Luminescent zeolite composites with outstanding external quantum efficiency using silver clusters as dopants

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Abstract
Silver-zeolite composites are a versatile family of materials. Their applications range from catalysts, to antibacterial materials, information storage, and pressure or chemical sensors. The use of zeolites as molecular scaffolds for the fabrication of luminescent materials by incorporating transition metals has widely been explored. The creation of such oligoatomic metal clusters in zeolite voids is based on a ship-in-a-bottle approach, taking advantage of the high cation exchange capacity of zeolites. One of the most popular methods to produce metal clusters in zeolitic matrices is by exchanging the original charge-balancing cations present in the zeolites with the desired metal ions, followed by a thermal treatment. Small clusters are thus formed, whose size is ideally limited by the cage/pore dimensions of the zeolite topology. The mechanism of cluster formation has been proposed as an “autoreduction” mechanism, in which the electrons needed for metal ion reduction are provided by zeolite framework oxygen (resulting in local lattice damages) and/or by oxygen of the hydration water in the zeolite. Alternatively, chemical reduction and photoactivation, have been employed for the creation of metal clusters and nanoparticles in zeolite matrices.
We recently reported the production of luminescent silver-clusters in zeolites. In this study, the effect of zeolite topology, silver loading, and counter-ion on the luminescence color, was systematically evaluated; green and red emitters were mainly found in LTA zeolite, while for FAU zeolite green and yellow emitters were observed. The photo-, chemo- and hydro-stability of the materials were investigated in detail. The study revealed dramatic differences among the different types of silver clusters; most of the samples presented a high photo and chemo stability. Based on these results, silver containing zeolites were suggested to be used as potential phosphor substitutes for the fabrication of fluorescent lamps or as wavelength converters in solar cells because of their large stokes shift and luminescent performance. Next to price, the major decisive factor for such application is the external quantum efficiency (EQE). The EQE of a luminescent material is defined as the ratio of the amount of photons emitted to the amount of photons absorbed by a material, this measure takes into account losses associated with the absorption of photons by non-emissive species, like for instance in this case silver ions and impurities associated with the starting material. The EQE parameter is of paramount importance to carefully select the luminescent materials for different applications. To the best of our knowledge there are no data available concerning the measurement of EQE of silver-clusters zeolite composites. One of the reasons for this lack of information on the luminescent of silver-clusters zeolite composites, is the difficulty of correctly measuring the EQE on highly scattering solid materials, especially when approaching the UV region for excitation.
Since the report published by de Mello and collaborators, in which an integrating sphere was used to measure the absolute EQE of thin dye doped films, many other studies were carried out to obtain the EQE of a wide range of solid samples showing the versatility of the method. For instance, the EQE of fluorescent dye-loaded zeolites, fluorescent nanopigments incorporated in solid matrices, and polymer light emitting films have been reported using the integrating sphere method. Unlike the silver zeolites, most of the reported materials present a small stokes shift for which re-absorption problems are obviously expected. Furthermore, their optimal excitation wavelengths fall in the visible area, while the silver-clusters zeolite composites are mainly excitable by ultraviolet light. Remarkably, while all reports agreed on the usage of the integrating sphere, the set-up configuration and the methodology of the EQE experiments was sometimes different and often depending on the sample requirements. In order to obtain reliable results, it is critical to perform appropriate calibrations, taking into account the nature of the sample; thin film, loose powder, powder incorporated in a polymer, etc., and corrections for re-absorption processes.
We have measured for the first time the external quantum efficiency (EQE) of silver-clusters containing zeolites. These materials, fabricated by cation exchange followed by a thermal auto-reduction process, have EQE's up to 69 percent. Due to their unique spectral features such as large stokes shift and high EQE, these materials could be potentially used as phosphors for the fabrication of fluorescent lamps and as wavelength convertors in solar cells.

References

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Figures

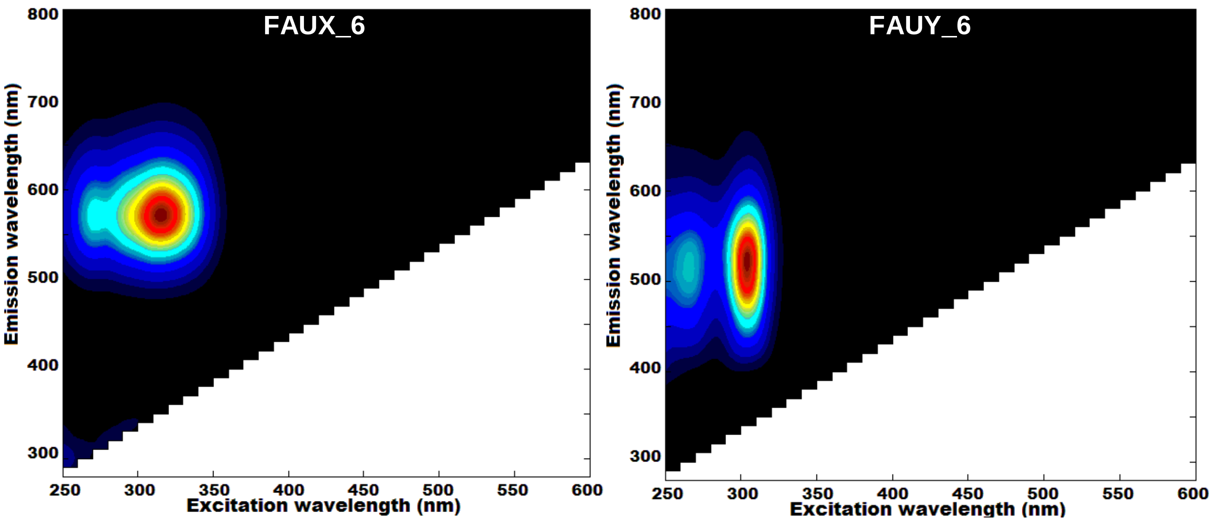

Figure 1. Emission-excitation 2D plots of two different luminescent silver-zeolite composites. Faujasite X zeolite with intermediate silver loading (left). Faujasite Y zeolite with intermediate silver loading (right).

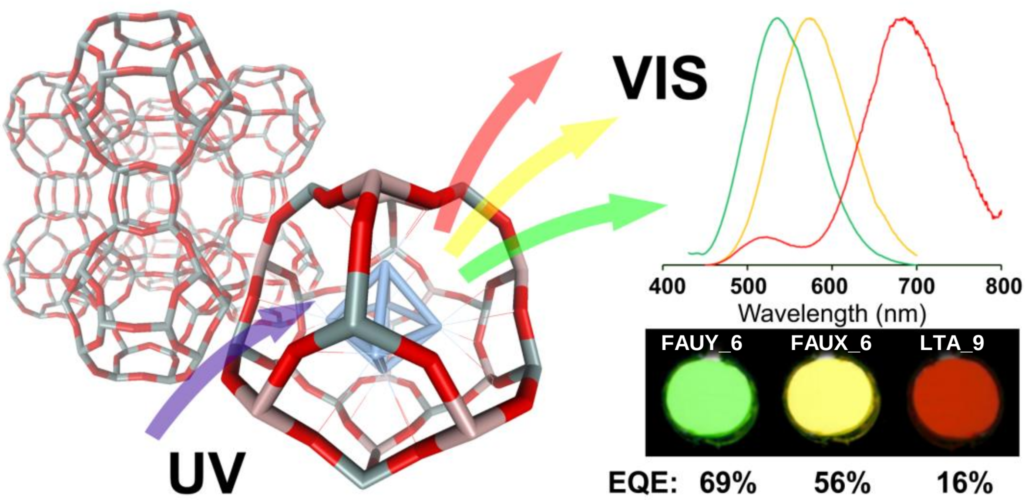

Figure 2. Schematic representation of the silver clusters contained in a sodalite cage (faujasite and LTA unit cage). Emission spectra of three luminescent silver-zeolite composites upon UV excitation (right side up), and photographs under 366 nm irradiation with their respective EQE values (right side low).