APTES duality and nanopore seed regulation in homogeneous and nanoscale-controlled reduction of Ag shell on SiO_2 microparticle for quantifiable single particle SERS

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SUPPLEMENTARY INFORMATION

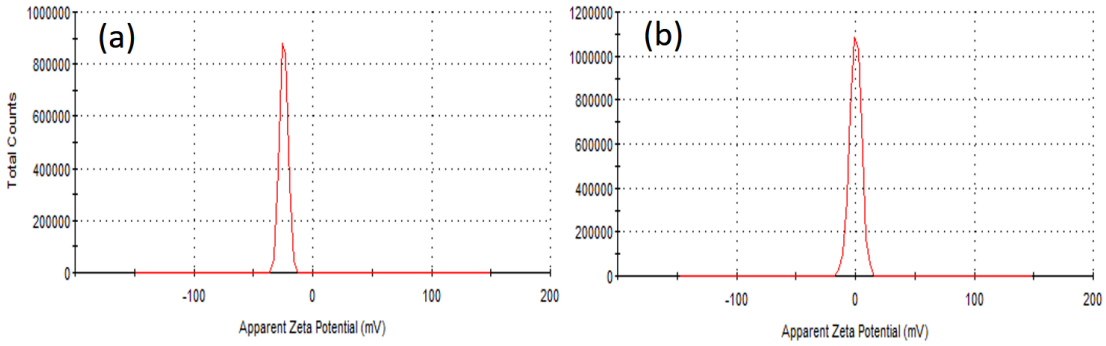

Figure S1. (a) Zeta potential (ζ) for SiO_2 microspheres 0.1mg/ml in ethanol with ζ= -24.4 mV, measured with a Zetasizer (Malvern) within a polystyrene zeta potential cell and estimated with the Hückel approximation for non-aqueous solvent. (b) Same after addition of 1 mM $AgNO_3$, showing ζ now more positive and at ca. 0 mV, suggesting coverage of the silanols with Ag^+ ions.

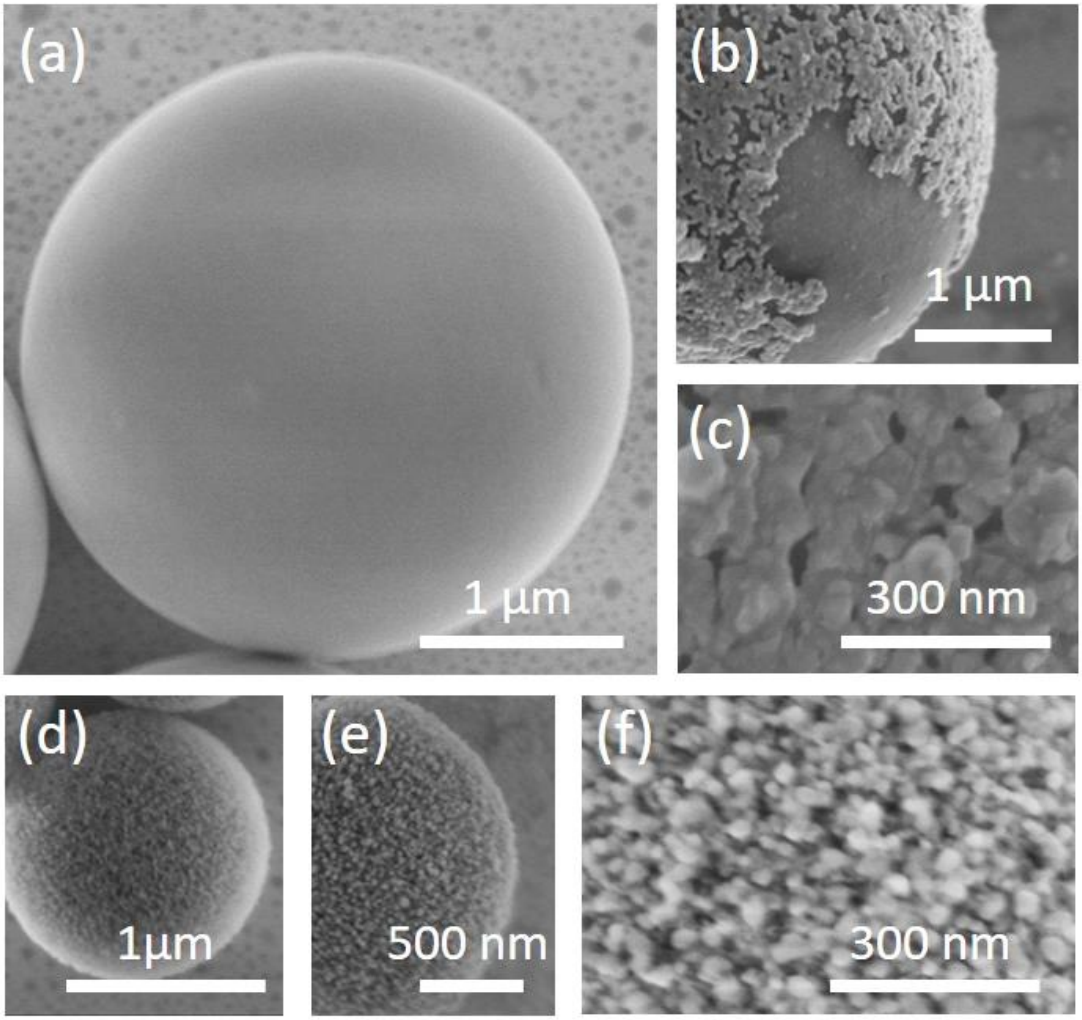

Figure S2. (a) SEM image of a silica microparticle (ca. 3 µm) with 22 Å nanopores. (b,c) Same after Ag reduction in ethanol ($AgNO_3$ 1 mM, APTES 1 mM), (d) SEM image of a silica microparticle (ca. 1.5 µm) with 92 Å nanopores. (e,f) Same after Ag reduction in ethanol ($AgNO_3$ 1 mM, APTES 1 mM). Larger nanopores lead to an increase in nucleation centres and achieve more homogeneous and uniform Ag nanoparticles coverage.

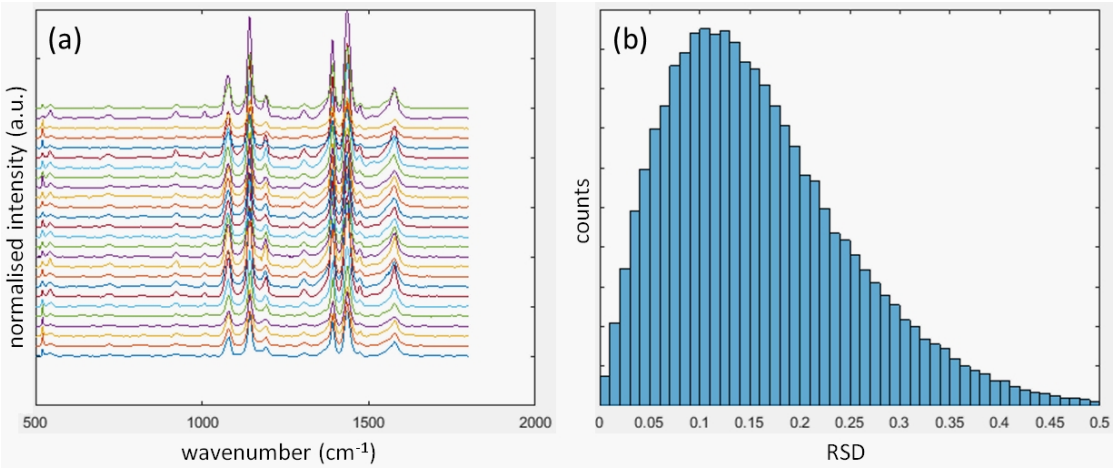

Figure S3. (a) Raman spectra of individual 4-ATP on Ag/SiO_2 microparticles recorded on 2 sets of 13 microparticles. The first 13 spectra from the bottom are from a first batch of microparticles and the 13 others from a second batch. The two batches were prepared with same conditions but are otherwise independent. The data are normalized as per main text. The RSD between the 26 spectra altogether is 36% and the RSD between the 2 sets after average of the corresponding spectra is 18%. (b) Histogram of the RSD calculated between two sets of 10 averaged spectra, mimicking the RSD determined from an experiment where a large amount of sets of 10 microparticles are measured and compared. This statistical RSD is 11% as the histogram peaks at this value. The two average spectra are computed by randomly picking 20 spectra from (a) and splitting these in 2 series of 10. The histogram is built for 10^5 randomly picked sets without excluding repetitions.