

Supporting Information (SI)

Glass Fibre Paper-based Test Strips for Sensitive SERS Sensing

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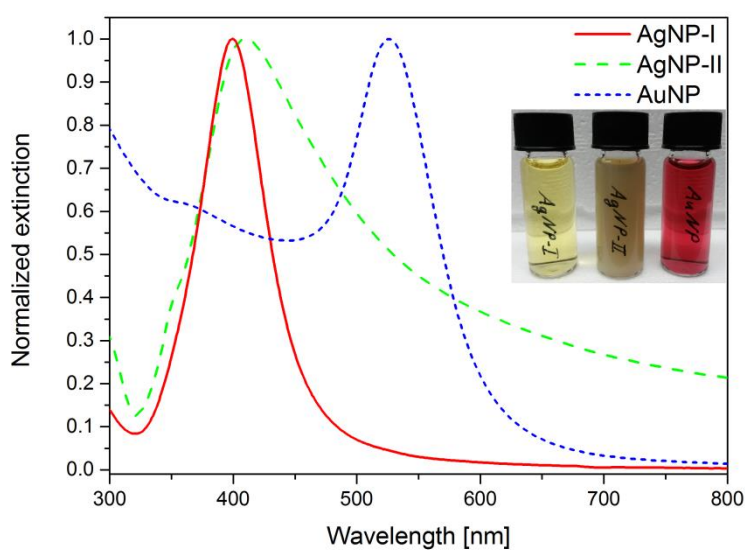


Fig. S 1 Extinction spectra (normalized) of the three NP solutions: AgNP-I (red, $\lambda_{\max} = 399$ nm), AgNP-II (green, $\lambda_{\max} = 410$ nm) and AuNP (blue, $\lambda_{\max} = 526$ nm).

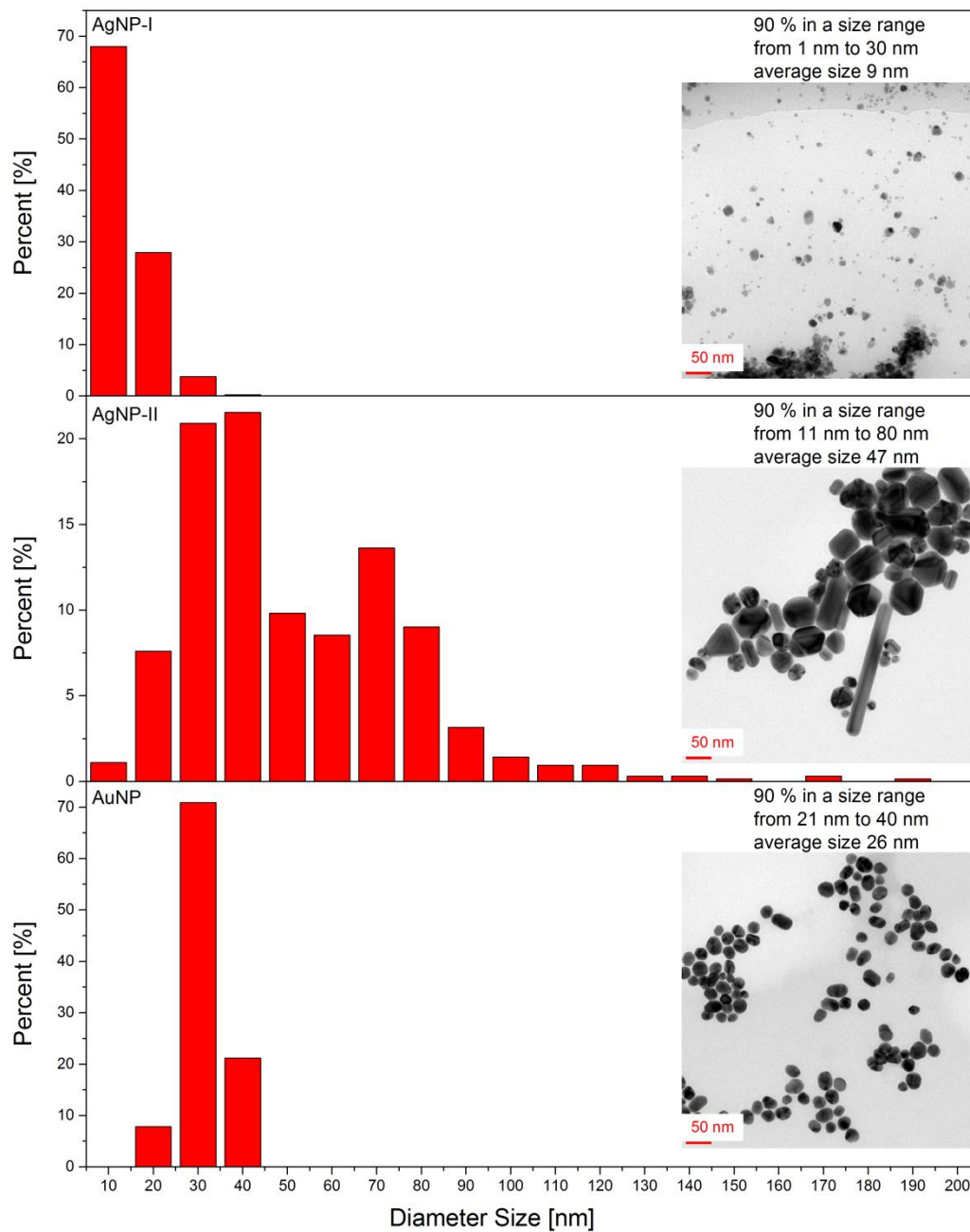


Figure S 2

TEM images of dried solutions of AgNP-I, AgNP-II and AuNP and the derived size distribution of the NPs from the TEM images (image analysis with the program ImageJ (Analyze Particles; National Instituted of Health, USA)). The average diameter of the NPs was calculated by the arithmetic average over all NP sizes.

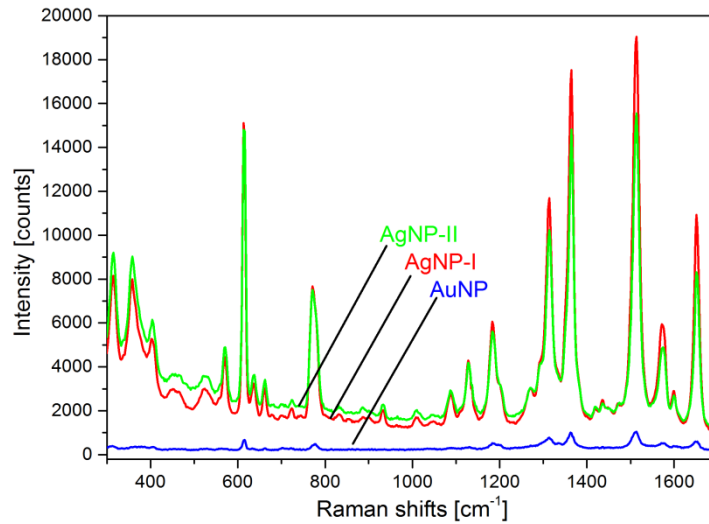


Figure S 3 SERS spectra of rhodamine 6G ($c = 10^{-6}$ M) with the three different NP solutions pre-aggregated with sodium chloride (mixture of 89 vol% of the synthesized NP solution, 1 vol% sodium chloride solution (1 M) and 10 vol% analyte solution (10^{-5} M)): AgNP-I solution (red), AgNP-II solution (green) and AuNP solution (blue). Parameters of the Raman setup were excitation at 632.8 nm, 60x objective, detection time 1 s and average over 20 spectra.

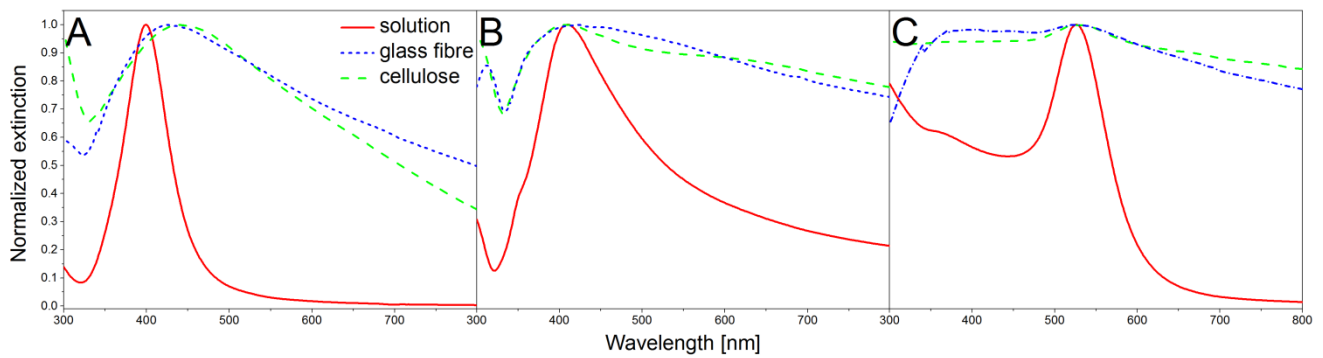


Figure S 4 Extinction spectra of AgNP-I (A), AgNP-II (B) and AuNP (C) in solution (red solid line), on glass fibre (blue dotted line) and on cellulose paper (green stroked line). The papers were coated with NPs by the spray method.

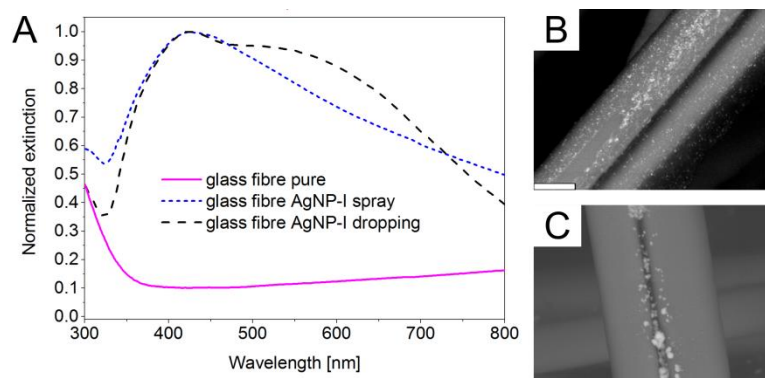


Figure S 5 Extinction spectra of glass fibre paper (A) without coating (magenta) and coated with AgNP-I by spraying (blue) and by dropping (black). The spectrum of the uncoated paper is not normalized and was measured with BaSO₄ powder as reference. The extinction spectra of the coated paper were measured with a spectrum of the pure paper as reference. SEM image of glass fibre paper coated with AgNP-I by spraying (B) and by dropping (C) (the scale bar is 5 μm).

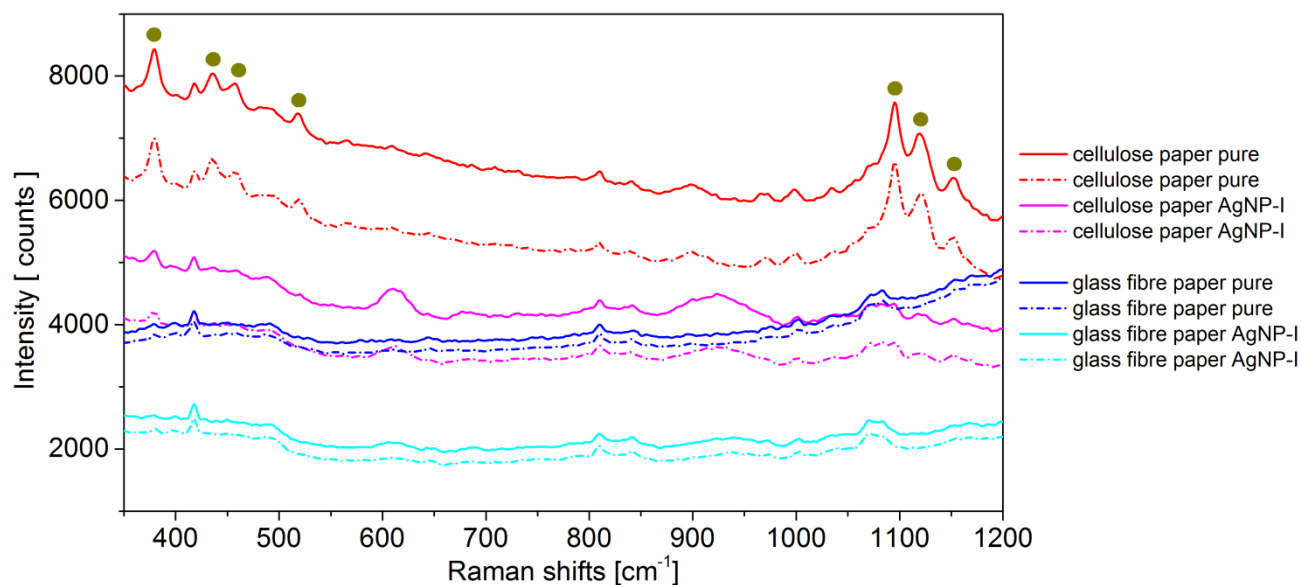


Figure S 6 Raman spectra (785 nm, 20 s detection time, average of 3 spectra) of cellulose paper and glass fibre paper uncoated and coated with silver NPs. The first Raman spectrum (0 min, solid lines) and a Raman spectrum after 5 min (stroked lines) irradiation of the laser for measurement is shown. The dots mark cellulose Raman bands.

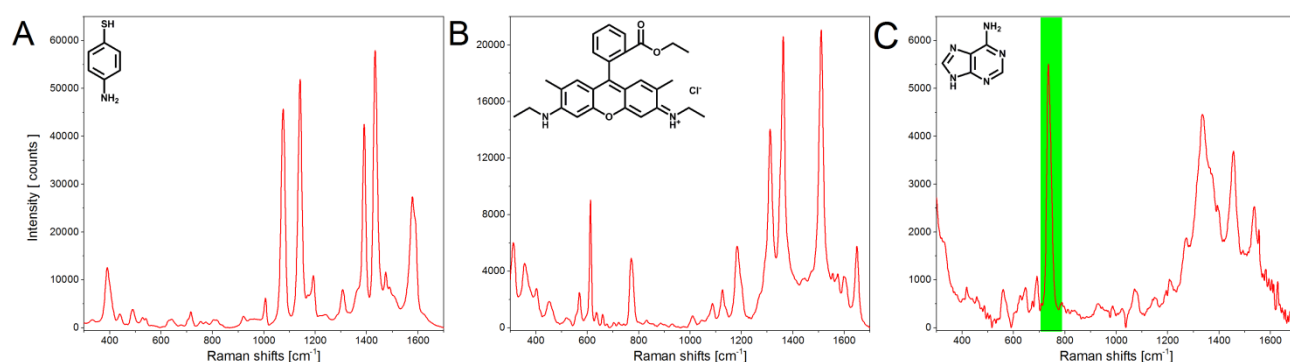


Figure S 7 SERS spectra of 4-aminothiophenol (A), rhodamine 6G (B) and adenine (C) ($c = 5 \cdot 10^{-5}$ M) on AgNP-I coated glass fibre paper test strips (10^{12} NPs mm⁻²) measured with the process Raman setup.

RSD calculation:

The relative standard deviations of the sample (RSD; Eq. S 3) were calculated from adenine spectra (solution: 10^{-4} M, 5 μ L) on glass fiber paper test strips. The measurements were performed with the Raman microscope (detection time 4 s and accumulation 3x) and the process Raman setup (laser power 200 mW, detection time 20 s and accumulation 3x). The Raman band at $735 \text{ cm}^{-1} \pm 1 \text{ cm}^{-1}$ after background correction (Origin 9G \rightarrow Subtract Baseline \rightarrow End Point Weighted) in the area from 710 cm^{-1} to 770 cm^{-1} was used for the calculation. The standard deviations s of the samples (Eq. S 1) were calculated for the intensities at $735 \text{ cm}^{-1} \pm 1 \text{ cm}^{-1}$ and for the peak areas from 710 cm^{-1} to 770 cm^{-1} . \bar{x} is the average of the data points (Eq. S 2, intensity or peak area), n is the number of samples and x_i is the intensity or area value.

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (\text{Eq. S 1})$$

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (\text{Eq. S 2})$$

$$RSD = \frac{s}{\bar{x}} \cdot 100 \% \quad (\text{Eq. S 3})$$

Data Processing of the spectra of the concentration series:

The raw data of the concentration series of adenine in the concentration region of 10^{-4} M to 10^{-8} M were measured with the process Raman setup (laser power 300 mW, detection time 20 s and accumulation 3x). The data in the area from 710 cm^{-1} to 770 cm^{-1} were extracted from the raw data (Fig. S 7 C green area). From the extracted data the background was removed (Origin 9G \rightarrow Subtract Baseline \rightarrow user-defined) and the intensity at 735 cm^{-1} was evaluated. In the next step, the average of the blank was subtracted from all intensity values. Then the first fit of the intensity data with the Langmuir isotherm (Eq. 1) in Origin 9G was performed. The fit gives for all values the error to the fitting curve. These errors were converted into relative errors to the absolute values of the fitting curve. Next, for the highest relative error it was checked if the error is higher than 10 % and, if it was true, was classified as outlier and the value was removed from the fitting values. For the rest of the values, the fitting procedure and outlier identification was repeated until the highest relative error was lower than 10 %. This fit and the values are accepted as the fit function and values and were used for the calculation of the linear Langmuir fit and all parameters. From the linear regression the parameter for the slope ($a = 4.03 \cdot 10^{-9} \text{ mol L}^{-1} \text{ counts}^{-1}$) and the y axis intercept ($y_0 = 1.13 \cdot 10^{-4} \text{ counts}^{-1}$) with the maximum SERS intensity ($I_{\text{SERS,max}} = 8827 \text{ counts}$) and the adsorption coefficient for the test strip analyte system ($K = 28103 \text{ L mol}^{-1}$) were obtained.

Dynamic Range:

The dynamic range for the measurements of the analytes is calculated from the blank measurement and the linear regression of the corrected values. The limit of detection (LOD, Eq. S 4) is calculated by using Eq. S 5. The values for the fits have been corrected with the average of the blank. Therefore, the LOD is the standard deviation of the blank multiplied by a factor of three (Eq. S 5). The upper limit is the axis intercept plus the standard error of the axis intercept. The values of the LOD and the upper limit give the dynamic range of the test strip analyte system.

$$LOD = 3 s + \overline{x_{blank}} \quad (\text{Eq. S 4})$$

$$LOD = 3 s \quad (\text{Eq. S 5})$$

Table S 1

Concentration of the analyte solution dropped on the test strips and the intensity of the Raman signal of the Raman band at 735 cm^{-1} of adenine. The intensities are corrected by a base line correction (Origin 9G \rightarrow baseline subtraction \rightarrow user-defined in the range of 710 cm^{-1} to 770 cm^{-1}) and an average blank spectrum was subtracted. The identified outliers are marked green in the last column.

c	Intensity	c^{-1}	Intensity $^{-1}$	Outliers (green)
[M]	[counts]	[M $^{-1}$]	[counts $^{-1}$]	
9.9E-05	6638	1.0E+04	1.5E-04	
7.4E-05	5912	1.3E+04	1.7E-04	
5.0E-05	5021	2.0E+04	2.0E-04	
2.5E-05	3670	4.0E+04	2.7E-04	
9.9E-06	2276	1.0E+05	4.4E-04	
7.4E-06	1750	1.3E+05	5.7E-04	
5.0E-06	1078	2.0E+05	9.3E-04	
2.5E-06	818	4.0E+05	1.2E-03	
9.9E-07	402	1.0E+06	2.5E-03	
7.4E-07	346	1.3E+06	2.9E-03	
4.9E-07	279	2.0E+06	3.6E-03	
2.5E-07	154	4.1E+06	6.5E-03	
9.9E-08	155	1.0E+07	6.5E-03	
9.9E-09	87	1.0E+08	1.2E-02	

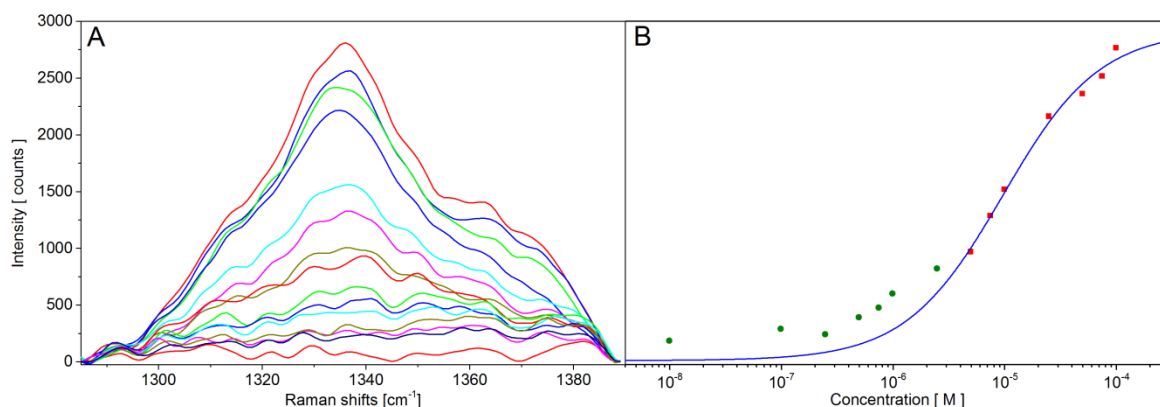


Figure S 8

SERS band at 1336 cm^{-1} at different concentrations (A) and an intensity vs concentration plot with the Langmuir curve (B). The red squares were used for the fit of the curve and the green circles were identified as outliers.

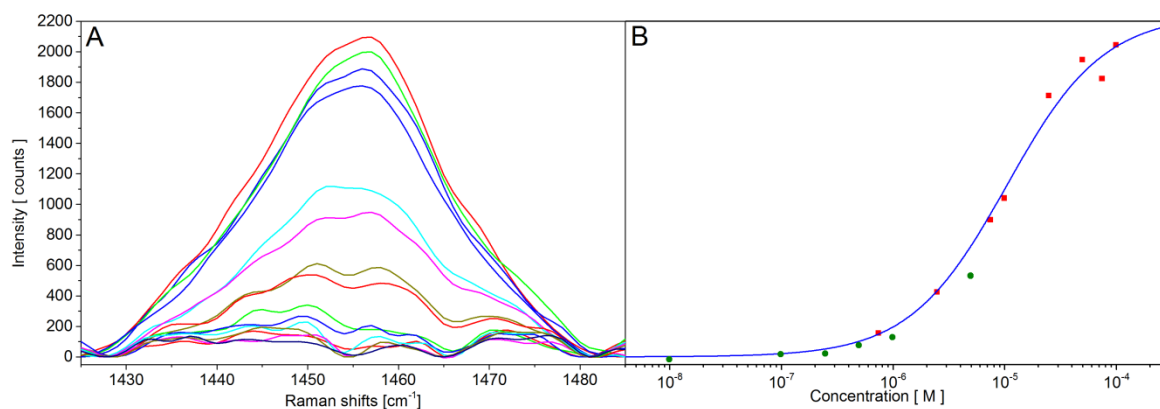


Figure S 9

SERS band at 1457 cm^{-1} at different concentrations (A) and an intensity vs concentration plot with the Langmuir curve (B). The red squares were used for the fit of the curve and the green circles were identified as outliers.