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Citation: [Applied Physics Letters](#) **105**, 211903 (2014); doi: 10.1063/1.4902530

View online: <http://dx.doi.org/10.1063/1.4902530>

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## Reversible emission evolution from Ag activated zeolite Na-A upon dehydration/hydration

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(Received 27 October 2014; accepted 12 November 2014; published online 25 November 2014)

Reversible emission evolution of thermally treated Ag activated zeolite Na-A upon dehydration/hydration in vacuum/water vapor was observed. The phenomenon was observed even for the sample with low Ag<sup>+</sup>-Na<sup>+</sup> exchanging (8.3%), indicating that the emission from Ag activated zeolites may not come from Ag clusters while from the surrounding coordinated Ag<sup>+</sup> ions or Ag<sup>0</sup> atoms. It was disclosed that the characteristic yellow-green emission at  $\sim 560 \pm 15$  nm is strongly associated with the coordinating water molecules to the Ag<sup>+</sup> ions or Ag<sup>0</sup> atoms, which is clear evidence for that the efficient emission from Ag activated zeolites may not originate from the quantum confinement effect. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4902530>]

Silver (Ag) activated guest-host systems in various forms including DNAs,<sup>1</sup> proteins,<sup>2</sup> or polymers<sup>3</sup> encapsulated Ag clusters, Ag activated zeolites,<sup>4</sup> and glasses<sup>5,6</sup> have been demonstrated as highly efficient luminophores, which may have promising application in bio-labeling,<sup>7</sup> white light emitting diodes (LEDs),<sup>8</sup> down-converter for solar cells,<sup>6</sup> probes for some specific hazardous chemicals or ions,<sup>2,9</sup> optical recording/encoding,<sup>10,11</sup> dosimetry,<sup>12</sup> etc. However, till now, the exact luminescence mechanism from Ag activated materials is still not sufficiently clear. One of the most proposed explanations is that the emission is from the sub-nm scale molecule-like Ag clusters complying with the quantum confinement effect, that is, when the size of the metal clusters is comparable to the electron Fermi wavelength ( $\sim 0.5$  nm for Ag), discrete energy levels can be formed and fluorescent molecule-like emission properties will be exhibited.<sup>13,14</sup> The concept of metal clusters is amazing since it bridges the gap between individual metal ions/atoms and metal nanoparticles in the luminescence and photonics community. Concerning the host materials to stabilize the highly agglomerable Ag clusters, zeolites is known to be one of the few solid matrices owing to its spatially well confined cages and channels. Among the various types of zeolite matrices, Ag activated zeolite A is intensively investigated, from which the strong and broad yellow-green emission peaked at 530–590 nm is the most often observed. Previously, this emission was tentatively attributed to the linear Ag<sub>3</sub><sup>+</sup> (Ag<sup>+</sup><sub>6-ring coordinated</sub>-Ag<sup>0</sup><sub>4-ring coordinated</sub>-Ag<sup>+</sup><sub>6-ring coordinated</sub>) trimer cluster formed in the sodalite cage (also called  $\beta$ -cage).<sup>4</sup> Formation of Ag cluster in zeolite A can be achieved via various activations such as thermal treatment,<sup>15,16</sup> UV illumination,<sup>17</sup> and X-ray irradiation.<sup>18</sup> The existence of Ag clusters in zeolite A has been demonstrated by X-ray absorption fine structure (XAFS),<sup>19,20</sup> far-infrared spectroscopy,<sup>21</sup> electron spin resonance (ESR),<sup>4</sup> scanning tunneling electron microscopy (STEM),<sup>22</sup> etc. However, recently it has been proposed by Miyanaga *et al.* that based on the *in situ* XAFS and photoluminescence (PL) spectra in different gas

environmental conditions, the emission from the Ag<sup>+</sup> fully exchanged zeolite Na-A (denoted as Ag<sub>12</sub>, Na<sub>0</sub>-A) may be due to structural change of the zeolite framework induced by the formation and breakdown of Ag clusters other than the Ag clusters itself. Their conclusion was supported by the fact that emission from the sample exposed in air was of the highest intensity, while in this situation Ag clusters were actually “broken up.”<sup>23</sup> Indeed, the existence of Ag clusters does not ensure that the emission comes from clusters. Furthermore, theoretically, the quantum confinement effect applies only for those Ag clusters with the diameter less than 2 nm. In fact, efficient emission from large Ag dots with the average diameter of  $18 \pm 3$  nm was still observed. From the high resolution transmission electron microscopy images of the luminescent and the non-luminescent Ag nano dots of the same size, the origin of emission from such large nano dots was explained in the way of a multi-domain, polycrystalline structure with an average (single crystalline) domain scale of 0.9 nm.<sup>24</sup> Still, this reminds that the luminescence mechanism of Ag species may not simply be the quantum confinement effect, since no obvious gaps or “walls” were observed between the domains (the single crystalline sub-nm grains) to prevent the electron migration. It has been shown that two key factors influence the emission properties of Ag species: one is the quantum confinement effect, specifically, the size and the configuration (including the shape and the electronic charges),<sup>13,14</sup> the other is the coordinating environment.<sup>25,26</sup> However, it seems that size and configuration were too much emphasized as the main origin of the emission, with the influence of coordinating environment left behind. Very recently, it was proposed by Chen *et al.* that the emission mechanism of Ag clusters conjugated by carboxylate ligands with the nanocomposite size in the range of 2–5 nm is the ligand (oxygen) to-metal (Ag<sup>+</sup>)-metal (Ag<sup>0</sup>) charge transfer transition.<sup>27</sup> Meantime, the strong dependence of emission wavelength on excitation was assigned to the surface plasmon resonance (SPR) absorption from the Ag metal nano core. This is an attempt for the exploring the mechanisms of emission from metal clusters in another way. However, since the total size of the nanocomposite is 2–5 nm (Ag<sup>0</sup> nano core is below 5 nm), efficient SPR cannot be

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expected generally. Compared with the complicated cation sites in organic and glass matrices, situations for zeolites may be simplified due to the almost definite cation sites located in the cages and channels, thanks to the long-distance periodical structure due to its inorganic crystalline nature. Furthermore, the definite sizes of the pores, cages, and channels are selectively permeable to certain kinds of molecules, so environmental change for the Ag species is feasible to achieve. Here, in this work, we report the reversible emission evolution of Ag activated zeolite A via the hydration/dehydration process in water vapor/vacuum. It is disclosed that the bright yellow-green emission at  $\sim 560 \pm 15$  nm and the near infrared (NIR) emission at  $\sim 855$  nm are possibly originated from the charge transfer transitions from the framework oxygen to the  $\text{Ag}^0$  atoms/ $\text{Ag}^+$  ions with the assistance of  $\text{H}_2\text{O}$  molecules, rather than the previously most proposed confinement effect.

Ag activated zeolite Na-A samples were prepared by ion exchanging and thermal treatment. Details for the sample preparation were described elsewhere.<sup>28</sup> 3g zeolite 4A powders (Tosoh, Japan) were stirred at room temperature for 24h in  $\text{AgNO}_3$  solutions, in which nominal  $\text{Ag}_1$ ,  $\text{Na}_{11}$ -A ( $\text{Ag}^+/\text{Na}^+$  exchanging is 8.3%) and  $\text{Ag}_{4.4}$ ,  $\text{Na}_{7.6}$ -A ( $\text{Ag}^+/\text{Na}^+$  exchanging is 36.7%) samples can be achieved, respectively. The actual loading content of  $\text{Ag}^+$  ions into the zeolite's framework is somehow lower than the nominal value since  $\text{Ag}^+$  can still be examined in the filtrate after the  $\text{Ag}^+/\text{Na}^+$  exchanging process. The  $\text{Ag}^+$  loaded zeolite powders were washed by centrifuging, dried at  $50^\circ\text{C}$  and then finally annealed at  $550^\circ\text{C}$  for 2h in air. To get a clear view of the emission characteristics of Ag species confined in zeolites, it is necessary to know the luminescence properties of pure zeolites upon heat-treatment first. So pure zeolite 4A powders without any treatment and thermally treated at  $350^\circ\text{C}$ ,  $550^\circ\text{C}$ , and  $650^\circ\text{C}$  in air for 2h were also prepared. The samples were loaded into a cryostat for measuring the PL spectra in vacuum/water vapor and the temperature dependent PL. The first spectrum at room temperature in vacuum for the temperature dependent PL measurement was taken when the emission evolution in vacuum almost stopped in terms of the converting rate within our experimental conditions. Excitation-emission 3D contours and PL spectra taken at room temperature in air were directly measured on a fluorospectrometer (Jobin Yvon, Fluorog 3, Horiba, Japan).

From the excitation-emission 3D contours of the pure zeolite 4A annealed at different temperatures presented in Fig. S1,<sup>29</sup> it is shown that similar emission features to that of the thermally treated Ag activated zeolite Na-A appear.<sup>4,28</sup> This phenomenon leads us to infer that the emission from pure zeolite Na-A upon thermal treatment might come from the  $\text{Na}^+$ -zeolite guest-host interaction. Compared with the  $\text{Ag}^+$  activated zeolite Na-A, the emission intensity is of 2 orders of magnitude weaker, which can be attributed to the weak coordination between the  $\text{Na}^+$  ions and the framework oxygen.<sup>30</sup>

For zeolite 4A, the critical size of the  $\alpha$ -cage is  $\sim 4.2 \text{ \AA}$ , and the critical size of the  $\beta$ -cage is  $\sim 3.0 \text{ \AA}$ .<sup>31</sup> The dynamic diameter of  $\text{H}_2\text{O}$  and  $\text{O}_2$  molecules is  $\sim 2.7 \text{ \AA}$  and  $\sim 3.6 \text{ \AA}$ , respectively. So  $\text{H}_2\text{O}$  molecules can enter and stay at both

the  $\alpha$ -cages and the  $\beta$ -cages, while only the  $\alpha$ -cages are available for oxygen molecules. PL spectra evolution of the  $\text{Ag}_{4.4}$ ,  $\text{Na}_{7.6}$ -A sample from air to vacuum and then to water vapor or oxygen are presented in Fig. 1. As the evacuating time goes by, the intensity of the  $\sim 560 \pm 15$  nm and the  $\sim 855$  nm emissions simultaneously decreased, while a new broad emission peaked at  $\sim 678$  nm started to appear, grow, and finally became the dominant emission. When water vapor was introduced into the cryostat's chamber, the  $\sim 560 \pm 15$  nm emission was immediately ( $<30$  s) recovered. Though it was proposed that dehydration is a common method for forming Ag clusters;<sup>4</sup> here, it is clearly shown that involvement of a proper amount of  $\text{H}_2\text{O}$  molecules is vital to the bright  $\sim 560 \pm 15$  nm emission. The NIR emission peaked at  $\sim 855$  nm was partially quenched, which may be caused by over-adsorption of the highly vibrational  $\text{H}_2\text{O}$  molecules. The  $\text{H}_2\text{O}$ -sensitive emission feature might enable Ag activated zeolites to be a sensor or gauge for humidity. In Ref. 23, the visible emission was totally quenched after the  $\text{Ag}_{12}$ ,  $\text{Na}_{40}$ -A sample being exposed in oxygen for 24h. On the contrary, after being exposed in oxygen for 24h, intensity of the  $\sim 560 \pm 15$  nm emission remained unchanged;

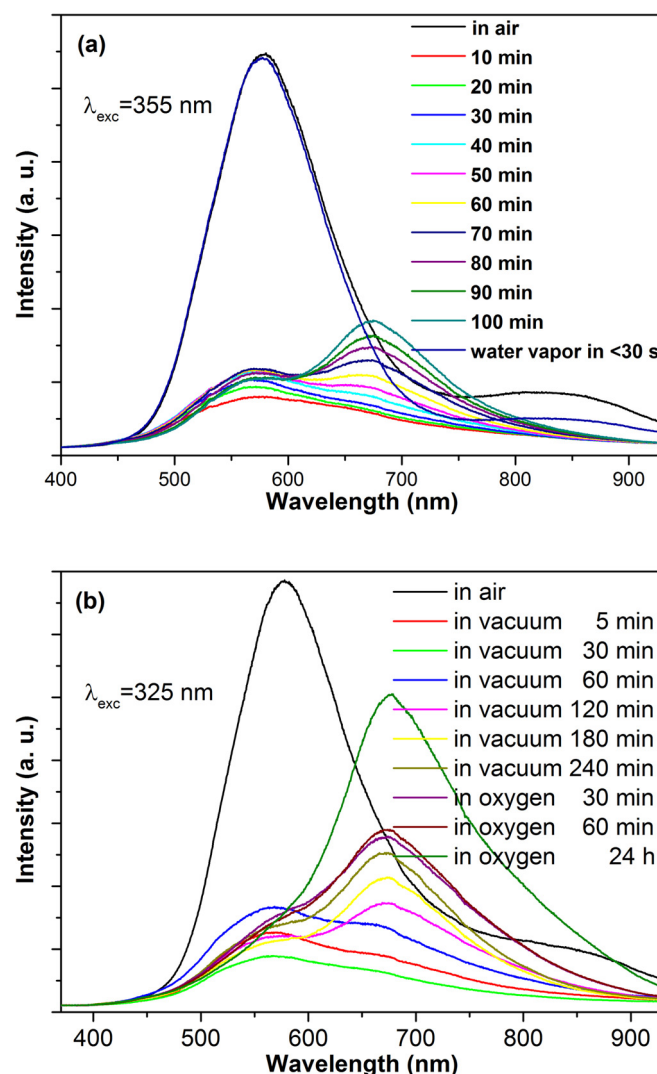


FIG. 1. PL evolution of  $\text{Ag}_{4.4}$ ,  $\text{Na}_{7.6}$ -A from air to vacuum then to water vapor (a) or oxygen (b).

while the intensity of the  $\sim 678$  nm emission was increased by almost 100% in our experiment (see Fig. 1(b)). Here, it should be noted that the above emission evolution is reversible and does not show obvious emission quenching after five cycles of repetition. The enhancement of the  $\sim 678$  nm emission in oxygen may be attributed to the further dehydration of the zeolite A framework by the extremely dry oxygen introduced from the gas cylinder, since the same phenomenon was observed when nitrogen was introduced instead. The inner surface of zeolite A has strong ability of capturing small polar molecules like  $\text{H}_2\text{O}$  due to the strong electric field between the cations and the framework  $\text{O}^{2-}$ . While for non-polar molecules such as  $\text{O}_2$  and  $\text{N}_2$ , the poor affinity with the pore walls<sup>32</sup> makes the coordination with the zeolite A framework (including the cations) negligible.

In Ref. 4, good homogeneity of the emission spectra was exhibited for different individual  $\text{Ag}_6$ ,  $\text{Na}_6$ -A zeolite microcrystals, indicating that the broad  $\sim 560 \pm 15$  nm emission is mainly not caused by inhomogeneous broadening. Seen from the temperature dependent PL spectra presented in Fig. 2, the emission peaks are still quite broad even at 10 K, which indicates that the broad emission feature is not only attributed to the phonon-electron coupling either. The broad emission feature of Ag activated zeolite at 10 K also seems to be against the explanation based on quantum confinement effect as the emission origin. Namely, since the configuration, especially, the ion and atom number and the shape of the Ag clusters, are perfectly confined in the cages and channels of zeolites, sharp emission line(s) is expected to be observed at cryogenic temperatures. However, this is completely not the case for Ag activated zeolites.

Excitation-emission 3D contour in the visible range for  $\text{Ag}_1$ ,  $\text{Na}_{11}$ -A exposed in air for 30 min after annealing at  $550^\circ\text{C}$  is shown in Fig. S2(a), from which the  $\sim 560 \pm 15$  nm emission still can be well observed. Besides the emission evolution upon dehydration/hydration in vacuum/water vapor, the same phenomenon was also observed upon dehydration/hydration by thermal annealing/(being exposed in air for 30 min), as shown in Fig. 2(b). It should be noted that according to the X-ray diffraction data of the vacuum dehydrated silver hydrogen zeolite A, it is shown that the ratio of the possibility for the  $\text{Ag}^+$  ions or  $\text{Ag}^0$  atoms to occupy the

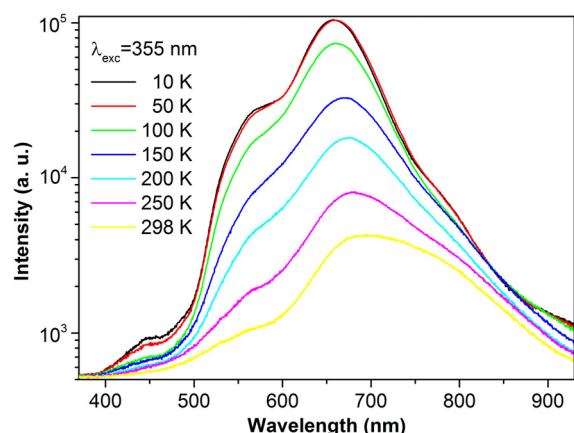


FIG. 2. Temperature dependent PL spectra for  $\text{Ag}_{4.4}$ ,  $\text{Na}_{7.6}$ -A under the 355 nm excitation.

6-ring ( $\alpha$ -cage), 6-ring ( $\beta$ -cage), 8-ring ( $\alpha$ -cage), and 4-ring ( $\beta$ -cage) co-cation sites is 44:9:7:6.<sup>33</sup> While in Refs. 34 and 35, it is disclosed that the yellow color appearance of the dehydrated  $\text{Ag}^+$  exchanged zeolite Na-A is only associated with the  $\text{Ag}^+$  ions sitting on the 4-ring coordinated sites in the  $\alpha$ -cages and the 4-ring coordinated sites in the  $\beta$ -cages are not available for  $\text{Ag}^+$  ions. In this case, formation of Ag clusters in the  $\beta$ -cages for  $\text{Ag}_1$ ,  $\text{Na}_{11}$ -A and  $\text{Ag}_{4.4}$ ,  $\text{Na}_{7.6}$ -A is almost impossible. Furthermore, from the results reported in Ref. 23 where it is shown that Ag clusters cannot be formed even for the  $\text{Ag}^+$  fully exchanged zeolite A when the samples are exposed in air or in water vapor, it seems that the possibility of forming Ag clusters for  $\text{Ag}_1$ ,  $\text{Na}_{11}$ -A and  $\text{Ag}_{4.4}$ ,  $\text{Na}_{7.6}$ -A in water vapor or air is negligible. Further investigation of the specific configuration of Ag activated zeolite A with low  $\text{Ag}^+$  loading concentration by XAFS will be conducted in our future work.

Noteworthy, similar to the reversible emission color change, reversible appearance color changes of Ag-exchanged zeolite A upon dehydration was reported early in the 1960s.<sup>36</sup> During the following four decades, the yellow and brick-red appearance was assigned to the formation of  $\text{Ag}_3^{2+}$  clusters and the interaction of two (or more)  $\text{Ag}_3^{2+}$  clusters, respectively.<sup>37</sup> Calzaferri *et al.* proposed that the color appearance of Ag activated zeolite A is due to the optical absorption from the ligand to metal charge transfer transition (specifically, from the framework oxygen to the empty 5s orbit of  $\text{Ag}^+$  ions).<sup>38</sup> In 2003, the same group further proposed that the electronic structure of the  $d^{10}$  ions-zeolite guest-host materials is dominated by the charge transfer transitions from the framework oxygen to the  $d^{10}$  ions, and these transitions can be influenced a lot by specific coordination conditions.<sup>30</sup> Meantime, it was also pointed out that  $\text{Cu}^+$  exchanged and  $\text{Ag}^+$  exchanged zeolites showed dynamic luminescence characteristics associated with the hydration state. The optimal amount of water for achieving the maximal emission intensity depends on the co-cations and on the types of zeolites, due to the different electrostatic interaction between the co-cations and the  $\text{H}_2\text{O}$  molecules.<sup>30,34,35</sup> Interestingly, the co-cations in the zeolite framework also strongly influences the luminescence property of semiconductor clusters such as  $\text{Ag}_2\text{S}$  and  $\text{PbS}$ .<sup>39</sup> In Ref. 23, the *in situ* XAFS results in various gas environment show that the nearest Ag-O distance (with coordination number  $>4$ ) is always below  $2.4 \text{ \AA}$  (the Ag-O bond length in  $\text{Ag}_2\text{O}$   $2.087 \text{ \AA}$ ), making strong coordination of  $\text{Ag}^+$  ions or  $\text{Ag}^0$  atoms by the framework oxygen possible. Though the emission of  $\text{Ag}^+$  ions is generally reported to be located at high energies,<sup>40,41</sup> it is shown that emission at lower energies is possible via the ligand-to- $\text{Ag}^+$  ion charge transfer transition,<sup>42</sup> especially, when reducing ligands are present.<sup>43</sup> Amazingly, zeolite framework is famous for its abundance of negative charge centers hence it can be a hotbed for the charge transfer process. Combined with the previous reports from which it is shown that partial reduction of the  $\text{Ag}^+$  ions into  $\text{Ag}^0$  atoms is essential for emission either in the case of Ag activated zeolites or the DNA (or protein) encapsulated Ag clusters, we infer that  $\text{Ag}^0$  atoms coordinated by  $\text{H}_2\text{O}$  molecules and the zeolite A's framework oxygen may also participate in the emission process. Here, we tentatively

assign the  $\sim 560 \pm 15$  nm and the  $\sim 855$  nm emissions to the charge transfer transitions from the framework oxygen to  $\text{Ag}^+-\text{Ag}^0$  involving the participation of  $\text{H}_2\text{O}$  molecules. Though, at present, we are incapable of assigning the emission peaks to exact coordination conditions, it is clear that origin of the emission from Ag activated zeolites is not mainly influenced by the existence of clusters while by the variation of coordinating environment. The almost invariable emission wavelength within a considerably wide excitation wavelength range for Ag activated zeolite Na-A<sup>4,28</sup> indicates the homogeneous coordinating environment for  $\text{Ag}^0$  atoms or  $\text{Ag}^+$  ions, due to the long-distance periodical lattice structure of the zeolite A matrix. Meantime, the invariable emission wavelength under different excitation wavelengths also excludes the existence of SPR absorption due to the large Ag nanoparticles on the surface of the zeolite A microcrystals. For glass matrices in Refs. 44 and 45, large red shifts are usually observed under longer excitation wavelengths, which were assigned to the wide size distribution of Ag clusters. Now, it seems that the non-periodical structure of the glass matrix, in results that the inhomogeneous coordination of  $\text{Ag}^+$  ions and  $\text{Ag}^0$  atoms may be an alternative explanation.

Based on the reversible emission evolution of thermally annealed Ag activated zeolite Na-A with low Ag loading content upon dehydration/hydration in vacuum/water vapor, it is proved that origin of the emission from Ag activated zeolite A may not be the quantum confinement effect, but may be the charge transfer transition from the framework oxygen to  $\text{Ag}^+-\text{Ag}^0$  with the participation of  $\text{H}_2\text{O}$  molecules. The  $\text{H}_2\text{O}$ -sensitive emission feature might enable Ag activated zeolites to be a sensor or gauge for humidity. This work also demonstrated that zeolites is a group of excellent matrices for investigating the luminescence physics of sub-nm scale Ag species activated materials for its inorganic crystalline nature.

Hui Lin would like to express his sincere thanks to Prof. Dr. Kanna Aoki for her generous and valuable discussion on the gas permeation properties of zeolite A.

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- <sup>29</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4902530> for Fig. S1 Excitation-emission 3D contours of pure zeolite 4A under different thermal annealing temperatures; Fig. S2 Excitation-emission 3D contour and emission evolution of  $\text{Ag}_1, \text{Na}_{11}$ -A upon dehydration/hydration.
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