Inkjet Printing of Silver Rainbow Colloids for SERS Chips with Polychromatic Sensitivity

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Synthesis of rainbow hydrosols

Fig. S1a shows TEM image of Ag seeds; Fig. S1b shows standard extinction spectra of the seeds after 10 min and 30 min after injection of $NaBH_4$ solution under vigorous stirring. The spectra correlate with particle size distributions confirming that their aging processes are negligible when just prepared seeds are applied.

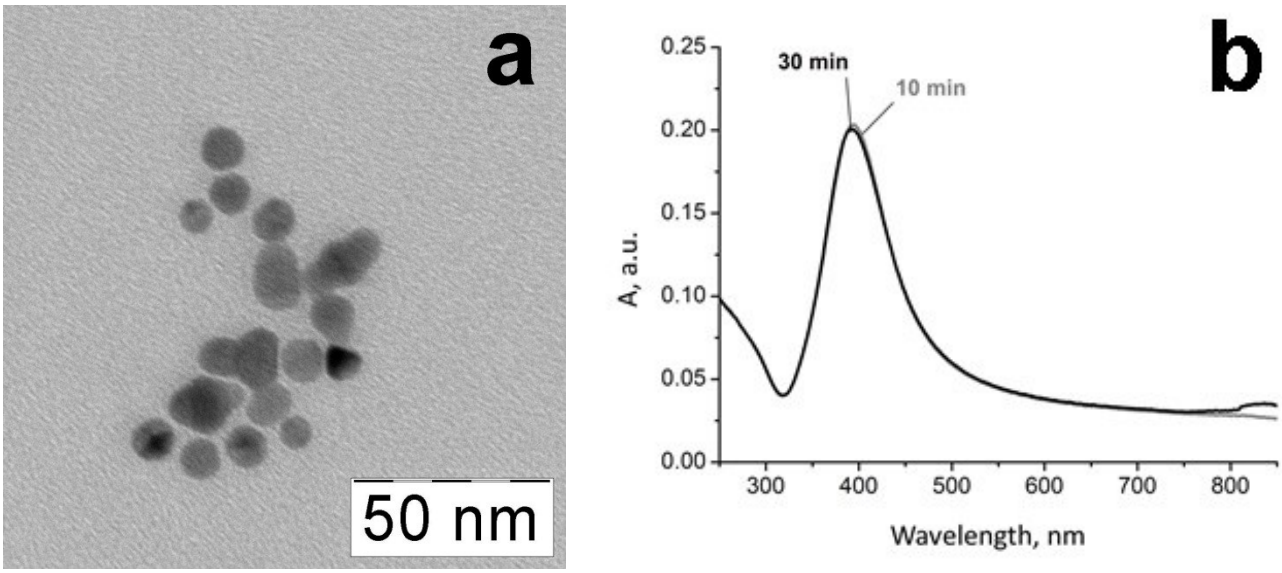


Fig. S1. (a) TEM image of Ag seeds (primary silver hydrosols); (b) UV-vis absorption spectra of primary silver hydrosols (silver seeds) after 10 min and 30 min of interaction with $NaBH_4$ solution.

An analysis of the micromorphology of nanoparticles grown up in aqueous media confirms the anticipated silver particles evolution with a volume of silver seeds aliquot added. It is seen (Table S1) that the samples are different in their microstructure so that the lateral dimension of particles rises up with a decrease of silver seeds aliquot. The growth of a particle size occurs along the (100) direction while the (111) one remains blocked by stronger PVP macromolecules as reported by Jana et al.[1] Larger particles have a triangular or truncated trigonal prism habitus being different from original round-shaped one.

[1] D. Jana and G. De, *J. Mater. Chem.*, 2011, **21**, 6072.

Table S1. Characteristics of silver hydrosols synthesized using the performed two-step method.

Characteristics	**Medium – H_2O (18.2 MΩ·cm)**					
Seeds aliquote, µl	3.2	12.8	25.6	51.2	76.8	153.6
Particle size (TEM), nm	26±8	18±4	14±3	11±2	9±2	10±2
Kinematic viscosity, mm^2/s	1.268±0.005	1.270±0.006	1.263±0.007	1.256±0.007	1.264±0.004	1.264±0.005
Characteristics	**Medium – H_2O : Ethylene glycol = 77% : 23%**					
Seeds aliquote, ml	3.2	9.6	12.8	19.2	22.0	51.2
Particle size (DLS), nm	52.5(75.3%) 5.5(24.7%)	47.8(76.2%) 2.9 (23.8%)	51.2(73.2%) 4.3(26.8%)	41.5(79%) 2.7(21%)	34.8(77.9%) 2.6(22.1%)	28.7(89.5%) 2.6(10.5%)
Particle size (TEM), nm	48 ± 12	41 ± 8	39 ± 14	32 ± 12	25 ± 6	22 ± 7
Density, g/ml	1.027±0.001	1.021±0.001	1.018±0.001	1.014±0.001	1.014±0.001	1.004±0.001
Kinematic viscosity, mm^2/s	1.767±0.003	1.764±0.003	1.763±0.003	1.764±0.003	1.722±0.004	1.680±0.004
Characteristics	**Medium – H_2O : Ethylene glycol = 50% : 50%**					
Seeds aliquote, ml	3.2	9.6	12.8	19.2	22.0	51.2
Particle size (DLS), nm	78.7(83.1%) 2.5(16.9%)	56.8(65.9%) 3.5(22.3%)	49.9(73.1%) 5.5(26.9%)	38.6(78.6%) 2.1(21.4%)	38.8(76.6%) 2.7(23.4%)	38.6(69.2%) 2.3(30.8%)
Particle size (TEM), nm	51 ± 7	40 ± 9	42 ± 6	34 ± 13	26 ± 6	20 ± 6
Density, g/ml	1.047±0.001	1.046±0.001	1.034±0.001	1.041±0.001	1.042±0.001	1.041±0.001
Kinematic viscosity, mm^2/s	2.847±0.005	2.836±0.005	2.826±0.005	2.728±0.006	2.720±0.005	2.585±0.006
Characteristics	**Medium – H_2O : Glycerol = 77% : 23%**					
Seeds aliquote, ml	3.2	9.6	12.8	19.2	22.0	51.2
Particle size (DLS), nm	52.4(70.5%) 6.6(29.5%)	43.5(73.1%) 3.3(26.9%)	39.9(74.2%) 2.6(25.8%)	37.2(74.5%) 2.6(25.5%)	55.5(85.5%) 2.4(14.5%)	29.7(88.5%) 2.1(11.5%)
Particle size (TEM), nm	44 ± 10	36 ± 11	31 ± 10	30 ± 10	26 ± 12	20 ± 8
Density, g/ml	1.041±0.001	1.039±0.001	1.044±0.001	1.043±0.001	1.041±0.001	1.005±0.001
Kinematic viscosity, mm^2/s	1.901±0.007	1.872±0.006	1.866±0.008	1.846±0.006	1.845±0.007	1.832±0.008
Characteristics	**Medium – H_2O : Glycerol = 50% : 50%**					
Seeds aliquote, ml	3.2	9.6	12.8	19.2	22.0	51.2
Particle size (DLS), nm	80.7(75.5%) 8.7(24.5%)	52.5(72.7%) 3.9(27.3%)	58.0(83%) 8.0(17%)	54.2(81.8%) 7.9(17.2%)	41.7(73.5%) 2.4(26.5%)	39.2(77.9%) 2.3(22.1%)
Particle size (TEM), nm	58 ± 13	54 ± 18	53 ± 15	47 ± 17	32 ± 11	24 ± 3
Density, g/ml	1.112±0.001	1.078±0.001	1.095±0.001	1.087±0.001	1.098±0.001	1.105±0.011
Kinematic viscosity, mm^2/s	5.116±0.008	4.826±0.009	4.826±0.008	4.678±0.008	4.588±0.009	4.445±0.010

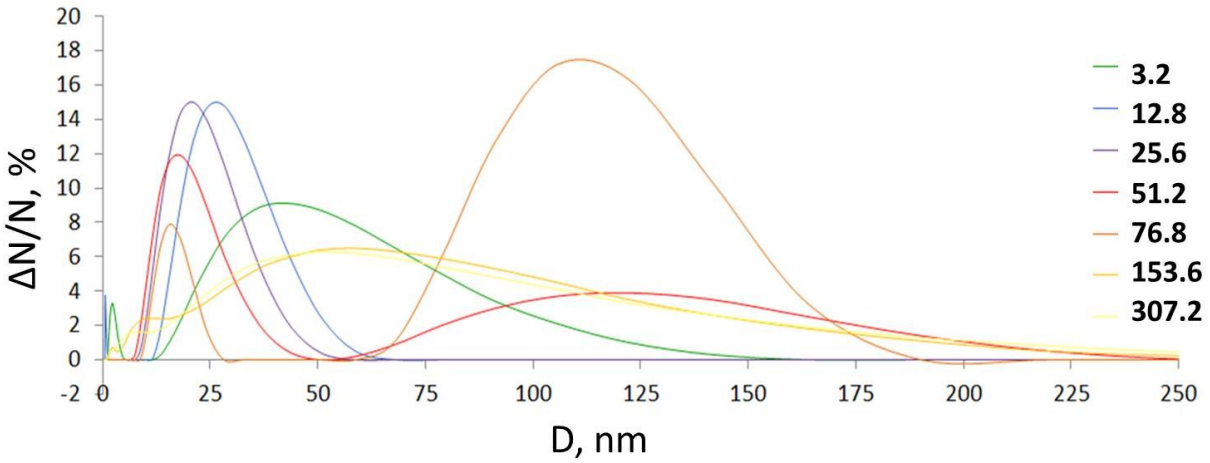


Fig. S2. DLS data for silver hydrosols of a variable plate-like to round morphology in respect with the seed volume added as marked to the right.

The lateral diameter subsidence is evenly demonstrated also by DLS data (Fig. S2). Smaller maxima in the range of 5 - 50 nm (which are the most permissible for analysis) shift to smaller sizes with an increase of the silver seeds aliquote. This correlates well enough with TEM statistics summarized in Table S1.

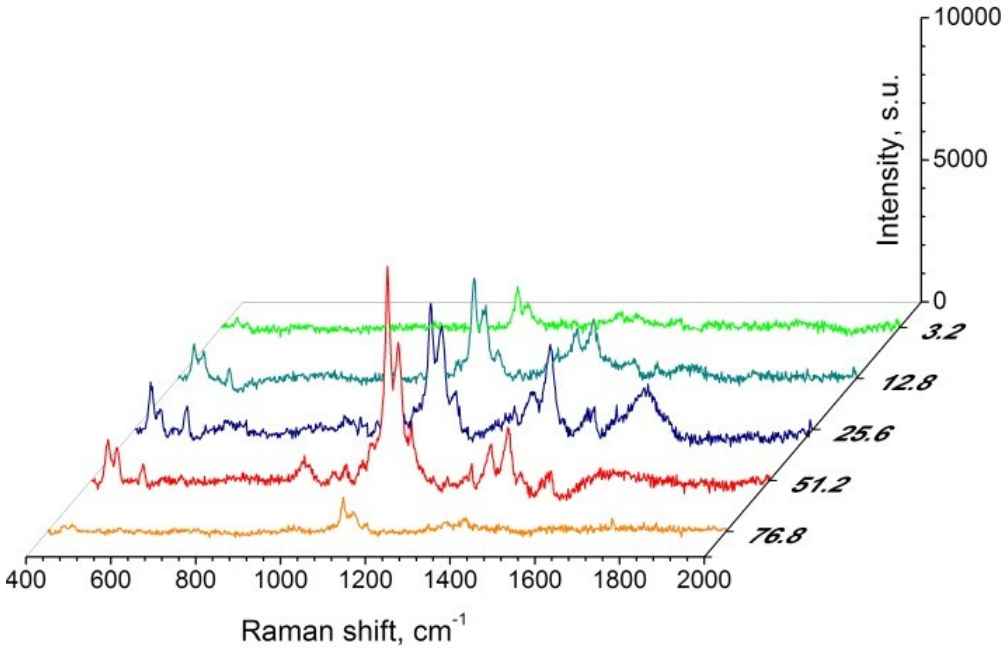
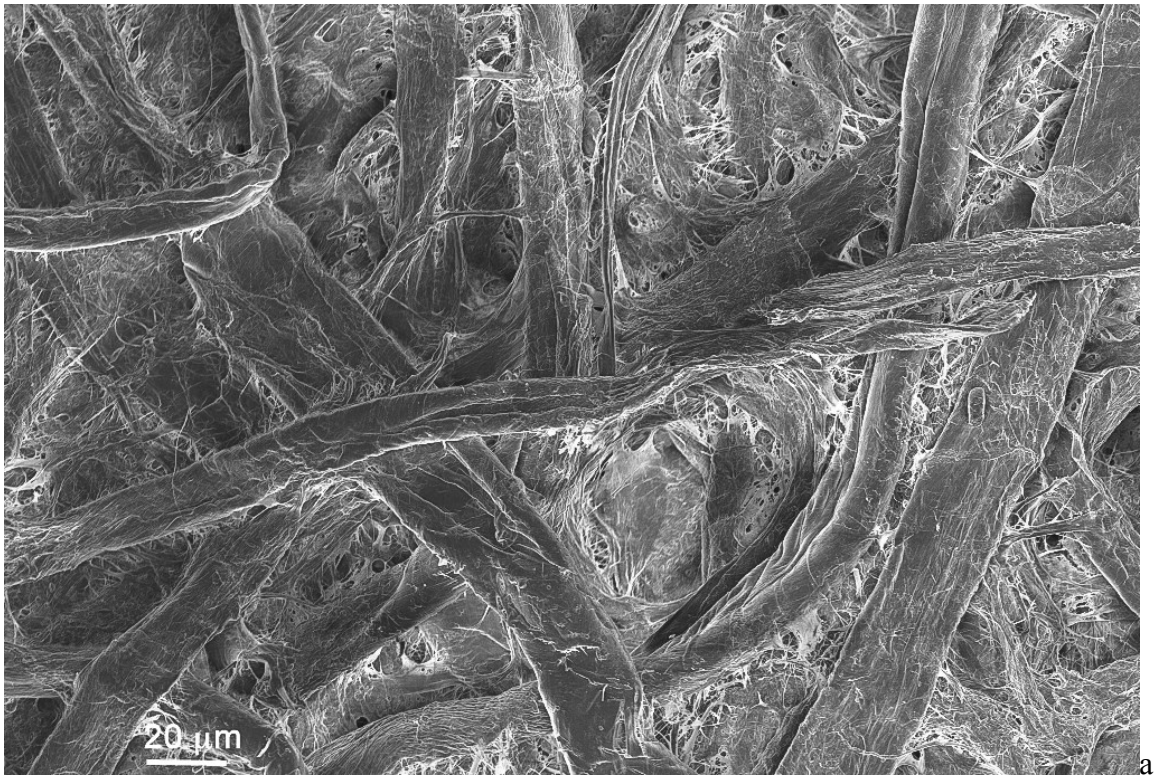
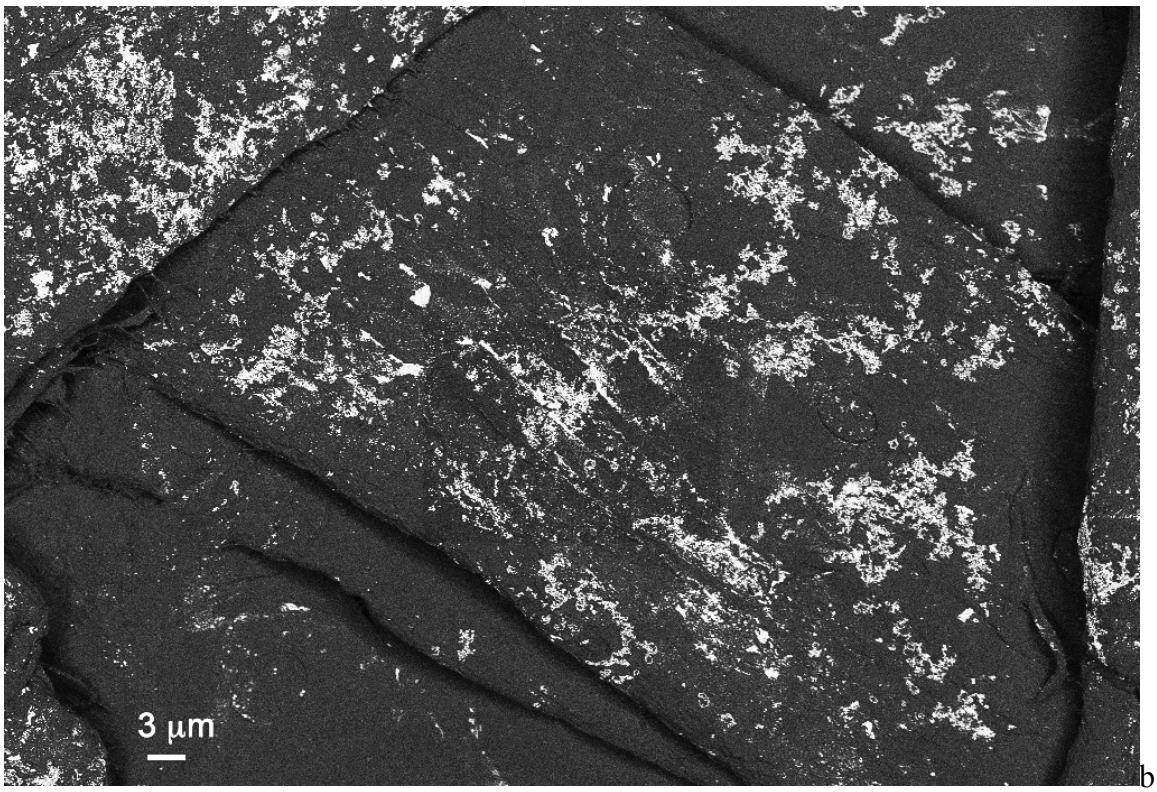


Fig. S3. Raman spectra with 632.8 nm He/Ne 20 mW laser source: characteristic modes of cellulose. The strongest SERS modes of cellulose in spectra are 436(s), 459(s), 520(m), 612(s), 898(m), 915(m), 971(m), 999(m), 1040(w), 1099(vs), 1121(s), 1153(s), 1239(w), 1294(w), 1339(s), 1379(s), 1412(w), 1461(m), 1479(m) cm^{-1}.



a



b

Fig. S4. (a) An overall SEM view of cellulose porous substrate, (b) Silver nanoparticles deposited on paper fibrils in a back scattering mode showing compositional contrast."