

SUPPORTING INFORMATION

A Raman-Based Imaging Method for Characterizing the Molecular Adsorption and Spatial Distribution of Silver Nanoparticles on Hydrated Mineral Surfaces

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This file has a total of 6 pages and consists of two tables (tables S1 and S2) and four figures (figures S1, S2, S3, and S4).

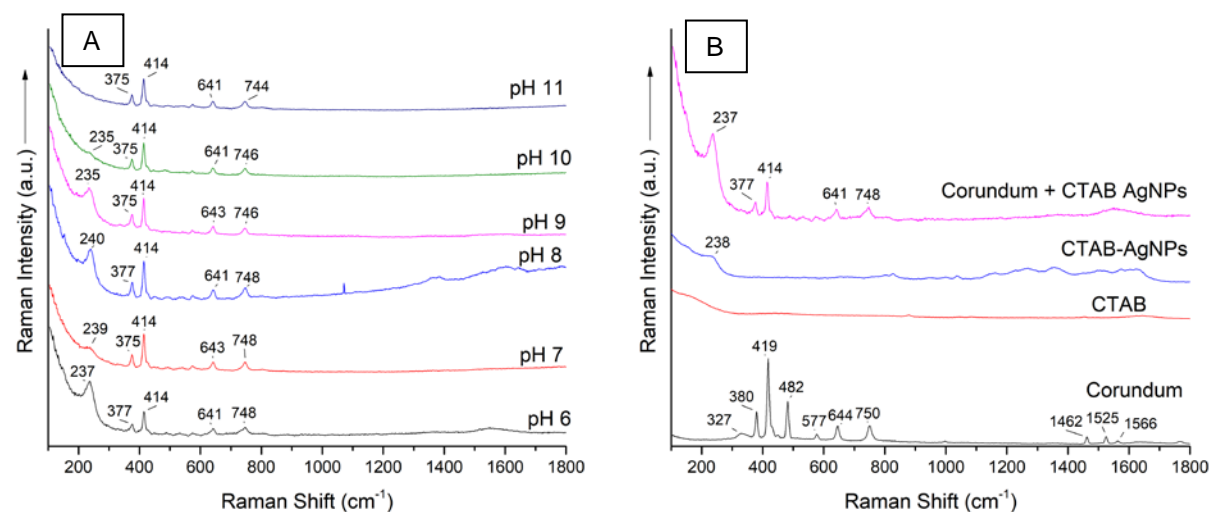


Figure S1. A) Raman spectra of micro-corundum exposed to 1 mg L⁻¹ of CTAB-capped AgNPs⁺ with ISA for 30 min at all experimental pH values (6-11). **B)** Raman spectra of the same sample in comparison with the corresponding controls on corundum, CTAB, and CTAB-capped AgNPs⁺. Spectra were shifted for comparison reasons.

Table S1: Raman vibrational modes of muscovite control and their tentative assignments according to references 51-54 from the manuscript. The experimental reference spectrum was obtained with a 633 nm HeNe Laser and 1 s acquisition time.

Literature Raman modes (cm ⁻¹)	Experimental Raman modes (cm ⁻¹)	Tentative Assignment
85		Sheet yz-trans. + K y-trans.
124	122	Sheet xz-trans. + K xy-trans. (minor)
172	170	M2-OH stretch (M2 z-trans.)
198	195	M2-OH stretch + Od xz-trans.
217	215	OH-M2-OH bend + M2-Oa stretch
265	267	Ob, OH y-trans. + Oc,e z-trans. + K y-trans.
265		T1-Oa z-trans. + T2-Ob -z-trans. + M2 xy-trans. + K xy-trans.
295		M2-OH stretch + M2-Oa stretch
316	317	M2-OH stretch + M2-Ob stretch + tetrahedral rot. z
382	382, sh	M2 z-trans. + Oc z-trans. + Od,e -z-trans.
411	413	M2 xz-trans. + Od z-trans. + Oc,e xz-trans.
442		Oa-M2-Ob bend + Oc,e z-trans. + Od xy-trans.
527		T-Obr-T xy-bend
583		M2 xy-trans. + T z-trans.
583		Od,e xy-trans. + T y-trans. + K xy-trans.
638	638	Onb yz-trans. + Obr -yz-trans.
703	707	Onb z-trans. + Ob r -z-trans. + M2-Ob stretch
754	757	Oa-M2-Ob bend
800		T-Oc,d-T bend
811		T-Oc,e-T bend
913	915	Tetrahedral breathing
958	959	T-Onb stretch (n1)
1024	1020	T-Onb stretch (n1) + Obr in/out tetr. base center
1098	1079	T1,2-Oc,e xy-stretch (n10)
1116	1120	T1,2-Oc,d xy-stretch (n10)

Abbreviations: M2 – Octahedral site occupied by Al³⁺ (M1 site is vacant), T – Tetrahedral site, Onb - non-bridging O atoms, Obr - bridging O atoms, and sh – shoulder.

26 **Table S2.** Raman vibrational modes of corundum control and their tentative assignment
 27 according to references 57-59 from manuscript.

Experimental Raman Modes (cm⁻¹)	Literature Raman Modes (cm⁻¹)	Tentative assignment
378 (m)	379	E_g external
416 (s)	417	A_{1g}
429 (m,sh)	429	E_g external
451 (w)	451	E_g internal
574-576 (w)	576	E_g internal
644 (m)	644	A_{1g}
750 (m)	750	E_g internal

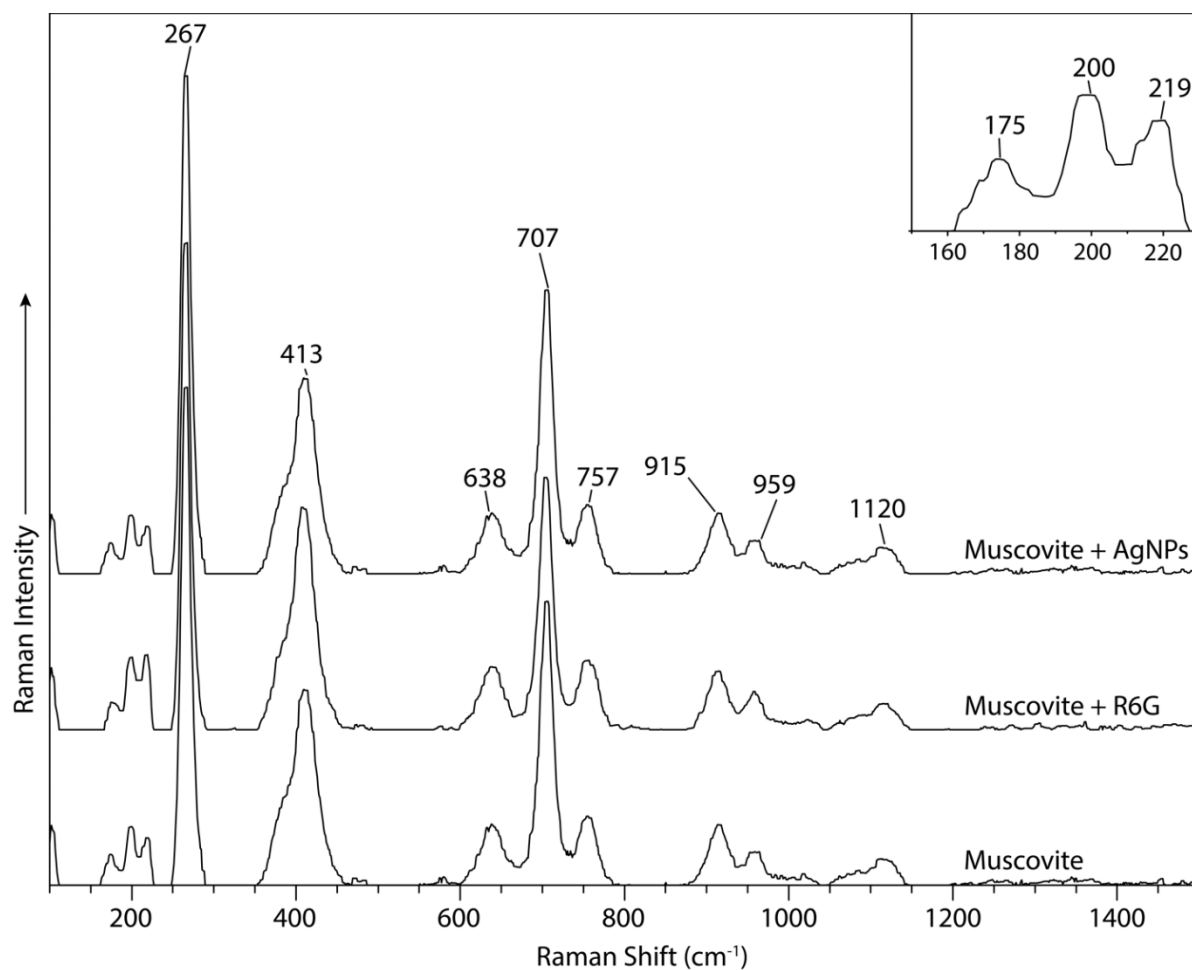


Figure S2: Representative Raman spectra of muscovite controls. No evidence of R6G or AgNPs⁻ is present in the controls. The upper two spectra were shifted for comparison reasons. Inset displays the low cm^{-1} region.

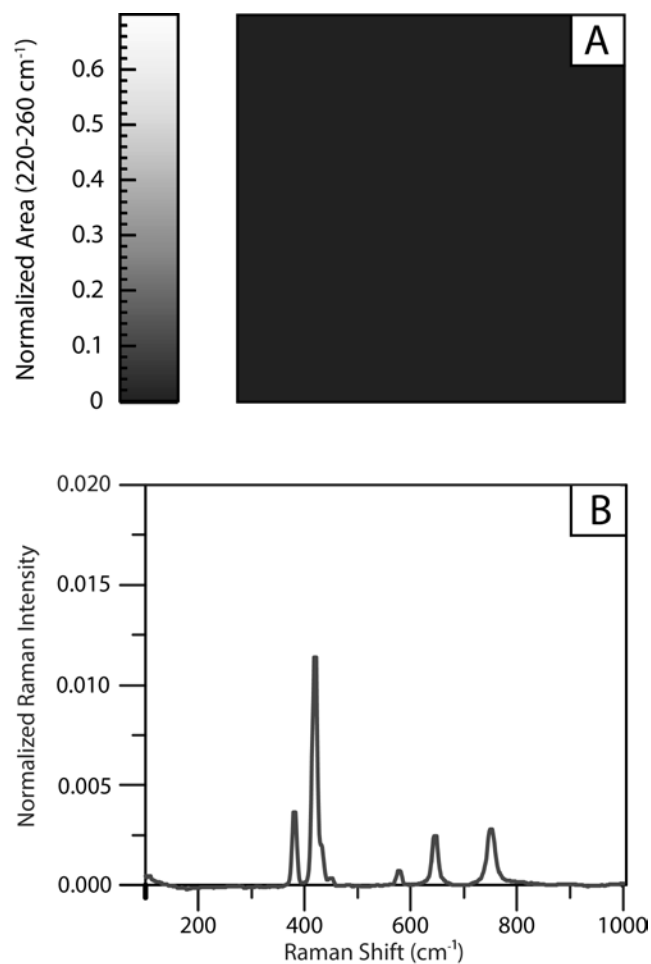


Figure S3: Raman image of a AgNP⁻-macro-corundum control window (52 μm x 52 μm) prepared by immersing corundum into 1 mg L⁻¹ of AgNPs⁻ for 30 min. The color scale in (A) is the same as in Figure 2. There is no evidence of silver in any spectrum; only the characteristic peaks of corundum were detected.

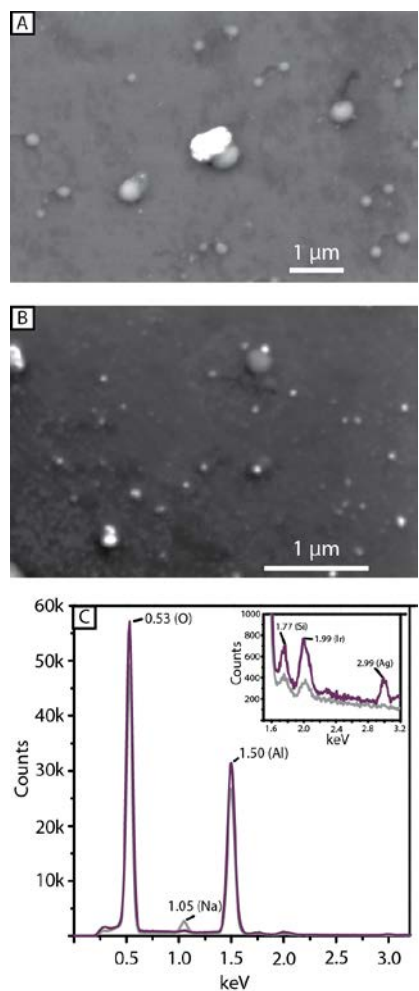


Figure S4. Backscattered SEM images of a macro-corundum window utilizing a backscatter, secondary electron detector. **A)** Mineral control with ISA (no AgNPs) leading to the formation of nano-sized features due to the ISA precipitation on the surface (large white spot in the center). **B)** Mineral sample with AgNPs⁻ showing the absorption of AgNPs⁻ onto the same window (smaller but more frequent white spots). **C)** EDX spectra collected from the described areas in images A) (silver gray spectrum) and B) (violet spectrum). The inset confirms the chemical nature of the Na (from image A) and Ag nanofeatures (from image B).