

Supporting Information

Uniform Generation of Sub-nanometer Silver Clusters in Zeolite Cages Exhibiting High Photocatalytic Activity Under Visible Light

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Characterization techniques

X-ray diffraction analysis: The crystallinity and phase purity of zeolite samples was studied by powder X-ray diffraction analysis (PXRD) using a PANalytical X'Pert Pro diffractometer with $\text{CuK}\alpha$ -moy wavelength ($\lambda = 1.5418 \text{ \AA}$). Rietveld refinements were then performed with the JANA2006^[1] software on PXRD data recorded on a Bruker D8-vario1 diffractometer equipped with a primary germanium (111) Johansson monochromator ($\lambda\text{K}\alpha 1 = 1.5406 \text{ \AA}$) and a LynxEye detector. The PXRD diagrams were recorded at room temperature between 3 and $120^\circ(2\theta)$ with a step size of $\sim 0.014^\circ(2\theta)$. Variable divergent slits with a constant illuminated sample length of 6 mm were used. Phase identifications were performed with the PANalytical HighScore plus program. The crystal structure of Ag@ZX-V was solved by *ab initio* method using the SUPERFLIP software.^[1]

UV-vis: UV-vis spectroscopy measurements were performed using a Cray 4000 UV-vis spectrophotometer at room temperature in transmission mode using a quartz cuvette with a 1 cm path length. The transmission spectra were corrected by subtracting the spectrum of pure zeolite (ZX). The DR-UV-vis spectra of the dried powder samples were recorded by using a RSA-CU40 Diffuse Reflectance cell. The spectrum of non-irradiated sample was subtracted from the spectra of irradiated samples.

FTIR spectroscopy: Powder samples were pressed ($\sim 10^7 \text{ Pa/cm}^2$) into self-supported discs (2 cm^2 area, $\sim 20 \text{ mg}$) and placed in an IR cell equipped with KBr windows. IR spectra were recorded using a Nicolet 6700 IR spectrometer equipped with a DTGS detector and an extended-KBr beam splitter was used. Spectra were recorded in the $400\text{--}5500 \text{ cm}^{-1}$ range at a resolution of 4 cm^{-1} and 128 scans were collected for each spectrum. A movable quartz sample holder was used for recording spectra and moving it into a furnace at the top of the cell for thermal treatment and activation.

SEM: Zeolite nanocrystals were analyzed by field-emission scanning electron microscope (SEM) using a JEOS JSM6700F with an accelerating voltage 30.0 kV .

TEM: The morphological features of the samples were investigated with a transmission electron microscope (Technai G2 30UT LaB_6 operated at 300 kV). Specimens for transmission electron

microscopy studies were suspended in ethanol and drop cast onto a Cu holey carbon grid. Advanced transmission electron microscopy (TEM), high-angle annular dark field scanning TEM (HAADF-STEM) together with EDX mapping experiments were carried out on an aberration probe and image corrected JEM ARM200F cold FEG microscope operated at 200 kV equipped with a CENTURIO EDX detector and GIF Quantum spectrometer.

Section I.

ZX-V synthesis

Al powder (325 mesh, 99.5 %, Alfa Aesar), NaOH (97 %, Sigma-Aldrich), SiO₂ (Ludox-HS 30, 30 wt. % SiO₂, pH = 9.8, Aldrich), NaO₃V (99.9 %, Sigma Aldrich) were used without further purification.

The nanosized FAU zeolite based samples were synthesized from a clear precursor suspension with a molar composition: 10 SiO₂ : 1.1 Al₂O₃ : x V₂O₅ : 9 Na₂O : 122 H₂O. Sodium vanadate was selected as a precursor of the photoactive sites due to the efficiency of the vanadate sites for silver ion reduction versus water oxidation (formation of OH radicals and oxidant species are prevented). The properties of this precursor are fully compatible with the synthesis of nano ZX zeolite (same counter ions, low polymerization at high pH, etc.). The initial reactants were mixed to prepare two initial solutions denoted A and B. **Solution A** was prepared by dissolving 0.296 g aluminum powder (325 mesh, 99.5%, Alfa Aesar) and 2.5 g NaOH (Aldrich, 97%) in 3 g double distilled H₂O. Vanadium containing samples were prepared by adding 0.061 g of VO₃Na (1 wt.%, in respect to the Silica and Alumina content; ZX-V; Aldrich, 98%), 0.122 g (2 wt.%; ZXV-2) or 0.304 g (5 wt.%; ZX-V-5) to this solution and stirring for 3 h. **Solution B** was prepared by mixing of 10 g colloidal silica (Ludox-HS 30, Aldrich) with 1.095 g (for pure ZX sample), 1.084 g (for sample ZX-V), 1.077 g (ZX-V-2) or 1.049 (ZX-V-5) NaOH and 1 g double distilled H₂O. The resulting turbid suspensions were placed in an oven at 100 °C for 5 minutes to obtain water clear suspensions. Solution A was added drop wise under vigorously stirring to the solution B at 4 °C using an ice-bath. The resulting colorless suspensions were stirred 24 h at room temperature followed by

dehydration of 6.9 g H₂O (equivalent to 45 M H₂O from the general gel composition). Hydrothermal crystallization was conducted at 50 °C for 36 h for samples ZX, ZX-V, ZX-V-2 and ZXV-5. The system yielding ZX-V-5 sample remained amorphous after 10 days synthesis at 50°C. ZX-V-5 was synthesized at 80 °C for 3 days. The obtained solid partially precipitated at the bottom of the reaction vessel. Except ZX-V-5 sample, very stable suspensions were obtained. The solid was recovered by centrifugation (25 min, 20000 rpm) followed by redispersion in double distilled water. The procedure was repeated till reaching pH ~ 8.

Section II.

1. Preparation of Ag@ZX-V

Step 1: ZX samples with high crystallinity were obtained (**Figure S1**). The crystallinity is partially affected by the amount of vanadate precursor added to the initial synthesis solution. The optimal amount, under our synthesis condition, was found to be 1.0 wt.% with respect to the total amount of alumina and silica used. Increasing the loading of vanadate precursor above 3 wt.% requires modification of the synthesis parameters (temperature and synthesis time) to promote zeolite crystallization (**Figures S2**). In addition, isolated vanadium oxides particles were detected when more than 1 wt.% of vanadate precursors were used (**Figure S3**). Therefore, only the sample prepared with 1 wt.% of vanadate (called ZX-V) is used for the preparation of sub-nanometre silver clusters (Ag@ZX-V) and discussed in the main text.

The ICP and EDX analyses showed vanadium content of 0.25 wt. % in ZX-V sample. The relatively low amount of vanadate species makes difficult their characterization and localization with conventional techniques.

DR-UV-visible spectroscopy was used to provide additional information on the nature of the vanadate species. In general, the low-energy charge transfer band (LCT) associated with O to V electron transfer falls in the 330-500 nm region,^[2-6] corresponding to V⁵⁺ ions in an octahedral (O_h) environment. For lower coordination, such as tetrahedral (T_d) environment V⁵⁺, the low energy charge transfer (LCT) band falls in the 285-330 nm region.^[5] The LCT band for O_h-V⁴⁺ falls at higher frequencies in the 250-285 nm region.^[6] In our case, only the later band (250-285 nm; 4.6-

4.9 eV) with a maximum at 265 nm was observed (**Figure S4**). This points out that the amount of polymeric V^{5+} oxides is negligible and that namely isolated interstitial V^{4+} species (e.g. $Na_2O_5V_2$, etc.) are present.

Step 2: Most of the work on silver sub-nanometer particles preparation was performed on the sample containing ca. 0.25 wt.% of vanadate (ZX-V), due to its good crystallinity and homogeneity. Ag@ZX-V samples were prepared by dispersing a variable amount of ZX-V in water solutions containing ethanol as an electron donor and silver nitrate as a silver precursor. There is no reduction of silver ions observed without adding ethanol to the ZX-V suspension, even after 10 min of UV irradiation. The same result was obtained by irradiation of the vanadate free zeolite (ZX) suspension in presence of ethanol and silver nitrate. However, the irradiation of ZX-V suspension in presence of ethanol and silver nitrate led to a significant color change of the solution. Less than 3 minutes of UV irradiation was enough to change the color of the milky suspension to green. This typical colour modification is due to the formation of reduced silver (nano)particles in the solution. The essential role of vanadate and ethanol confirms the photocatalytic behaviour of the process. It should be noted that the experiments were realized on 3 ml and 20 ml of ZX-V suspensions and similar results are obtained.

2. Optimization of ethanol and silver nitrate concentrations

The concentration of ethanol was found to be critical for the stability of zeolite suspension. When the water/ethanol ratio is lower than 1, a total precipitation of the suspension was observed. This is probably related to the concentration of the sub-products resulted from the photocatalytic oxidation of ethanol (e.g. formation of photosensible silver acetate). Therefore, the optimal concentration of ethanol was found to be around 4.5 ± 1.0 M giving rise to a stable suspension (**Figure S5**).

The concentration of the silver precursor relative to the zeolite quantity influences also the Ag clustering process. **Figure S6** demonstrates that increasing the concentration of Ag^+ promotes the formation of silver nanoparticles with characteristic plasmonic UV-visible bands at ≈ 430 nm. Based on the UV-visible spectra of the samples prepared with different silver concentrations and treated under the same condition, the optimal concentration of silver was found to be 5 mM for a

suspension containing 3 mg/ml of ZX-V. Therefore, the optimal concentrations are 4 M, 5 mM, and 3 mg/ml of ethanol, silver, and zeolite, respectively. The irradiations were performed using a Xe-Hg lamp (200 W) without (irradiance 205 mW/cm²) or with band pass filter at 365 nm (irradiance around 15 mW/cm²).

3. Hydrothermal preparation of Ag@ZX-V(HT)

The synthesis of Ag@ZX-V(HT) was carried out using common hydrothermal method as described elsewhere.^[7-9] 160 mg of ZX-V were dispersed in 8 mL aqueous solution of 4 M and 5 mM of ethanol and AgNO₃ respectively. The mixture was sonicated for 10 min, and transferred into a Teflon-lined autoclave. The autoclave was sealed in a stainless-steel tank and heated at 180 °C for 24 h. After the reaction, the reactor was cooled to room temperature naturally. The products were washed 3 times with distilled water. The final products were placed into an oven at 50°C overnight for drying.

3. Photocatalytic tests

The photocatalytic tests were performed using a homemade in-situ FTIR reactor (total volume capacity = 170 ml) equipped with CaF₂ windows (for IR analysis) and with gas inlet and outlet for purging the mixture and analyzing the gas headspace. 50 mg of each sample was dispersed in 10 ml of acetonitrile (AcN) with 0.35 ml of formic acid. Afterward, the mixture was bubbled with argon for 30 min to ensure an inert atmosphere. The irradiations of the samples were performed, under magnetic stirring, using a Xe-lamp (LC8 Hamamatsu, 200 W) with pass-high filter at 400 nm. The subsequent H₂ and CO generation was quantified by Thermo Scientific Trace 1310 equipped with a MolSive5 A column (30 m × 0.53 mm, 50 μm). For this purpose, injections (1 ml) of gas headspace were made in GC and the resulting peak areas were converted into H₂ and CO concentrations by using a calibration with the corresponding standard gases (operating conditions: carrier gas, He; split flow rate = 60 mL/min; split ratio = 1/12; inlet temperature = 423 K; column temperature 393 K). CO₂ formation was monitored in-situ IR study in real time (2 min/spectrum). IR spectra of headspace of IR cell were recorded using Nicolet 6700 IR spectrometer equipped with a MCT detector.

Section III.

1. Stability of the Ag@ZX-V under the electron beam

The Ag@ZX-V sample is extremely sensitive to the electron beam inside the microscope column. Using lower accelerating voltage, for instance 80 kV instead of 200kV, does not really improve stability of the material under electron beam. Despite using short dwell time for HAADF-STEM imaging, even at intermediate magnifications the ZX framework is destroyed after two or three frame scans, which also leads to agglomeration of the Ag sub-nanoparticles into larger size (around 10 nm) Ag nanoparticles (**Figure S10**). This behavior could be interesting for many applications which require delivering isolated silver nanoparticles at specific temperature ($>80^{\circ}\text{C}$). The localization of the Ag nanoparticles along the channels in the ZX framework is difficult to determine due to the two-dimensional nature of TEM imaging. In principle, electron tomography could provide 3D information, an experiment that could not be performed successfully due to mentioned high instability of the clusters under the electron beam.

2. Structural analysis

As confirmed by the FFT patterns of the high resolution HAADF-STEM image (**Figure 2 c**) possible [001] orientation the Ag sub-nanoparticles are oriented with their $\langle 001 \rangle$ axes parallel to $\langle 001 \rangle$ FAU. The high resolution HAADF-STEM image taking along $\langle 112 \rangle$ FAU (**Figure 2d**) shows that the Ag nanoparticles are arranged as rod-shape aggregates aligned along the channels parallel to the $\langle 011 \rangle$ FAU direction.

3. PXRD analysis

The initial analysis of the PXRD data of the ZX-V sample (**Figure S11**) showed two minor extra-phases are present besides main peaks belonging to the ZX-V phase; one of them was identified as quartz (SiO_2). The high level of the background at low angles as well as the large bump centered close to 29° (2θ) corresponding to diffuse scattering, indicating the presence of small amount of amorphous phase in the sample. The Rietveld refinements of the crystal structure of ZX-V were performed assuming a starting Faujasite model given by Calestani et al. ^[10] with a chemical

composition, close to our compound and presence of the quartz as extra-phase. The Si/Al ratio was fixed at 1.63 according to the ICP analysis since no distinction can be made between Si and Al atoms from PXRD data. As established already, the amount of vanadium in ZX-V is very low (0.25 wt.%) and remain undetectable by PXRD. Thus, the presence of V was ignored in the Rietveld refinements. The final refinement cycle gives good agreement factors: $R_{obs} = 2.95$; $R_{wp} = 2.83$; $gof = 1.07$. The following chemical formula $\text{Na}_{82}\text{Al}_{73}\text{Si}_{119}\text{O}_{384}(\text{H}_2\text{O})_{139}$ has been obtained. It should be noted that the number of sodium atoms slightly exceeds the number of aluminium atoms, as observed in the ICP analysis, while the stoichiometry of the zeolite requires the same amount of Al and Na atoms. Since some amount of SiO_2 (~ 2.7 wt.% of the identified crystalline) is present in the sample it is possible that the Si/Al ratio in the Faujasite is lower than expected. Comparing the PXRD spectra of Ag@ZX-V and ZX-V observe drastic changes of the relative intensities of the diffraction peaks can be clearly observed (**Figure S11**), corresponding to the change of the cationic composition between the two Faujasites. The Rietveld refinements of the PXRD data of Ag@ZX-V converged to the following agreement factors: $R_{obs} = 3.91$; $R_p = 2.79$; $gof = 1.71$. The deduced chemical formula is $\text{Ag}_{27}\text{Na}_{55}\text{Al}_{73}\text{Si}_{119}\text{O}_{384}(\text{H}_2\text{O})_{120}$ with the stoichiometric sum of the Ag^+ and Na^+ cations equal to 82, as previously observed for ZX-V. The apparent diameter of the crystallites does not change and corresponds to the size of the ZX crystallites. The unit cell parameter $a = 24.997(1)$ Å slightly is smaller compared to $a = 25.023(1)$ Å for ZX-V. This may be correlated with the smaller amount of water molecules in Ag@ZX-V. Apparently, the crystallographic sites for Na^+ , Ag^+ ions and oxygen atoms of the water molecules are not fully occupied. As a consequence, based on the PXRD data, an average structure of the Faujasite can be deduced with cations and water molecules randomly distributed among those crystallographic positions.

All details of PXRD data and Rietveld refinements of ZX-V and Ag@ZX-V structures are shown in **Table S1**. Site occupancies, atomic positions and isotropic atomic displacement parameters (U_{iso}) for ZX-V and Ag@ZX-V are given in **Table S2**.

Section IV- Supplementary Figures and Tables

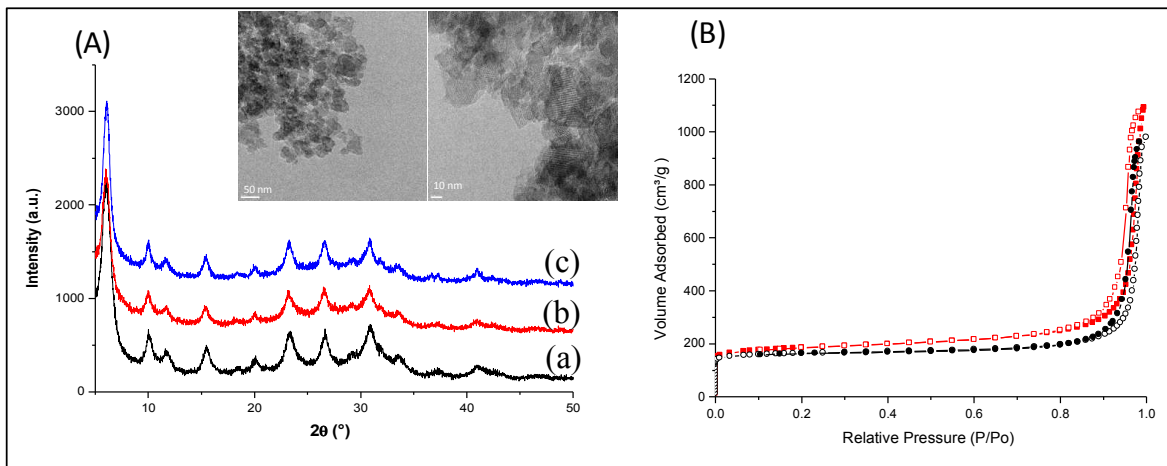


Figure S1. (A) XRD patterns of a) pure ZX and vanadium containing ZX b) prepared with 1 wt.% (ZX-V) and c) with 2 wt.% (ZXV-2) of vanadate precursor. The samples were prepared at 50°C for 34 h. Inset: HRTEM images of ZX-V (B) N₂ sorption (close symbol) and desorption (open symbol) isotherms of ZX (square) and ZX-V (circle) samples.

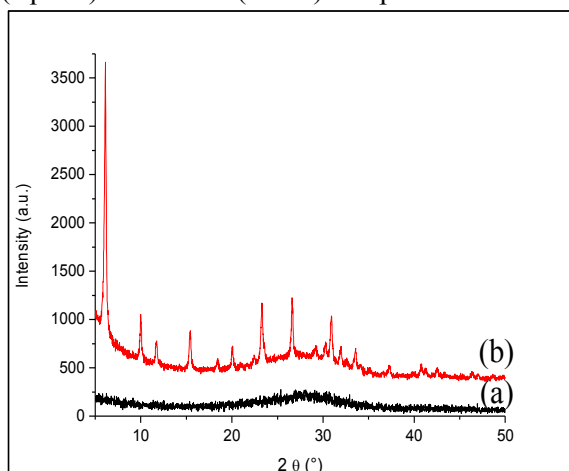


Figure S2. XRD patterns of ZX-V samples prepared with 5 wt.% of Vanadate (ZX-V-5): (a) 50°C (same condition of ZX-V and ZX-V-2) for 10 days; and (b) 80°C for 72 h.

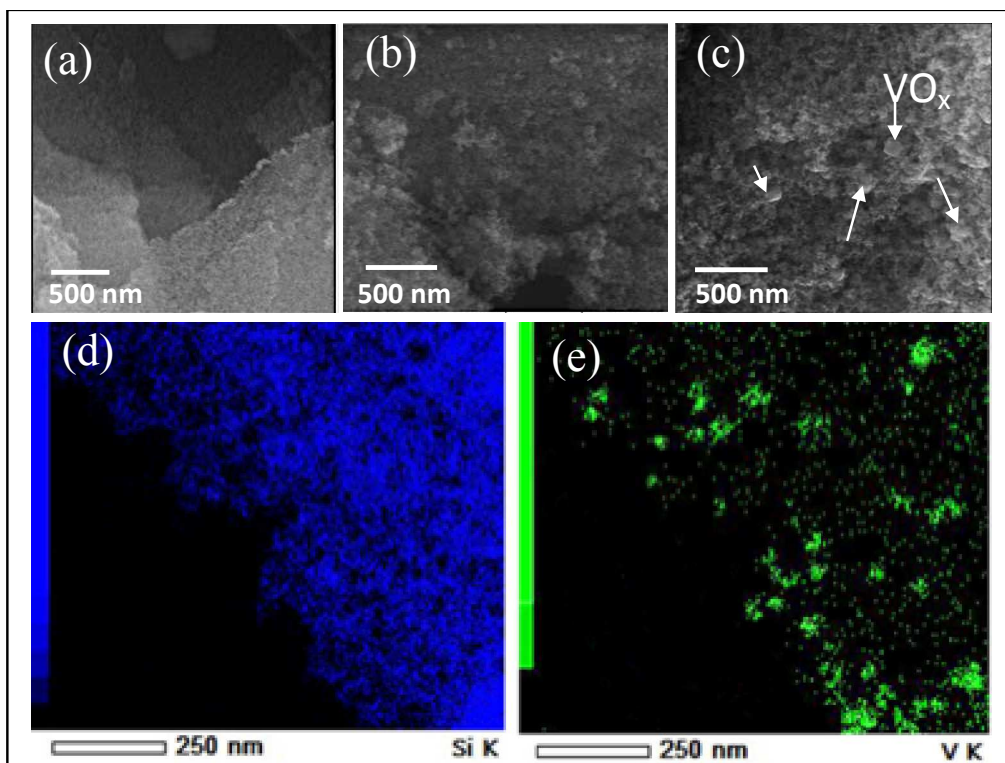


Figure S3. SEM images of a) ZX b) ZX-V and c) ZX-V-5 samples. In image c) the arrows indicate the presence of isolated vanadium oxide particles confirmed by the EDS mapping presented in e). d) and e) correspond to the Si (k) and V (K) EDS-mapping, respectively, of the ZX-V-5 sample. For ZX-V the EDS vanadium signal is under the detection limit.

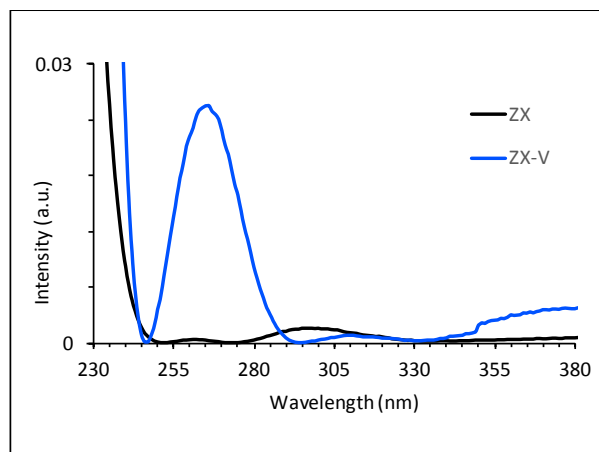


Figure S4. DR-UV-visible spectra of ZX (black) and ZX-V (blue) powders. The band at 290-250 is characteristic of isolated vanadate.

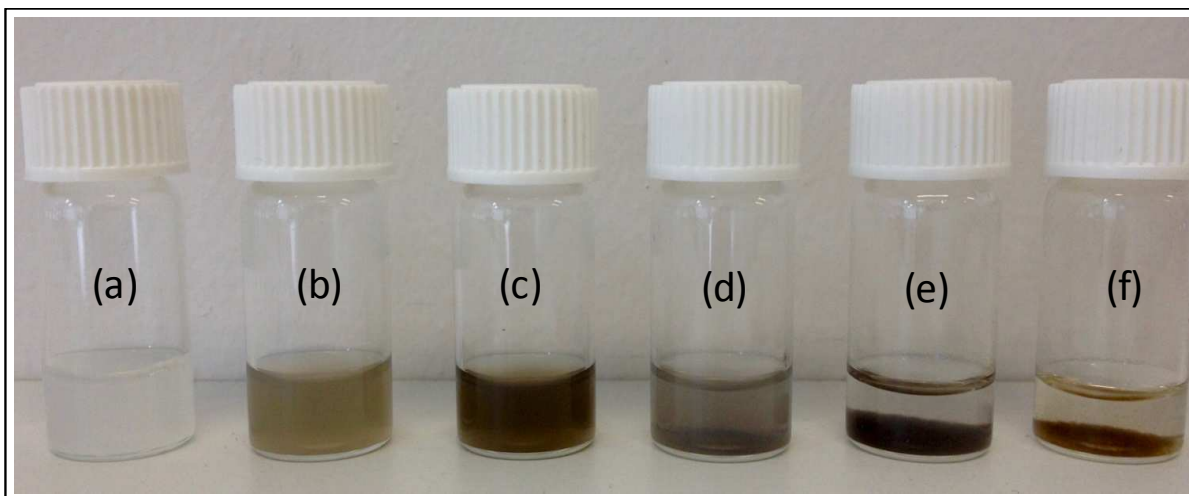


Figure S5. Optical photographs of $\text{AgNO}_3/\text{ZX-V}$ suspensions in (1/0) a), (0.95/0.05) b), (0.75/0.25) c), (0.5/0.5) d), (0.25/0.75) e), and (0.05/0.95) f) of $\text{H}_2\text{O}/\text{EtOH}$ (Vol./Vol.) after 300 s of UV irradiation. ZX-V content = 3 mg/ml. Hg-Xe Lamp (200 W), irradiance = $205 \text{ mW}/\text{cm}^2$, polychromatic irradiations. N.B. All suspensions were stable before irradiation; total volume = 3 ml. The grey precipitation could be due to the formation of photosensitive silver acetate. Acetate is resulted from ethanol photooxidation and probably promoted at high ethanol concentration (at low ethanol concentration complete photooxidation is promoted).

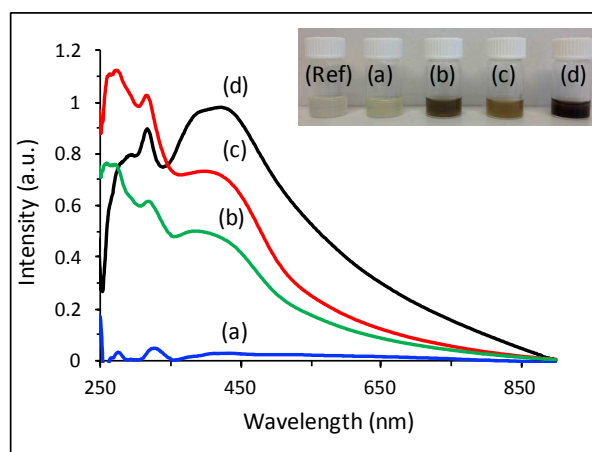


Figure S6. UV-visible spectra of ZX-V suspensions after 300 s of UV irradiation in presence of different concentrations of AgNO_3 : a) $1 \times 10^{-3} \text{ M}$; b) $5 \times 10^{-3} \text{ M}$; c) $1 \times 10^{-2} \text{ M}$; and d) $5 \times 10^{-2} \text{ M}$. Zeolite concentration = 3 mg/ml; $\text{EtOH}/\text{H}_2\text{O}$: 0.25/0.75 vol./vol; total volume= 3 ml. Hg-Xe Lamp (200 W), irradiance = $205 \text{ mW}/\text{cm}^2$, polychromatic irradiations. Spectra subtracted from the spectrum of the sample before irradiation. *Inset*: image of the corresponding samples. It is clear that the formation of silver nanoparticles is promoted with the time of irradiation.

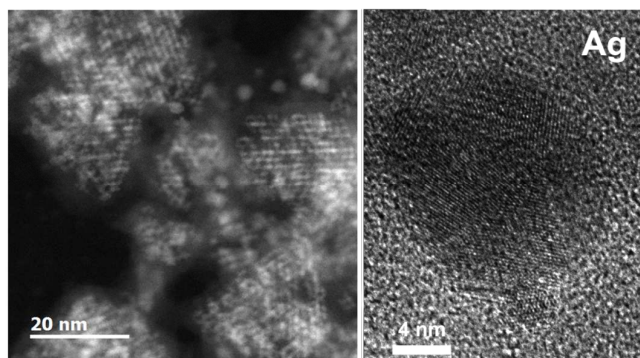


Figure S7. HAADF-STEM images of Ag@ZX-V. Notice silver nanoparticles on the external surface of some of zeolite crystals.

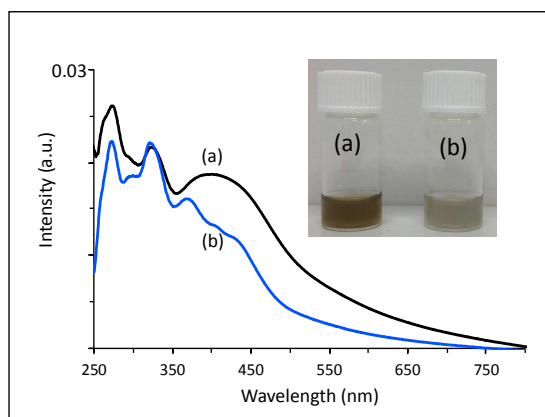


Figure S8. UV-visible spectra of ZX-V suspensions after 300 s of UV irradiation in presence of 5×10^{-3} M of AgNO_3 : (a) as prepared; (b) after washing and re-dispersion in water/ethanol. Zeolite concentration=3 mg/ml; EtOH/ H_2O = 0.25/0.75 vol./vol.; total volume = 3 ml. Hg-Xe Lamp (200 W), polychromatic irradiations. Spectra subtracted from the spectrum of the sample before irradiation. Inset: image of the corresponding samples. The results demonstrate the stability of the subnanometer particles of silver clusters while the silver nanoparticles can be easily removed with a simple wash.

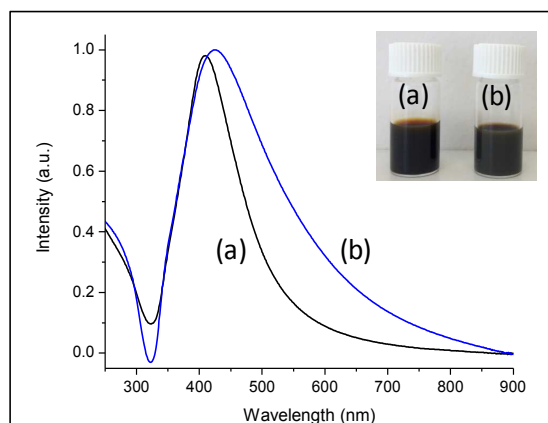


Figure S9. UV-visible spectra of ZX a) and ZX-V b) suspensions after 1 h of heating at 180°C in presence of 5×10^{-3} M of AgNO_3 . Zeolite concentration=3 mg/ml; EtOH/ H_2O = 0.25/0.75 vol./vol. Inset: image of the corresponding samples. The broad band is assigned to the plasmonic band of silver showing that the hydrothermal method promotes mainly the formation of the silver nanoparticles.

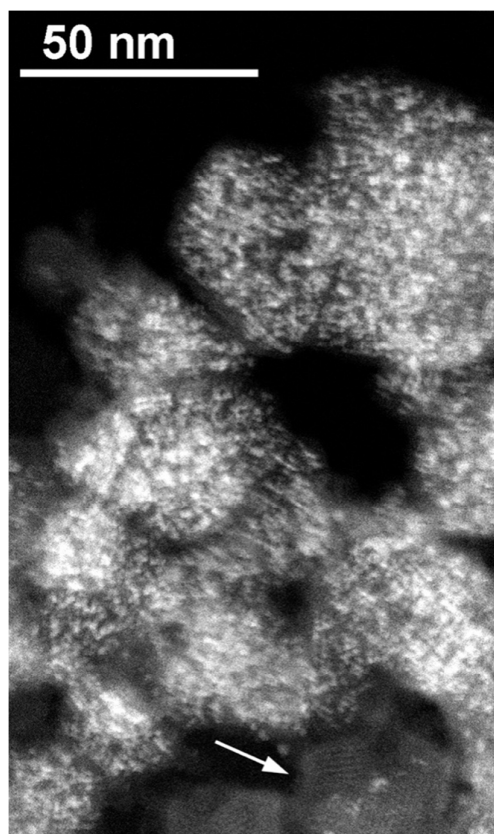


Figure S10. HAADF-STEM image of Ag@ZX-V sample. Non-loaded FAU nanoparticle with resolved lattice plains depicted by white arrow.

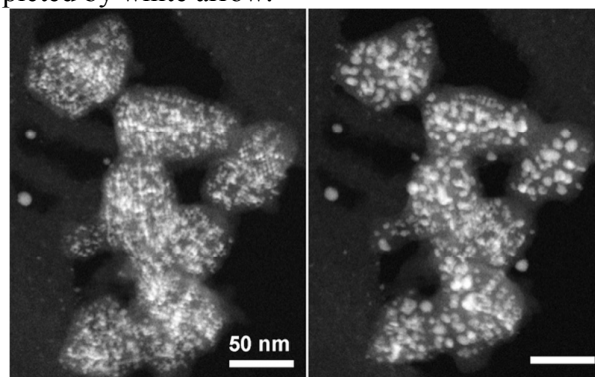


Figure S11. HAADF-STEM images of Ag@ZX-V nanoparticles obtained immediately (left) and after second scan (approximately 1 minute - right). Notice segregation of Ag nanoparticles from the pores into the large Ag nanoparticles after second scan by e-beam inside the microscope during imaging.

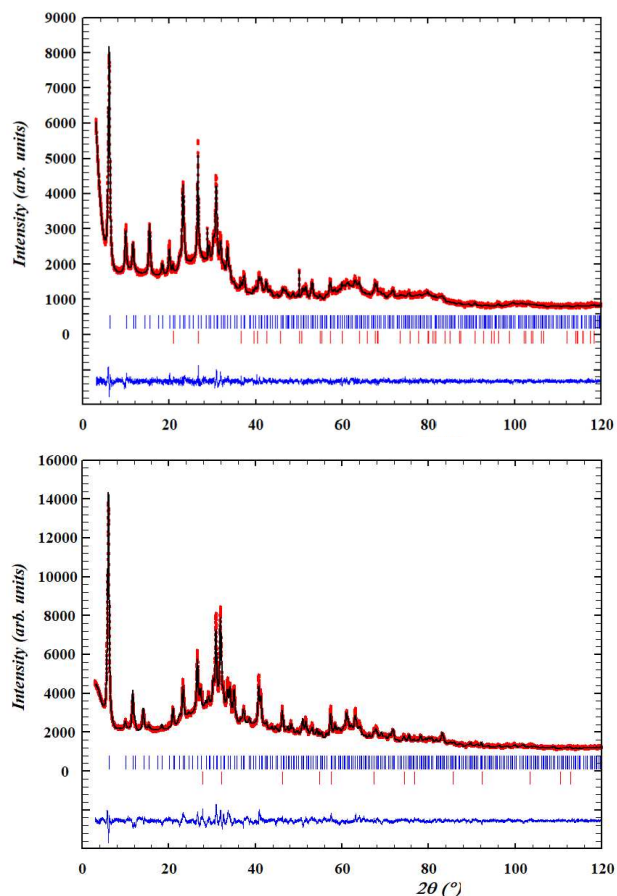


Figure S12. PXRD diagrams (Cu-K α 1 radiation; 1.5406Å) of ZX-V (a) and Ag@ZX-V (b) with observed (red dots), calculated (black solid line), difference profiles (blue solid line) and Bragg reflections (ticks) obtained after Rietveld refinements.

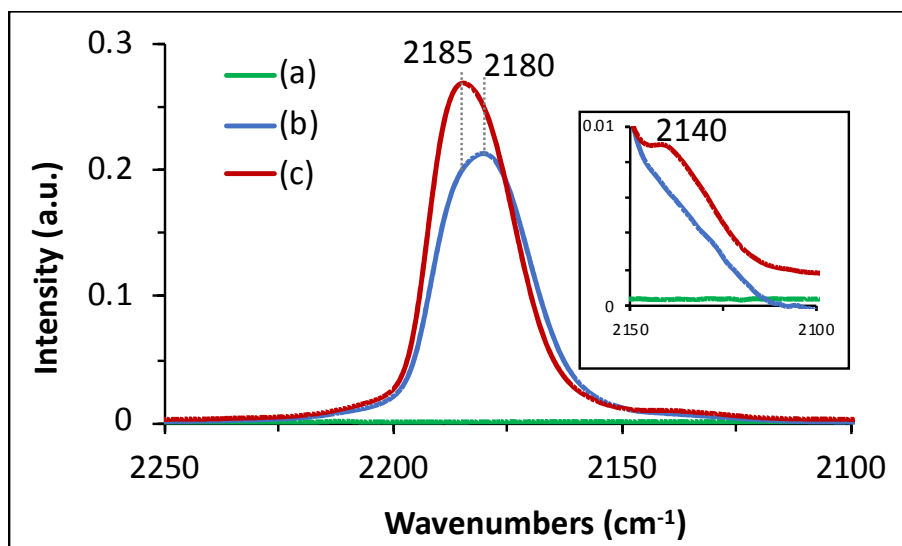


Figure S13. FTIR absorbance spectra in the range 2250–2100 cm^{-1} of adsorbed CO on self-supported pellets of (a) ZX-V (Na form) (b) ZX-V (Ag form) and (c) Ag@ZX-V samples. Inset: zoom of the range 2150–2100 cm^{-1} . The band at 2140 cm^{-1} is characteristic of adsorbed CO on reduced silver (Ag^0).

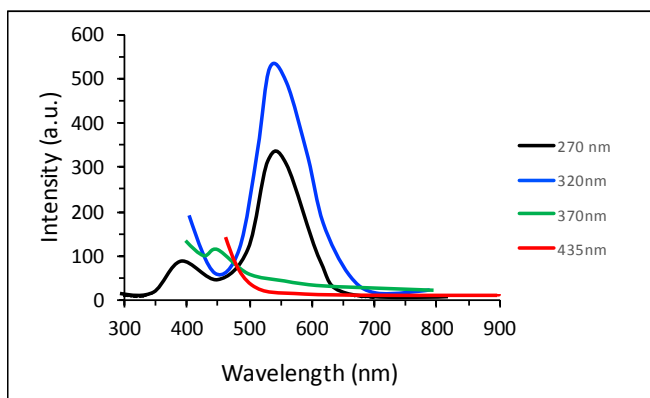


Figure S14. Emission spectra of the Ag@ZX-V suspension obtained at different excitation wavelengths.

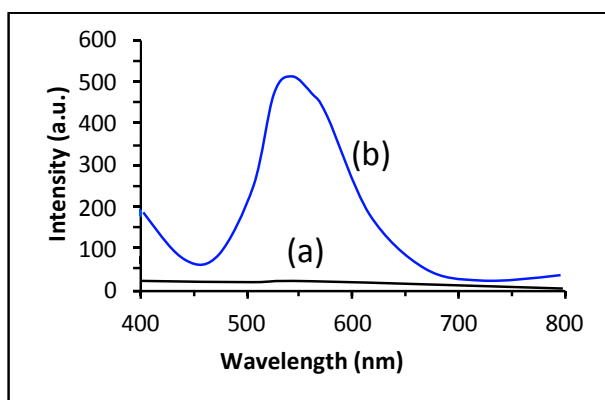


Figure S15. Emission spectra of $\text{Ag}^+/\text{ZX-V}$ (a) and Ag@ZX-V (b) suspensions during the excitation at 320 nm. $\text{Ag}^+/\text{ZX-V}$ is not photoluminescent. Ag@ZX-V is prepared by irradiation of the $\text{Ag}^+/\text{ZX-V}$ suspension after 300s under polychromatic irradiation. Zeolite concentration=3 mg/ml; $[\text{AgNO}_3]=5 \times 10^{-3}$ M; EtOH/ H_2O : 0.25/0.75 vol./vol.; total volume= 20 ml.

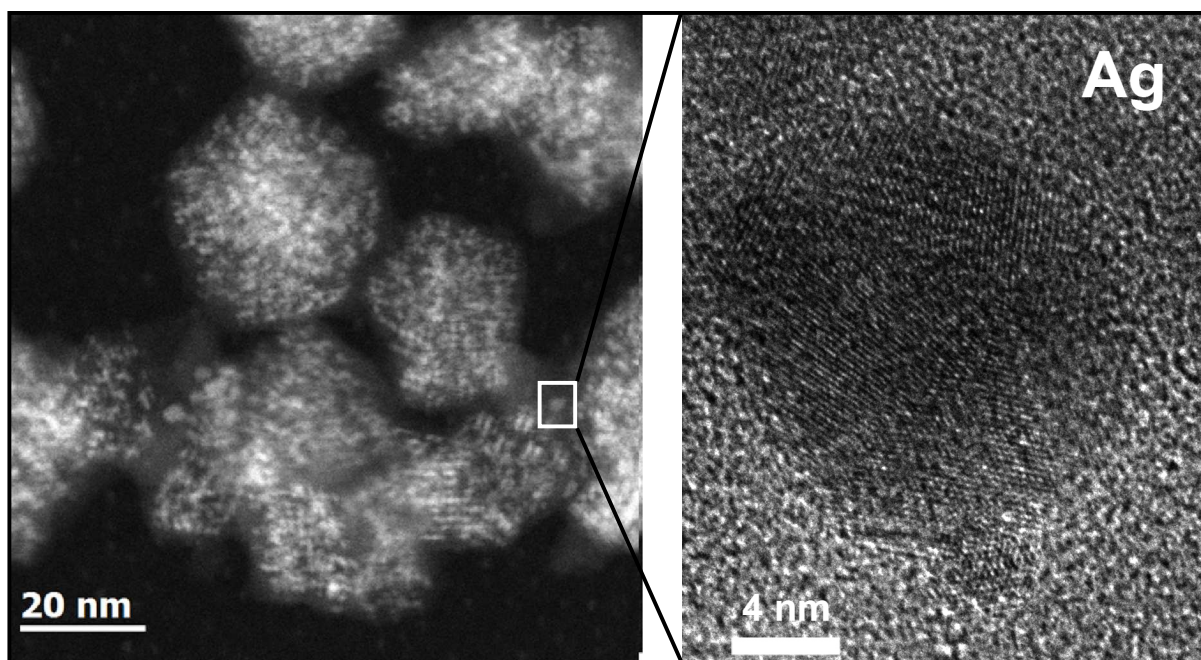


Figure S16. HAADF-STEM images of Ag@ZX-V showing the presence of external silver nanoparticles.

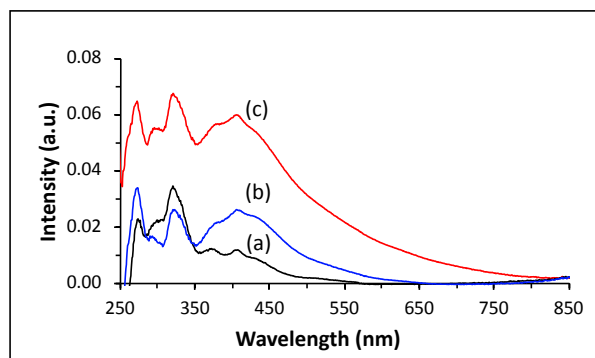


Figure S17. UV-visible spectra of $\text{Ag}^+/\text{ZX-V}$ suspensions: (a) after 30 s of polychromatic UV irradiation; (b) after 30 s of polychromatic UV irradiation (205 mW/cm^2) followed by 300s of monochromatic irradiation at 365nm (15 mW/cm^2); (c) after 30s of polychromatic UV irradiation followed by 300s of irradiation with Xe visible lamp ($\lambda > 390\text{nm}$; $I_0 = 150 \text{ mW/cm}^2$). Zeolite concentration=3 mg/ml; $[\text{AgNO}_3] = 5 \cdot 10^{-3} \text{ M}$; EtOH/ $\text{H}_2\text{O} = 0.25/0.75 \text{ vol./vol.}$; total volume= 20 ml. Spectra subtracted from the spectrum of the sample before irradiation. N.B. The direct irradiation (without previous irradiation under polychromatic UV) of the $\text{Ag}^+/\text{ZX-V}$ suspensions with 365 nm or visible light for 10 min demonstrate that there is no reduction of silver (no development of UV-visible bands is observed).

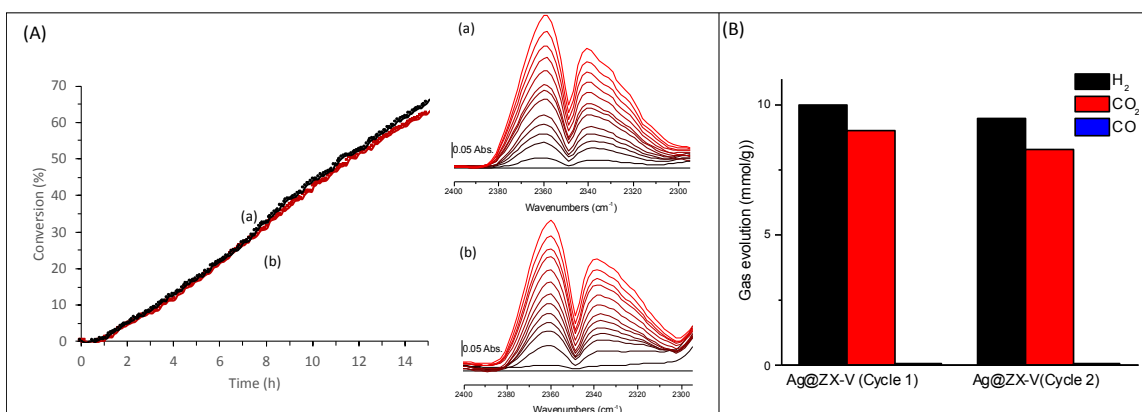


Figure S18. A) Evolution of the formic acid conversion versus the visible irradiation time over Ag@ZX-V during the first and the second cycle. The conversion was calculated by following the CO_2 IR band of headspace (Inset). (a) and (b) correspond to the cycle 1 and cycle 2, respectively. (B) H_2 , CO_2 and CO content as determined by GC after 5h of visible-light irradiation of formic acid solution (0.35 ml in 10 ml of AcN) in the presence of Ag@ZX-V as photocatalysts.

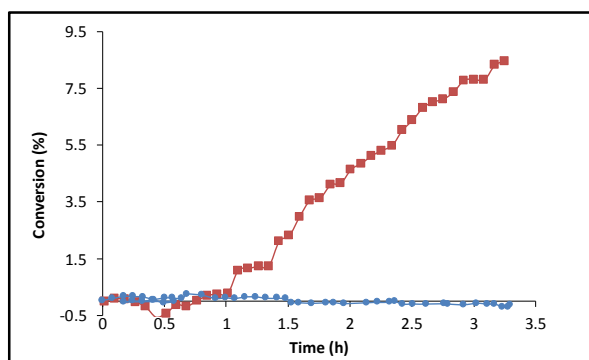


Figure S19. Evolution of the formic acid conversion upon the polychromatic visible irradiation with $\lambda > 390 \text{ nm}$ (square) and monochromatic UV irradiation (circle) with $\lambda = 365 \text{ nm}$ using Ag@ZX-V .

V as photocatalyst: solution: 50 mg of catalyst with 0.35 ml of formic acid in 10 ml of AcN under Ag; t=0.5 h corresponds to the irradiation time.

Table S1. Details of PXRD data and Rietveld refinements for ZX-V and Ag@ZX-V.

Diffractionmeter	Bruker D8 advance vario1	
Radiation (Å)	Cu-K α_1 radiation $\lambda = 1.5406$	
Compound	ZX-V	Ag@ZX-V
Formula	Na ₈₂ Al ₇₃ Si ₁₁₉ O ₃₈₄ (H ₂ O) ₁₃₉	Ag ₂₇ Na ₅₅ Al ₇₃ Si ₁₁₉ O ₃₈₄ (H ₂ O) ₁₃₈
2 θ -range / step (°) / time per step (s)	3 – 119.998 / ~0.014 / 4.8	10 – 126.181 / ~0.012 / 1
Temperature (°C)	20	20
Space Group	<i>Fd</i> $\bar{3}$ (203)	<i>Fd</i> $\bar{3}$ (203)
Z	1	1
<i>a</i> / Å	25.0232(10)	24.9968(7)
<i>V</i> / Å ³	15668.6(10)	15619.0(5)
Molar mass (g.mol ⁻¹)	15565.8	17862.3
Rietveld refinement :		
Shape	Lorentzian	Lorentzian
Background	35 Legendre polynoms	30 Legendre polynoms
Asymmetry	Fundamental approach	Fundamental approach
Rietveld agreement factors		
<i>R</i> _{Fobs}	0.0295	0.0389
<i>R</i> _{Bobs}	0.0415	0.0718
<i>R</i> _{wp}	0.0283	0.0364
<i>cR</i> _{wp}	0.1284	0.1487
Gof	1.07	1.71
Relative phase amounts in mass (%)	97.3(4) - ZX-V-1	97.7(4) - AgZX-V-1
	2.7(5) - SiO ₂	2.3(5) - NaO ₂

Table S2. Site occupancies, atomic positions and isotropic atomic displacement parameters (U_{iso}) for ZX-V and Ag@ZX-V

Atom	Occ.	x	y	z	U_{iso} (Å ²)
ZX-V					
Na1	0.762(15)	0.2340(3)	0.0160(3)	0.0160(3)	0.018007
Na2	0.648(15)	0.0619(3)	0.0619(3)	0.0619(3)	0.018007
Na3	0.36(2)	0	0	0	0.018007
Na4	0.323(9)	0.1757(8)	-0.1874(9)	0.0405(8)	0.018007
Si1	1	0.1250(4)	-0.0553(4)	0.0355(5)	0.073(3)
Si2	0.24	0.1241(4)	0.0369(4)	-0.0490(3)	0.0261(18)
Al2	0.76	0.1241(4)	0.0369(4)	-0.0490(3)	0.0261(18)
O1	1	0.1073(7)	-0.1055(7)	-0.0027(11)	0.074(5)
O2	1	0.1471(3)	-0.0069(5)	-0.0012(4)	0.038(4)
O3	1	0.0764(4)	-0.0314(4)	0.0706(4)	0.051(4)
O4	1	0.1769(5)	-0.0701(4)	0.0714(4)	0.068(6)
O5 (H ₂ O)	0.454(17)	0.0878(6)	0.0878(6)	0.1622(6)	0.005686
O6 (H ₂ O)	0.686(19)	0.2831(5)	-0.0331(5)	-0.0331(5)	0.005686
O7 (H ₂ O)	0.355(10)	0.2326(13)	-0.1516(9)	0.0080(13)	0.005686
O8 (H ₂ O)	0.200(8)	0.295(3)	-0.1380(14)	-0.047(3)	0.005686
O9 (H ₂ O)	0.514(12)	0.0883(8)	-0.2040(7)	0.1007(9)	0.005686
Ag@ZX-V					
Ag1	0.632(7)	0	0	0	0.0271(18)
Ag2	0.533(7)	0.24066(14)	0.00934(14)	0.00934(14)	0.090(3)
Na1	1	0.0706(3)	0.0706(3)	0.0706(3)	0.013(3)
Na3	0.72	0.0878(4)	0.1622(4)	0.0878(4)	0.067(10)
Si1	1	0.0423(2)	0.12948(19)	-0.0480(2)	0.0239(16)
Si2	0.24	0.1297(3)	0.2185(3)	-0.0560(3)	0.0266(18)
Al2	0.76	0.1297(3)	0.2185(3)	-0.0560(3)	0.0266(18)
O1	1	-0.0084(3)	0.1446(3)	-0.0022(4)	0.0206(16)
O2	1	0.0725(3)	0.0671(3)	-0.0378(4)	0.0206(16)
O3	1	0.0804(3)	0.1854(3)	-0.0665(3)	0.0206(16)
O4	1	0.1426(4)	0.2604(5)	-0.1079(3)	0.0206(16)
O5 (H ₂ O)	0.865(15)	0.0113(5)	0.3652(6)	-0.0339(5)	0.037
O6 (H ₂ O)	0.70(3)	0.0360(7)	0.2140(7)	0.5360(7)	0.037
O7 (H ₂ O)	0.69(2)	0.0503(9)	0.375	0.875	0.037

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