Electronic Supporting Information for

Unravelling the structure of broadband white-emitting silver nanoclusters stabilized in sulfur-doped zeolites

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1. Photoluminescence

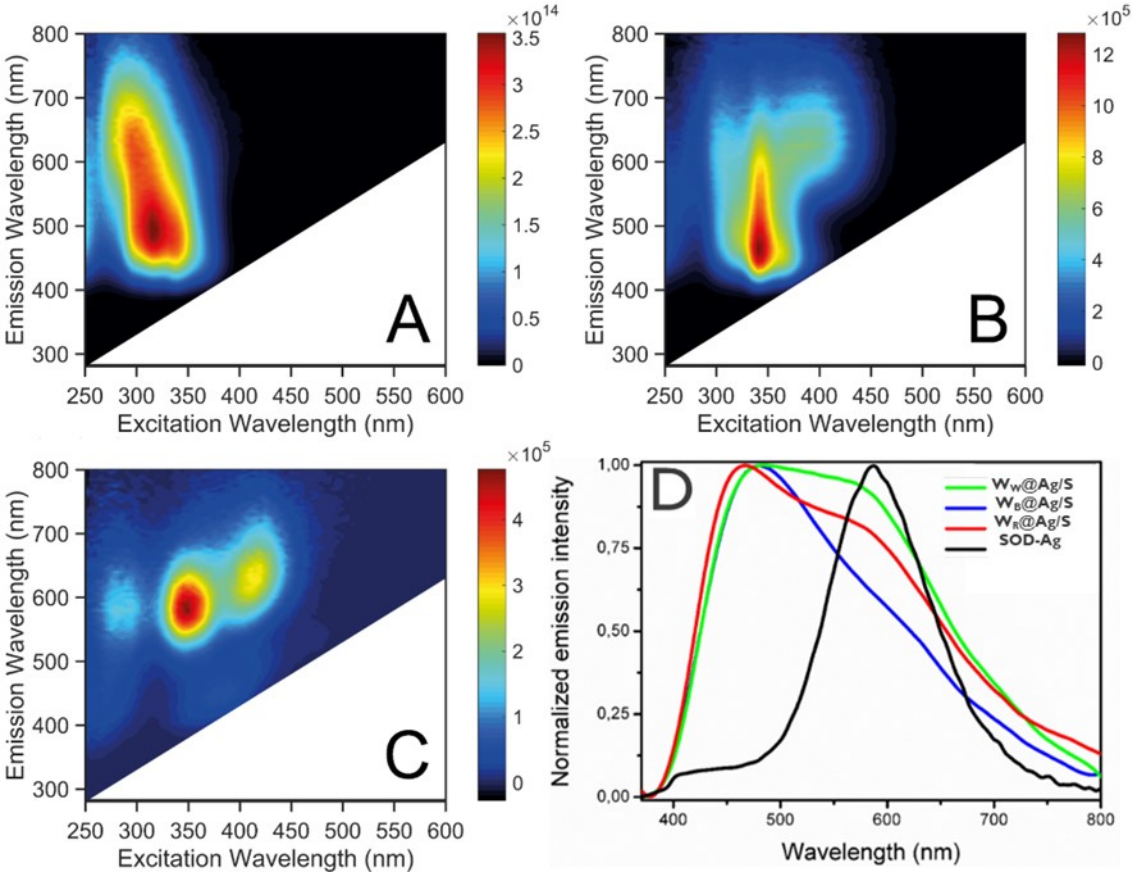

Figure S1. Two-dimensional (2D) excitation−emission plots of (A) W_B@Ag/S, (B) W_R@Ag/S, and (C) SOD-Ag. (D) Emission profile spectra of the investigated samples excited at 340 nm.

Figure S1 shows the 2D excitation–emission plots of the W_B@Ag/S, W_R@Ag/S, and SOD-Ag samples. After the incorporation of Ag species, a main emission peak is observed at 315 nm in W_B@Ag/S (**Figure S1A**), which shifts slightly to 300 nm for higher emission wavelengths. These emissive species also exhibit broad blue–white emission with a maximum around 495 nm. On the other hand, W_R@Ag/S (**Figure S1B**) exhibits a remarkable similarity to W_W@Ag/S (**Figure 1A**). However, the red orange emitting species, excited at 400 nm with an emission maximum at 635 nm, are more favoured, while the blue-emitting species are less prominent. In addition, a main emissive species is observed under excitation at 340 nm, producing broad emission centered around 465 nm. Likewise, the SOD-Ag sample (**Figure S1C**) prepared for comparative purposes shows two main peaks: one centered at 350 nm excitation with emission at 580 nm, and the other

at 415 nm excitation with an emission maximum around 635 nm. **Figure S1D** depicts the emission spectra profiles of the investigated samples under 340 nm excitation.

2. XANES

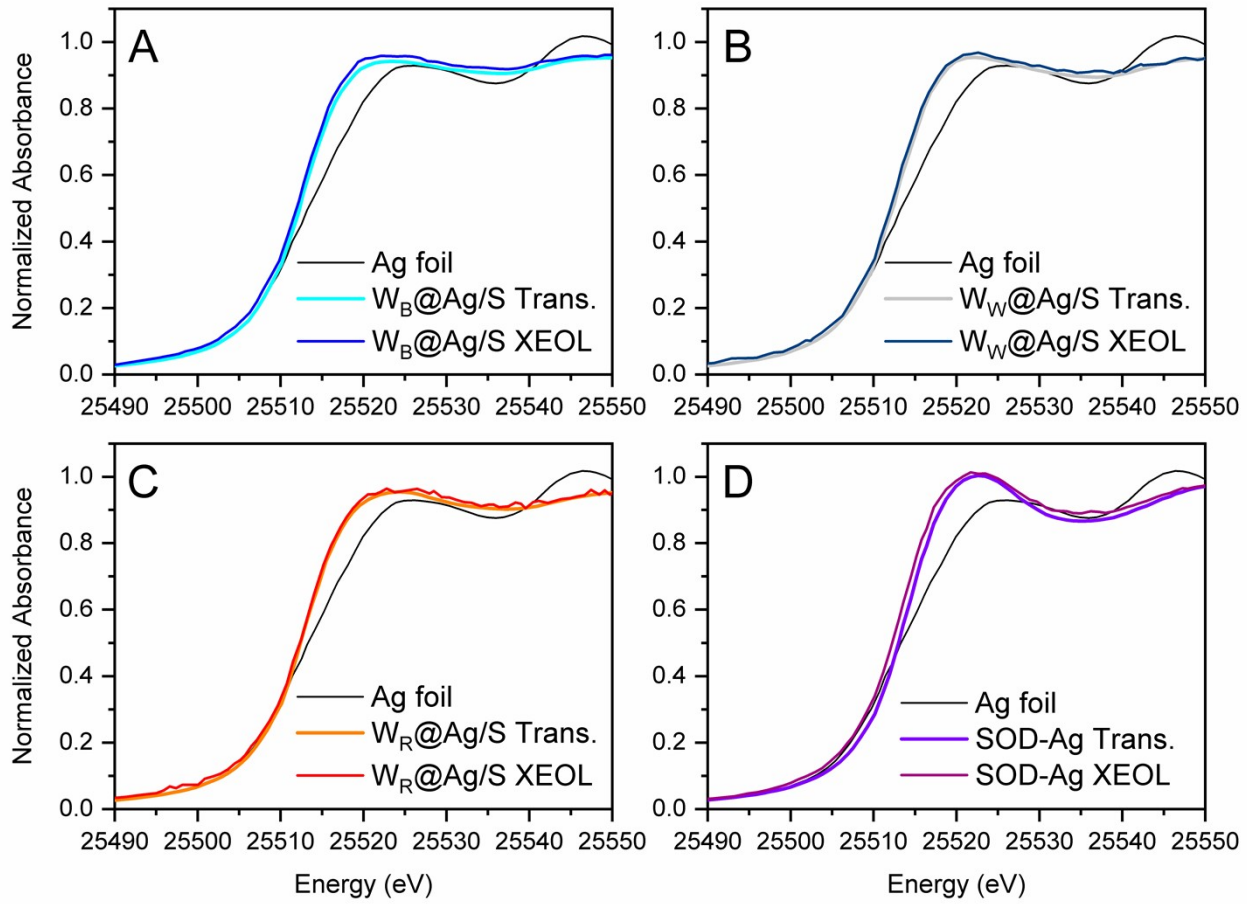

Figure S2. XEOL and transmission-detected Ag K-edge XANES spectra of (A) Ag/S-B, (B) Ag/S-W, (C) Ag/S-R, and (D) Ag-SOD along with reference Ag foil.

3. EXAFS

3.1. XEOL-EXAFS

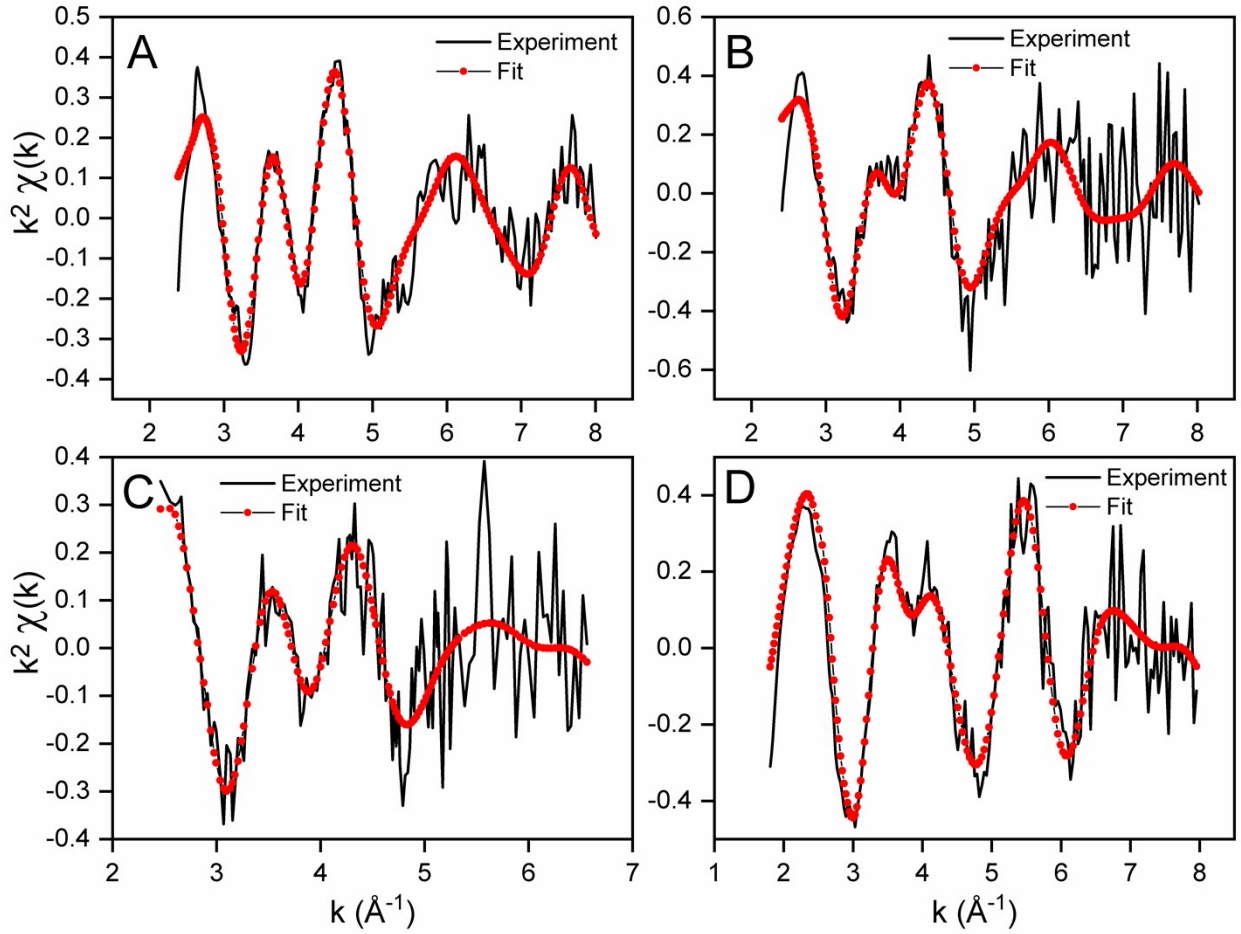

Figure S3. XEOL-detected Ag K-edge k^2-weighted EXAFS (A) W_B@Ag/S, (B) W_W@Ag/S, (C) W_R@Ag/S, and (D) SOD-Ag best fits.

Table S1. Summary of structural results of Ag K-edge EXAFS refinements of the Ag/S Sodalites in XEOL-detection mode.

Sample	W_B@Ag/S	W_W@Ag/S	W_R@Ag/S	SOD-Ag
AFAC	0.9	0.9	0.9	0.9
k weight	2	2	2	2
k-range	2-8	2-8	2-7	2-8
E_f (eV)	3.6 (10)	3.5 (10)	-7.6 (10)	-4.9 (5)
N_1	1.0 (1) O	1.9 (4) O	2.2 (9) O	2.5 (3) O
R_1	2.15 (2)	2.20 (3)	2.30 (9)	2.38 (1)
A_1	0.008 (6)	0.02 (1)	0.06 (4)	0.015 (6)
N_2	2.5 (9) Ag	2.9 (9) Ag	3.7 (9) Ag	3.8 (3) Ag
R_2	2.65 (5)	2.74 (7)	2.79 (9)	2.84 (3)
A_2	0.07 (3)	0.11 (5)	0.08 (7)	0.03 (1)
N_4	2.5 (9) Ag	2.4 (9) Ag	2.2 (9) Ag	1.1 (6) Ag
R_4	3.35(6)	3.39 (7)	3.5 (1)	3.7 (1)
A_4	0.022 (2)	0.03 (2)	0.01 (3)	0.03 (7)
N_5	4.4 (9) Ag	4.4 (10) Ag	2.4 (9) Ag	2.0 (9) Ag
R_5	3.60 (6)	3.63 (6)	3.8 (1)	3.96 (9)
A_5	0.02 (2)	0.018 (6)	0.01 (3)	0.03 (5)
R (%)	37 %	51 %	56 %	37%

E_f = contribution of the wave vector of the zero-photoelectron relative to the origin of k [eV]
AFAC = amplitude reduction due to many-electron processes
N_i = number of atoms in the i^{th} shell
R_i = radial distance of atoms in the i^{th} shell [Å]
A_i = Debye-Waller term of the i^{th} shell ($A=2\sigma^2$ with σ = Debye-Waller factor) [$Å^2$]
R factor in %

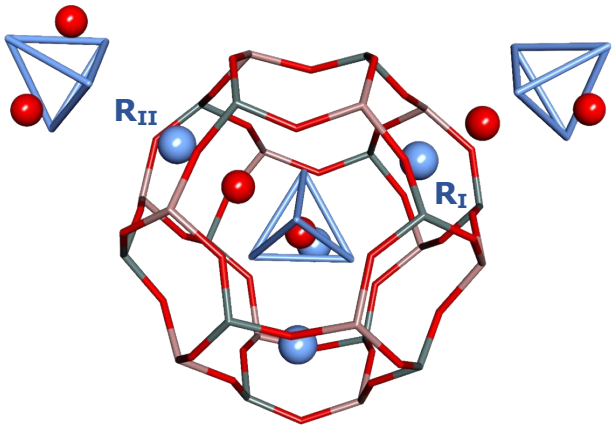

Figure S4. Schematic structural model showing the arrangement of several Ag_4O_2 NCs embedded in contiguous sodalite cages, highlighting the position of Ag_{RI} and Ag_{RII} cations in the single six-membered rings (S6Rs).

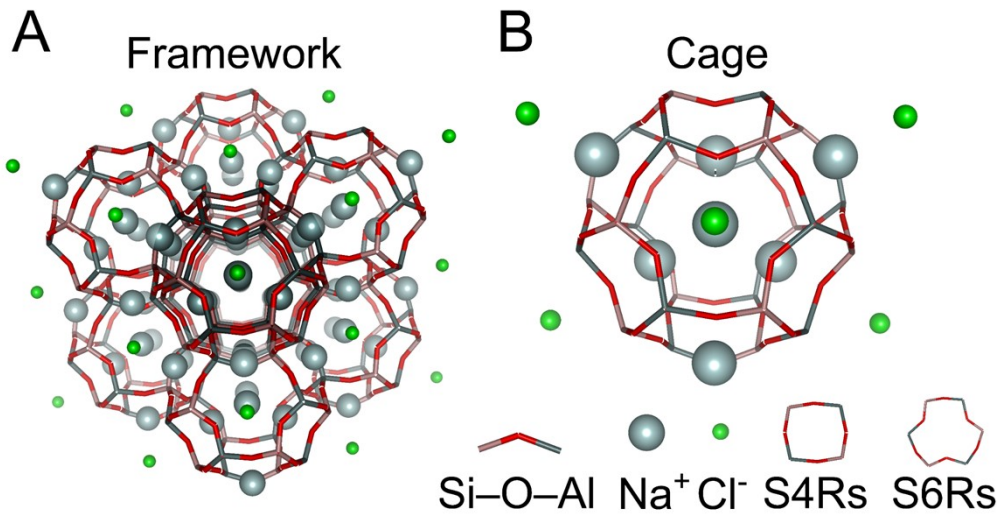

Figure S5. (A) Structural view of the SOD $(Na_8[Al_6Si_6O_{24})Cl_2)$ framework. (B) Enlarged sodalite cage showing Si–O–Al connectivity, extra-framework cations (Na^+, large spheres; Cl^-, small spheres), and the characteristic single four-membered rings (S4Rs) and S6Rs that result in a compact structure without supercages.

Comment [EC]: Referee 2.- We have included the chemical formula of the sodalite.

3.2. Transmission-EXAFS

Table S2. Summary of structural results of Ag K-edge EXAFS refinements of the Ag/S sodalite in transmission-detection mode.

Sample	W_B@Ag/S	W_W@Ag/S	W_R@Ag/S	SOD-Ag
AFAC	0.9	0.9	0.9	0.9
K weight	3	3	3	3
k-range	2-11	2-11.4	2-10.5	2-11
E_f (eV)	2.0 (9)	0.4 (9)	-2.8 (7)	0.5 (3)
N_1	1.7 (3) O	2.4 (3) O	2.5 (3) O	3.1 (1) O
R_1	2.22 (2)	2.29 (2)	2.28 (2)	2.341 (4)
A_1	0.049 (9)	0.041 (7)	0.047 (7)	0.025 (1)
N_2	2.1 (2) Ag	2.3 (6)Ag	3.0 (4) Ag	2.8 (2) Ag
R_2	2.61 (4)	2.71 (4)	2.71 (3)	2.74 (1)
A_2	0.08 (1)	0.06 (1)	0.07 (1)	0.047 (2)
N_3	1.1 (2) SA	1.2 (5) SA	0.9 (1) SA	1.4 (2) SA
R_3	3.27 (1)	3.33 (2)	3.33 (2)	3.289 (7)
A_3	0.014 (4)	0.014 (6)	0.012 (3)	0.014 (2)
N_4	4.3 (9) Ag	4.0 (9) Ag	1.8 (2) Ag	1.9 (3) Ag
R_4	3.44(2)	3.50 (3)	3.51 (2)	3.50 (2)
A_4	0.047 (7)	0.047 (8)	0.028 (4)	0.042 (6)
N_5	4.3 (6) Ag	4.2 (9) Ag	1.6 (7) Ag	3.0 (4) Ag
R_5	3.69 (4)	3.77 (4)	3.77 (3)	3.77 (1)
A_5	0.07 (1)	0.05 (1)	0.03 (1)	0.043 (4)
N_6	0.4 (2) Ag	0.4(3) Ag	1.0 (7) Ag	0.9(4) Ag
R_6	4.45 (2)	4.44 (3)	4.44 (4)	4.45 (1)
A_6	0.008 (5)	0.011 (7)	0.03 (1)	0.024 (7)
N_7	0.34 (3) S	0.25 (8) S	0.3 (2) S	
R_7	2.393 (6)	2.46 (1)	2.41 (1)	

A_7	0.003 (2)	0.009 (4)	0.013 (4)	
R (%)	26 %	30 %	25 %	13%
Ag_C - Ag_C Coordination	2.6	2.9	3.5	3.7
Ag_C-O_L Coordination	1.2	1.8	2.2	3.1
Ag_C /Ag_R (%)	82	80	85	77

E_f = contribution of the wave vector of the zero-photoelectron relative to the origin of k [eV]
AFAC = amplitude reduction due to many-electron processes
N_i = number of atoms in the i^{th} shell
R_i = radial distance of atoms in the i^{th} shell [Å]
A_i = Debye-Waller term of the i^{th} shell ($A=2\sigma^2$ with σ = Debye-Waller factor) [$Å^2$]
R factor in %

As in our previous work in Ag exchanged LTA zeolites, the Tr-EXAFS analysis of their sodalite counterpart is based on a the three-shell model (Ag–O, Ag–Ag, and Ag–Si/Al).[1] In this model, we include a virtual mixed Si/Al site corresponding to 0.5 Si:0.5 Al occupancy that better reflects the 1.3 Si/Al ratio of the sodalite. Crystallographic data of SOD [ICDD card 41190] were used to support the EXAFS analysis and to obtain information related to the nuclearity of these NCs from the fitting results. Details of the fitting parameters are provided in **Table S2**. EXAFS data were fitted with k^3 weighting as it is more sensitive to heavy atoms such as Ag and intensifies the high k-range of the spectra. Besides, as Ag-NC atoms do not occupy fixed crystallographic positions weak Ag–Ag bonds with relatively large static disorder (DWF) are observed, making them difficult to detect.[2] Thus, k^3 weighting provides more useful information on the Ag shells.

Figure S6 shows the $\chi(k)$ k^3-weighted EXAFS data and the corresponding phase-corrected FT best (**Figure S7**) fits of W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag. The first peaks in the FTs (**Figure S7**) could be fitted with 1.7, 2.4, 2.5, and 3.1 oxygen atoms at 2.22, 2.29, 2.28, and 2.34 Å in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag, respectively. This oxygen shell (N_1) corresponds to a combination of zeolite framework O atoms for the Ag cations occupying the center of the S6Rs. Among these cations, two distinct positions can be identified: R_{II} inside the sodalite cage when no extra-framework O ligand is present between the NC and the Ag_R cation, and $R_{II'}$ inside the neighboring sodalite cage when an extra-framework O or H_2O ligand is coordinated to Ag_C, forming the NCs (**Figure 4**).

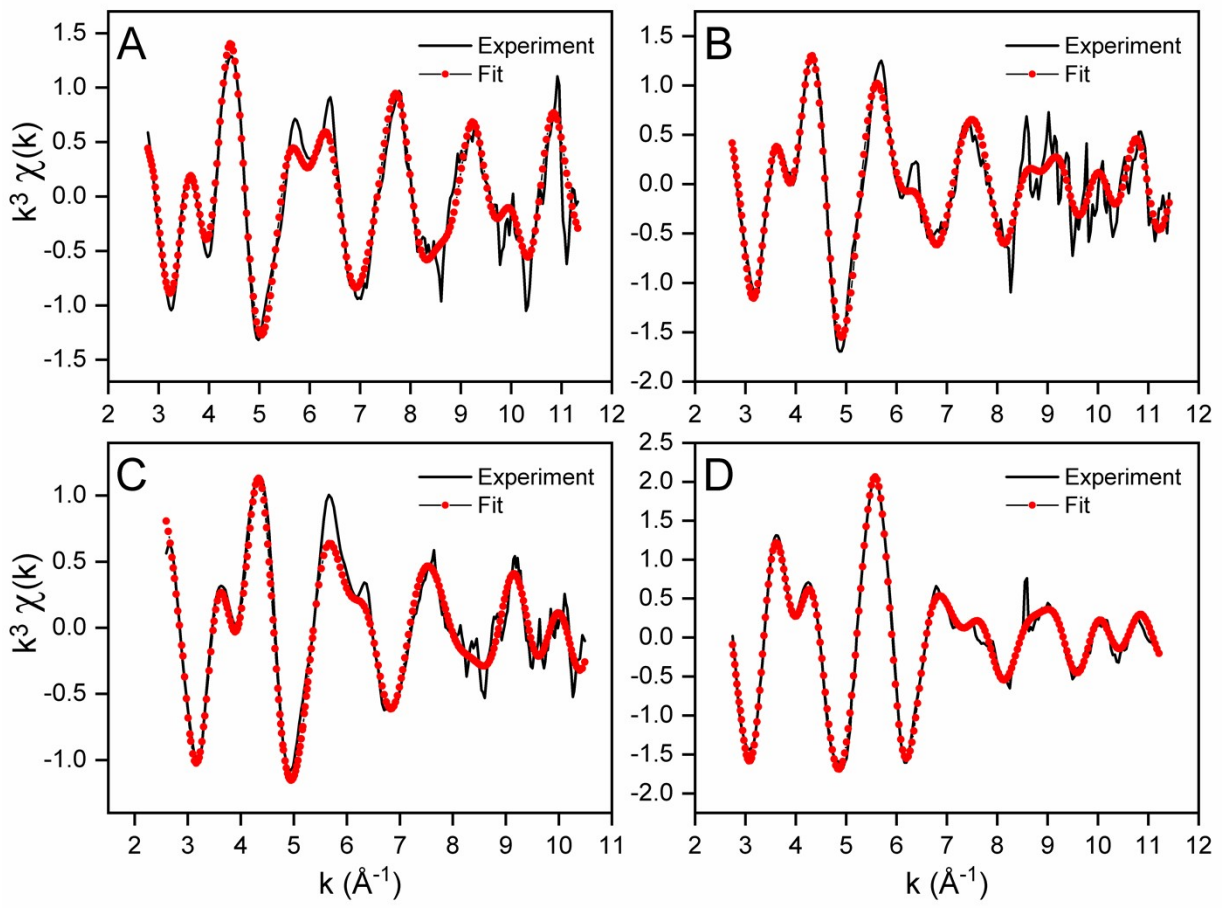

Figure S6. Transmission Ag K-edge k^3-weighted EXAFS of (A) W_B@Ag/S, (B) W_W@Ag/S, (C) W_R@Ag/S, and (D) SOD-Ag best fits.

The second multi-peaks in the FTs correspond to Ag-Si/Al and Ag-Ag contributions. The Ag-Si/Al shell consists of (N_3) of 1.1, 1.2, 0.9, and 1.4 Si/Al atoms at 3.27, 3.33, 3.33, and 3.29 Å in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag, respectively. These Si/Al contributions correspond to the Ag_{RII} and $R_{II'}$ which are strongly bonded to three framework oxygens (N_1) pointing towards the centers of the S6Rs. In the crystallographic model of sodalite, Ag_R located in the plane of the S6Rs, with the R_3 Ag_R–Si/Al distance obtained by the EXAFS analysis corresponding to crystallographic Ag_R–O distances of 2.27, 2.35, 2.35, and 2.30 Å in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag, respectively. This confirms that R_1 is a combination of long framework O and short extra-framework O atoms at shorter distances in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and extra-framework water molecules at longer distances in SOD-Ag. The Ag–Ag shell (N_2) consists of 2.1, 2.3, 3.0, and 2.8 Ag at 2.61, 2.71, 2.71, and 2.74 Å in W_B@Ag/S,

W_W@Ag/S, W_R@Ag/S, and SOD-Ag, respectively. This contribution corresponds to the remaining part of the Ag atoms forming oligomeric Ag-NCs located inside the sodalite cages.

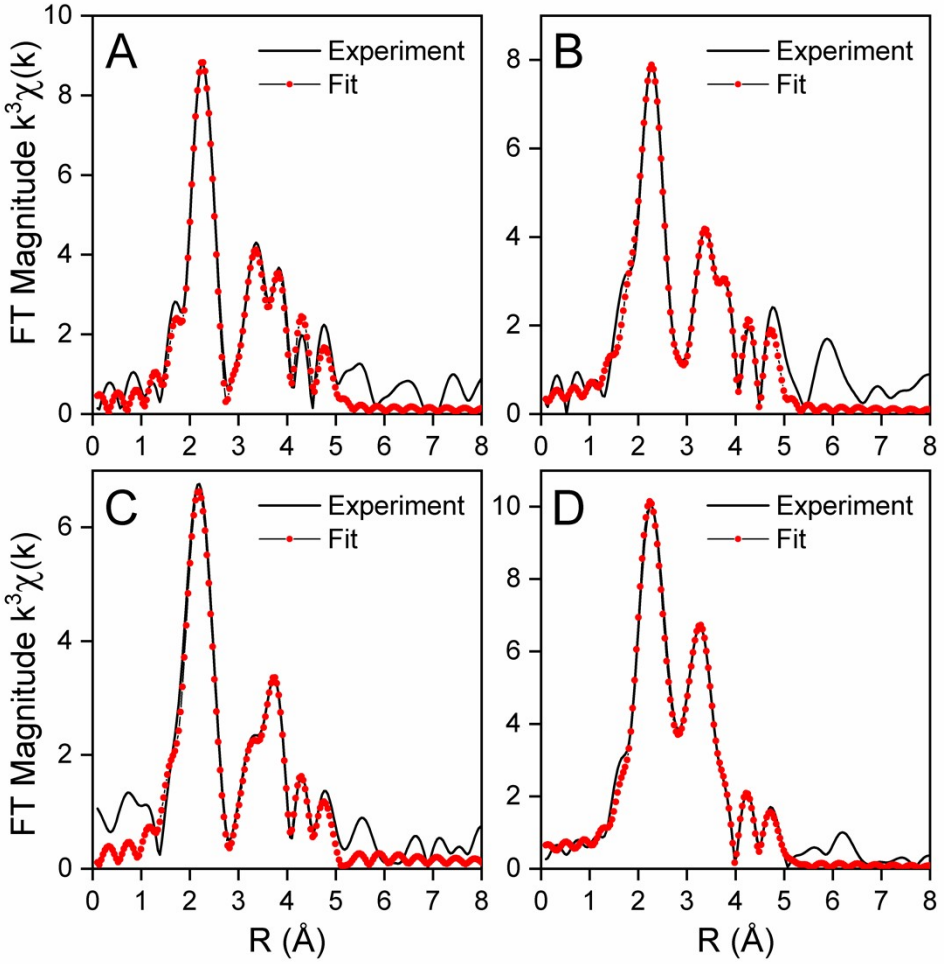

Figure S7. Transmission Ag K-edge k^3-weighted phase corrected FTs of (A) W_B@Ag/S, (B) W_W@Ag/S, (C) W_R@Ag/S, and (D) SOD-Ag best fits.

The total fraction of Ag cations located in the S6Rs (Ag_{RII} and $Ag_{RII'}$) can be derived as 18, 22, 15, and 22% (N_3/6x100) while the fraction of Ag-NCs is 82, 80, 85, and 77% in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag, respectively. The corrected equivalent Ag coordination (N_4/Ag_C fraction) are 2.6, 2.9, 3.5, and 3.7, suggesting that the NC nuclearity in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag spans from Ag_3 (CN2) to Ag_6 (CN4).

Each Ag-NC is then coordinated to 1.2, 1.8, 2.2, and 3.1 extra-framework O ligands [(N_1 – (3xAg_R fraction))/Ag_C fraction] in W_B@Ag/S, W_W@Ag/S, W_R@Ag/S, and SOD-Ag, respectively, in line with the corresponding XEOL-EXAFS determined values of 1.0, 1.9, 2.2, and 2.5. Oxygen ligands consist either of extra-framework O atoms in Ag/S-SOD or of water molecules in SOD-Ag. In W_B@Ag/S, the 1.2 O coordination corresponds to a mixture of a single extra-framework O atom in Ag_3O and Ag_4O_2 within the sodalite cage (Ag_C coordination of 1 and 1.5 respectively). In W_W@Ag/S, the 1.8 O coordination is in line with the coexistence of Ag_3O, Ag_4O_2, and Ag_6O_4 NCs (Ag_C coordination of 1, 1.5, and 3, respectively), while in W_R@Ag/S the CN of 2.2 matches a mixture of Ag_4O_2 and Ag_6O_4 NCs. Finally, in SOD-Ag the CN of 3.1 could correspond to a mixture of $Ag_6(OH_2)_2$, $Ag_6(OH_2)_4$, and $Ag_6(OH_2)_6$ isomers (Ag_C coordination of 1.5, 3, and 4 respectively).

The addition of three long-distance Ag–Ag shells (N_4-N_6) significantly improved the quality of the fit. Inspection of the SOD crystallographic structure suggests that these long Ag–Ag distances correspond to distances from Ag_C forming the NCs at the center of the sodalite cages to $Ag_{RII'}$ and Ag_{RII} sites positioned in the S6Rs within the same sodalite cage. N_4 shell of 1.8 to 4.3 Ag at 3.44 to 3.50 Å, and N_5 shell of 1.6 to 4.3 Ag at 3.69 to 3.77 Å, correspond respectively to Ag_C–Ag_{RII} and Ag_C–$Ag_{RII'}$ distances occurring in the presence or absence of a water molecule located near the center of the S6Rs and sandwiched between the two atoms. N_6 shell of 0.4 to 1.0 Ag at 4.44 to 4.45 Å correspond to Ag_C–Ag_{RII} in the presence of a water molecule when the neighboring cage does not contain a NC. The sharing of the Ag_R between two neighbor NCs that is specific of the SOD structure results in larger Ag_C–Ag_R CNs as compared to those found in the LTA zeolite. Finally, a shell of 0.25 to 0.34 S at 2.39 to 2.46 Å (N_7) was added to the fit of W_B@Ag/S and W_W@Ag/S, confirming the limited interaction of a small number of Ag cations with S atoms during the Ag exchange procedure, in line with the S K-edge XANES (**Figure 2A**).

References

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