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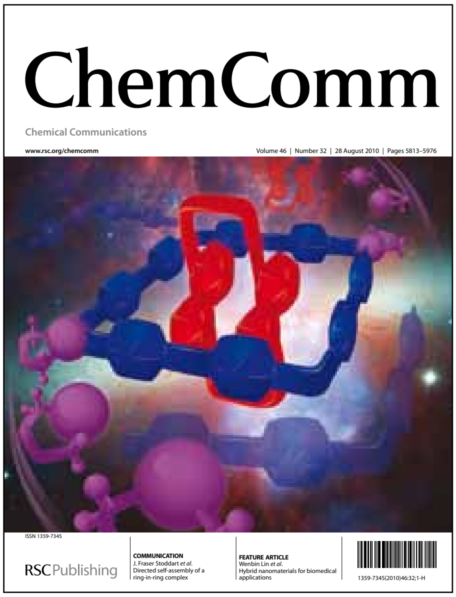

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ARTICLE TYPE

X-ray Irradiation-Induced Luminescent Silver Clusters Formation In Nanoporous Matrices

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We report the formation of luminescent silver clusters in zeolites by a fast, highly accurate, and controlled activation of silver ions entrapped in sodalite cages of LTA and FAU zeolites using high-brilliance soft X-rays. The activated luminescent samples were investigated by employing a combination of stationary and time-resolved spectroscopic techniques.

The peculiar optical and catalytic properties of oligoatomic (noble) metal clusters, which are significantly different from those displayed at bulk level, make them very attractive for different applications in diverse fields such as plasmonics,[1] catalysis,[2] and photonics.[3] However, at these small length scales and such level of atomic organization, rational design and synthesis is crucial since the functionality of these clusters is strongly influenced by their size, shape, charge, and interaction with the environment.[4] Template-mediated strategies are nowadays widely utilized to produce metal clusters with well-defined sizes and shapes; these methods are based on a self-organization approach in which the size and shape of the final metal cluster are ideally controlled by the dimensional restrictions induced by the hard template structure during the cluster formation. Popular templating host structures include glassy matrices,[5] metal-organic frameworks,[6] and zeolites.[7] The loading method of the precursor metal ions as well as the activation technique to form the metal clusters can vary significantly from host to host. Within the template-mediated strategies, ion exchange and ion implantation are popular doping methodologies, whereas heat-treatment[8] and/or electromagnetic radiation[9] have been widely utilized as activation methods to trigger the formation (reduction, migration of metal ions within the scaffold) of metal clusters. However, the development of highly reproducible synthesis methods that could allow a fine tuning of the cluster shape and size remains a challenge for the scientific community. In a recent study, a clear relationship between the luminescence properties and the clusters size was demonstrated in heat-treated[10] and photon-activated[7,11] silver clusters incorporated in zeolitic matrices. Their optical properties were shown to be strongly influenced by the host crystal structure, the silver content, and the nature of the remaining counter-balancing ions. Remarkably, these silver-clusters zeolite composites present high photo- and chemical stability and high external quantum efficiencies,[12] making them very attractive, for instance, as phosphors for several applications, such as in fluorescent lamps and upconverter materials. More recently, the formation of sub-nanometer luminescent silver clusters in photosensitive glasses via a thermal/photon-induced approach was reported.[13] Although the use of different host systems for the creation of well-defined luminescent oligoatomic metal clusters is emphasized in the previous examples, researchers have also recently focused on the development of highly controlled activation procedures. Eichelbaum and co-workers[14] have explored the use of X-ray irradiation for the generation of gold and silver luminescent clusters in glassy substrates. They found that upon X-ray irradiation followed by a thermal treatment, green and white emission centers were created in gold and silver doped soda-lime silicate glasses respectively. The green emission was assigned to gold dimers bound to silanol centers whereas the white emission was attributed to a mixture of small silver clusters, Ag_2, Ag_3 and Ag_4. Due to its short wavelength, high brilliance, high stability, and low divergence, synchrotron X-ray lithography is potentially suited for the fabrication of luminescent silver clusters in zeolites. However, as compared to heat-treatment activation, more sophisticated and less accessible instrumentation is needed. In this report we explore the selective formation of luminescent silver clusters via X-ray irradiation, without the need for subsequent heat treatment, in different zeolite topologies, all containing sodalite cages. The optical properties of the formed luminescent Ag-clusters were extensively studied and compared to heat and photo-activated samples with the same composition. To the best of our knowledge there have been no previous reports on the formation of luminescent silver clusters in zeolite matrices via X-ray irradiation.

To investigate the influence of the zeolite topology and counter-balancing ion, we chose two different topologies (LTA and FAU) and two different counter-balancing ions (Na & K) based on previous results found in heat-treated and photo-activated silver exchanged zeolites. In heat-treated silver loaded K-LTA samples, two main emission maxima were found when low (550 nm) and high (700 nm) silver loadings were respectively used; whereas in silver loaded Na-FAU, depending on the silicon to aluminium ration (Si/Al), green and yellow emitters were reported.[7,10] The silver loaded zeolites were prepared by suspending 1 gram of the zeolite material (K-LTA Si/Al = 1, FAU-X Si/Al = 1.2, FAU-Y Si/Al = 2.7; supplied by

Union Carbide) in 500 mL of a silver nitrate aqueous solution (1.1 to 3.5 mM; Sigma-Aldrich, 99.99% purity) for 2 h in the dark. According to their silver content and assuming a complete uptake of the silver ions in the solution by the zeolite host, the following samples were used in this study; Ag_3K_9-LTA and Ag_9K_3-LTA for K-LTA topology, and Ag_6Na_5-FAU-X & $Ag_3Na_{3.5}$-FAU-Y for FAU topology, where the subscripts refer to the amount of silver/counter-balancing ions in the normalized zeolite unit cell (see S2 ESI). After the ion-exchange process, the suspended powder was recovered by filtration using a Buchner filter and washed several times with miliQ water until no silver ions were present in the washing water; precipitation with sodium chloride was used to test this. The recovered powder was dried for 1 h at 50 °C to remove the excess of water in the sample. The dried powder was pressed in pellets (1.3 cm diameter, 1 mm thickness) with a mechanical press (1.5 tons), and stored in the dark prior X-ray activation. For each sample an area of approximately 1 x 1 cm^2 on the surface of the pellet was irradiated with a highly focused X-ray beam (high-flux) with energy close to the Ag L_2 edge (3524 eV) at the ID26 beamline of the European Radiation Synchrotron Facilities (ESFR Grenoble, France). This area corresponds to 100 separate measurements of X-ray absorption near edge structure spectra (XANES) in high energy resolution fluorescence detection mode (HERFD), each collected at a different location with fixed exposure time and beam spot separation using an automated translation stage. Three different short exposure times of 10, 50, and 60 seconds, corresponding to irradiation doses of $7.19x10^4$, $3.93x10^5$, and $4.88x10^5$ Jm^{-2} respectively, were used according to the stability of the samples which was determined after a preliminary calibration run with incremented exposure times (Table S2 ESI). Prolonged exposure at a fixed position in the centre of the pellets systematically gave a non-luminescent black trace (Fig. 1).

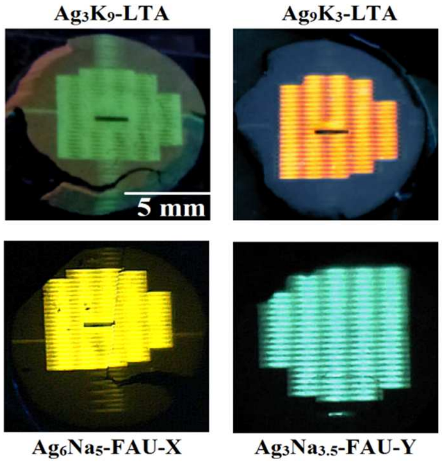

Fig. 1 Photographs of the X-ray irradiated silver-zeolites under 366 nm illumination.

We performed the steady-state photophysical characterization of the X-ray activated samples. In Fig. 2 the two-dimensional excitation-emission plots of the luminescent clusters formed by X-ray irradiation are shown. Two excitation wavelengths at 270 and 310 nm for Ag_6Na_5-FAU-X and $Ag_3Na_{3.5}$-FAU-Y resulted in emission at 570 nm for Ag_6Na_5-FAU-X and 520 nm for $Ag_3Na_{3.5}$-FAU-Y. However, higher intensities were found when the samples were excited at 310 nm. The K-LTA samples (Ag_3K_9-LTA and Ag_9K_3-LTA) display a more complex luminescent behavior. In the low silver loaded sample two principal excitation wavelengths were found (310 and 340 nm) with similar emission maxima with a peak at about 540 nm, whereas in the high silver loaded sample the excitation maximum was located around 400 nm giving rise to emission centered at 660 nm. Nevertheless, two other excitation maxima (300 and 350 nm) also resulted in emission at 600 nm, albeit weaker. Previous reports assigned a Ag_6^{n+} cluster to a red/orange emitter[10] in heat-treated loaded LTA zeolites with high silver loading whereas the green emission[15] at lower silver loadings was attributed to a Ag_{3-4}^{n+} cluster. For heat-activated silver FAU samples the luminescence was tentatively assigned[8] to a Ag_3^{n+} cluster. We observed that the different emission maxima found in the X-ray irradiated samples are very similar to the samples previously reported where heat-activation and UV irradiation was used.[7,10] Next, we measured the diffuse reflectance spectra (DRS) of X-ray activated as well as the corresponding non-activated samples to examine the presence of the different absorbing species. DRS spectra of the non-activated samples show two main absorption bands between 200 and 280 nm (Fig. S6 ESI). Such signals have been previously associated with isolated silver ions located at specific sites within the zeolite framework in silver exchanged LTA and FAU zeolites.[16] The absence of luminescent silver clusters in the samples not submitted to an activation process is further corroborated by their two-dimensional excitation-emission spectra (Fig. S3 ESI). On the contrary DRS spectra of the X-ray irradiated samples showed new absorbing bands, not present in non-activated samples. For silver exchanged FAU-Y-zeolites the absorbance of the X-ray irradiated samples resembles the analogous heat-treated hydrated sample (Fig. S7 ESI).

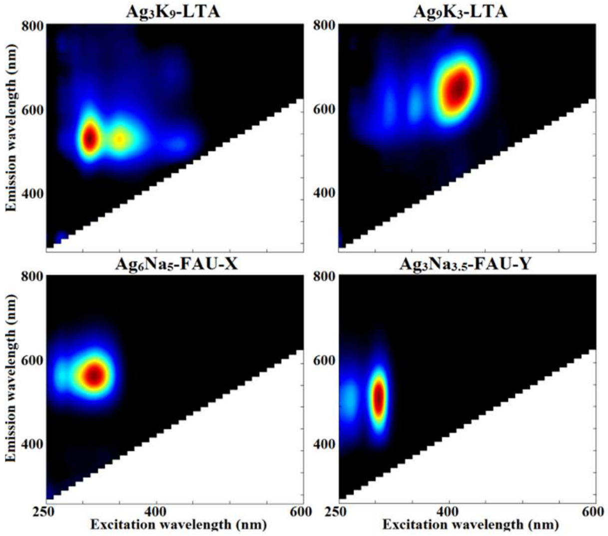

Fig. 2 Excitation-emission two-dimensional plots of the X-ray activated Ag_3K_9-LTA, Ag_9K_3-LTA, Ag_6Na_5-FAU-X and $Ag_3Na_{3.5}$-FAU-Y.

Time-resolved luminescence measurements of the X-ray activated samples revealed for the green emitting Ag_3K_9-LTA three decay components of 0.35 ns, 1.60 ns, and 4.10 ns, where each component has its maximum intensity at wavelengths ranging between 440 and 640 nm (see S6 ESI).These time constants have values close to those measured in the analogous heat-treated material in which they were related to at least three different local environments in which the clusters are present.[10] In Ag_9K_3-LTA only two components were observed (0.38 and 2.50 ns) whereas for Ag_6Na_5-FAU-X and $Ag_3Na_{3.5}$-FAU-Y similar decay kinetics were obtained with two components with average values of 0.60 and 3.30 ns. A detailed time-resolved spectroscopic investigation aiming at identifying all emitting species and revealing their excited state dynamics is currently ongoing.

The time resolution of XANES measurements did not allow us to follow in a time-dependent fashion the clusters formation nor the change in oxidation state at the early stage of the clusters formation. However, once the luminescence clusters were formed we could monitor their behavior until a non-luminescent phase was created. Inspection of the HEFRD-XANES spectra of the luminescent and non-luminescent Ag_3K_9-LTA X-ray irradiated material (Fig. S8 ESI) reveals that both present very similar shapes that are very distinct from those of Ag metal and Ag_2O bulk reference spectra (a similar behavior is found for the 3 other luminescent materials). The first sharp peak at ca. 3524 eV isolated from the rest of the spectral structures at higher energies could correspond to discrete empty electronic levels specific of small oligomeric Ag clusters.[17] This is supported by the much higher and constant absorption level observed in the low energy part of the spectra of the references (below 3540 eV) that correspond to the band structure expected in bulk materials. Comparison between the HERFD-XANES spectra of the non-luminescent and luminescent Ag_3K_9-LTA sample showed that the first sharp peak at ca. 3524 eV broadens whereas the resonance at 3532 eV is shifted to higher energy and the intensity of the main resonance at 3546 eV increases, suggesting structural changes and a more ordered and/or larger Ag-based nanosized phase in the non-luminescent sample. An investigation of the influence of X-ray irradiation on the location of exchangeable cations in FAU zeolites revealed the formation of a mixed oxide phase at prolonged exposure times.[18] The appearance of such mixed oxide phase was attributed to the reaction of the exchangeable cations with the oxygen of the damaged zeolite framework. In this case, the formation of a nanostructured silver oxide phase could be associated to the darkening of the samples (non-luminescent phase).

In this study, we report for the first time the formation of luminescent silver cluster in zeolites via X-ray irradiation and their detailed spectroscopic comparison with the analogous heat-treated silver zeolites. No significant differences in optical properties were found between X-ray irradiated and heat-treated silver zeolites indicating that very similar species were formed. However, activation of silver zeolites with X-rays provides a tightly controllable spatial production of luminescent silver clusters at fast time scales. Because of the short wavelength used it should be possible to create luminescent micro(nano)-structures in different silver zeolite arrays with X-ray lithography. This could provide an opportunity for the development of alternative light-emitting devices at micro and macro scales. This contribution also highlights the large modification that X-rays can induce on sub-nanometer metal structures included in zeolitic scaffolds, a very important issue to take into consideration in the data analysis and interpretation of the information obtained by X-rays based techniques. Further structural characterization of these luminescent clusters is ongoing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Silver zeolite synthesis, SEM, DRS, emission-excitation measurements, description of the X-ray irradiation set-up, lifetime measurements and additional referrences. See DOI: 10.1039/b000000x/

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