation of luminescent silver nanoclusters in the zeolite cavities. Heat-treated Ag-X single crystals display an intense yellow emission (560 nm emission maximum, Fig. 1b)) when excited at 310 nm with external quantum efficiency of maximum 41 %. The crystal structures of these heat-treated Ag-X were determined crystallographically with synchrotron X-radiation and refined in the cubic space group $Fd\overline{3}m$ (a = 25.0581(5)) (Fig. 1c)). The detail structural information could be used to identify the correlation between crystal structures and photoluminescence properties^[2,3] of Ag-X zeolites possessing luminescent silver nanoclusters, towards the rational design and synthesis of metal nanoclusters confined in zeolite cavities that could have potential applications in the design of lighting devices.

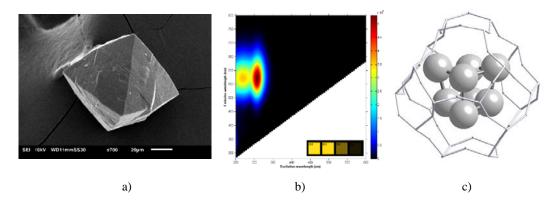


Figure 1. Luminescent silver nanoclusters confined in the zeolite cavities: a) SEM image of synthesized large single crystals of Na-X, b) Excitation-emission 2D-plot of heat-treated Ag-X, and c) Ag₈ nanocluster in the sodalite cavity of heat-treated Ag-X zeolite.

Funding: the Belgian Federal government (Belspo through the IAP VI/27 and IAP-7/05 programs), the European Union's Seventh Framework Programme (FP7/2007-2013 under grant agreements no. 310651 SACS and no. 307523 ERC-Stg LIGTH to M.B.J.R.), the Flemish government in the form of long-term structural funding "Methusalem" grant METH/15/04 CASAS2, the Hercules foundation (HER/11/14), the "Strategisch Initiatief Materialen" SoPPoM program, and the Fund for Scientific Research Flanders (FWO) grant G.0B39.15.

Acknowledgement: We gratefully acknowledge the support of the Swiss-Norwegian Beamlines (ESRF at Grenoble, France) for the use of their diffractometers and computing facilities.

References:

- [1] W. T. Lim, S. M. Seo, T. Okubo, M. Park, J. Porous Mater., 2011, 18, 305
- [2] G. De Cremer, E. Coutino-Gonzalez, M. B. J. Roeffaers, B. Moens, J. Ollevier, M. Auweraer, R. Schoonheydt, P. A. Jacobs, F. C. De Schryver, J. Hofkens, D. E. De Vos, B. F. Sels, T. Vosch, J. Am. Chem. Soc., 2009, 131, 3049
- [3] O. Fenwick, E. Coutino-Gonzalez, W. Baekelant, F. Richard, S. Bonacchi, M. B. J. Roeffaers, J. Hofkens, P. Samorì, *Nat. Mater.* **2016**, 15, 1017