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Full Paper

Efficient Passivation of Ag Nanowires with 11-Mercaptoundecanoic Acid Probed Using In Situ Total-Internal-Reflection Surface-Enhanced Raman Scattering Spectroscopy

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nanowires

passivation

noble metals

silver

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A promising passivation strategy of one class of Ag nanostructures of high interest for optoelectronics, namely Ag nanowires (AgNWs), with 11-mercaptoundecanoic acid (MUA) is described. Combining XPS, electron microscopy and original *in-situ* total-internal-reflection (TIR) surface-enhanced Raman scattering (SERS) spectroscopic measurements, the substitution of polyvinylpyrrolidone (PVP) molecules on as-synthesized PVP-coated AgNWs by their MUA counterparts is clearly demonstrated. The relevance of the SERS approach to examine the anchoring of the MUA onto the silver surface of specific AgNWs with

pentagonal cross-sections is supported by FDTD simulations. In particular, the TIR-SERS technique reveals that the PVP-MUA substitution process can be divided into two main steps, namely (i) the desorption of PVP molecules associated with the anchoring of MUA molecules via the formation of Ag-OOC and Ag-S bonds (accomplished within 40min), and (ii) the subsequent reorientation of MUA molecules to form only Ag-S bonds (finished in 90min). The resulting passivation of AgNWs with MUA significantly improves their resistance to corrosion, which is crucial for future commercial applications.

Introduction

The interest in silver nanowires has surged in recent years as they are becoming to be promising nanostructures in a growing number of applications. In particular, they have received intense attention for their use as flexible, transparent electrodes to replace conductive metal oxides, most commonly indium tin oxide (ITO), in optoelectronic devices such as liquid crystal displays, touch screens, light emitting diodes and solar cells.^[1--5] Although there are many synthetic routes to produce silver nanowires (AgNWs), control of their yield and chemical stability over time, both necessary for widespread commercial applications, remain a major challenge.^[6--10]

The most common way to prepare long silver nanostructures is the solution-phase approach.^[1,6--7] Several synthetic approaches have been reported in polyol medium or via hydrothermal routes.^[6--7] However, the synthesis often yields the formation of a high proportion of by-products (30% or greater). Secondly, the silver nanowires obtained from these approaches are often stabilized with the polymer polyvinylpyrrolidone (PVP), which serves as a surface adsorbing agent to control the growth morphology. PVP-coated AgNWs are sensitive to daylight and humidity leading to a gradual corrosion of the metal nanostructures and resulting in insufficient device lifetimes.^[8]

Various materials have been studied to passivate silver nanowires.^[11--17] Typically nanowires on a substrate can be encapsulated within a film of organic or inorganic material

such as metal oxide (Al_2O_3 , ZnO , TiO_2), graphene or polymers.^[11--14] However, these matrices affect the intrinsic properties of the nanowire film. Passivating the nanowire surface only, rather than blanketing the nanowires in a film, is a promising alternative strategy as it should not, for example, lower the transparency of a nanowire film or interfere with its mechanical flexibility.^[15--17] This can be achieved through passivating AgNWs with short molecules. Triphenylphosphine has shown to be effective, inexpensive and simple passivation solution,^[17] as we will shown here, MUA, a less toxic molecule, is similarly effective. Furthermore, short molecules permit electrical current to traverse nanowire junctions and go from nanowire surfaces to any active material above, thus maintaining electrode conductivity.^[15--17] Due to their promise, further studies on nanowire short-molecule passivation are in progress. However, it is still unclear whether these molecules fully passivate the silver surface and replace polymer polyvinylpyrrolidone (PVP) molecules which generally cover the surface of as-synthesized AgNWs in solution, and how long the passivation process can last.

In this paper, large quantities of AgNWs are first synthesized with high yield. To increase the chemical stability of AgNWs, their surfaces are the modified with 11-mercaptoundecanoic acid (MUA). UV-visible absorption spectroscopy, X-ray Photoelectron Spectroscopy (XPS) as well as a novel surface-enhanced Raman spectroscopy method (SERS) in total internal reflection (TIR) are used to prove the effective anchoring of the MUA onto the nanowires, and precise the dynamics of the passivation process.

Results and Discussion

AgNWs were prepared by a polyol synthesis process, using PVP as a capping agent and 1,2-propanediol rather than the typical ethylene glycol medium. Details of the synthesis have recently been patented.^[18] The wires obtained in this medium have a pentagonal cross-section. They are produced in a single run, at the gram scale (Figure 1). Their preparation in

the presence of an increasing amount of nitric acid allows one to gradually tune their overall dimensions. Their high symmetry and yield result from the specific properties (especially ~~its~~ the viscosity and thermal conductivity) of the 1,2-propanediol solvent.^[18]

While these nanowires are produced at the gram scale with high yield, their PVP-coating does not prevent the corrosion of silver,^[8,19--20] and a general strategy has thus been developed to chemically modify the surface of AgNWs and improve their resistance to corrosion. The AgNWs can be thiolated with short organic molecules^[15,17] such as MUA that spontaneously adsorb onto the surface and form an efficient protection against oxidation. The details of how MUA molecules anchor to the metallic nanostructure's surface^[21] and whether they fully replace the PVP layer is unclear. In our case, to modify the silver surface, the AgNW suspension was simply incubated in a fresh aqueous solution of thiolated MUA molecules overnight. Before surface modification, a thin amorphous layer of PVP polymer (few nm thick) could be seen on the silver surface (Figure 1). After surface modification, the amorphous polymer layer is substituted by a monolayer of MUA molecules, difficult to image even by atomic resolution microscopy (Figure S1 in Supporting Information (SI)). The initial PVP-stabilized silver sol typically has a main absorption band around 374nm and a shoulder at 350nm that corresponds to absorption along the short axis of the nanowires whereas the MUA-coated ones possess the same band slightly red-shifted by a few nm (Figure S2 in SI). Such a red shift is commonly observed upon modifying the surface of metal nanostructures with organosulfur compounds.^[22] The MUA-protected AgNWs remain stable in solution, even after several months at ambient temperature, in the presence of air. They are even stable in a strong oxidative medium such as H₂O₂ solution that can easily destroy PVP-coated nanowires (Figure S2 in SI). These observations suggest a full MUA coating of the wires. In order to get more insight of the interaction of the MUA onto the nanostructure, we characterize the metal surface by XPS and an original SERS method. Figure S3 displays the results of the XPS analyses. The results confirm the formation of the Ag-S bonds after the

ligand exchange and the absence of any sulfur oxide. For a better understanding of the mechanism of the PVP-MUA substitution process, surface-enhanced Raman scattering (SERS) of the AgNWs was exploited due to its high sensitivity for molecular sensing. As SERS strongly depends on the size, shape and dielectric environment of noble metal nanostructures,^[23] single PVP-coated AgNWs with different diameters were preliminarily characterized using AFM and dark-field Rayleigh scattering microscopic (DFRSM) imaging (Figure 2), this latter technique revealing localized surface plasmon resonances (LSPRs) of AgNWs.^[24,25] AgNWs appeared to lay with one facet on the glass substrate (Figure 2E). As the height of their pentagonal cross-section increases, their DFRSM band maximum shifts to higher wavelength (Figure 2A). This size effect on Rayleigh scattering spectra is well reproduced theoretically by means of FDTD simulations considering an incident excitation along the X-axis and a light polarization along the Z-axis, a situation close to the experimental one (Figure 2B and Figure S4 in SI). Pentagonal nanowires are known to support five modes resulting from a coupling of corner modes.^[26] One of these modes exhibits a scattering maximum at 525nm where the electric field is confined at the 4 corners best excited by a sloshing of the electrons in the Z-direction of the structure. An electric field enhancement of 4 with respect to the incoming excitation is then obtained, for example, in the case of a 45nm-high PVP-coated AgNW (Figure S4 in SI). Considering a 561nm irradiation wavelength, slightly off-resonance with the aforementioned mode, a similar electric field enhancement of 4 is observed (Figure 2E). As the electromagnetic SERS enhancement factor (EF) derives, in a first approximation, from the fourth power of this electric field enhancement at the laser wavelength ω_L , it reaches 2.6×10^2 . This value is at least 2 orders of magnitude lower than the one commonly reported for SERS-active nanostructures.^[24,25,27] Note that FDTD simulations considering light propagating along the Z-axis with a polarization along the X-axis leads also to scattering spectra very similar to the experimental ones (FigureS5 in SI).

DFRSM investigations on individual AgNWs suggest a better LSPR excitation for large AgNWs under 561nm irradiation (Figure 2A). However, the SERS EF is still too weak to probe the PVP-MUA substitution at the surface of a single AgNW in ethanol. Therefore, regions including several neighbor AgNWs were excited to take advantage of the presence of *hot spots* at contact points between AgNWs that are vertically stacked.^[28--30] The DFRSM spectrum is then significantly red-shifted (Figure S6 in SI). Such a shift is commonly reported upon decreasing the interparticle gap between nanostructures, and increasing the amount of *hot spots*.^[26] Moreover, the scattering signal at 561nm rises for AgNWs with small pentagonal cross-sections, such as 45nm-high nanostructures that will be exclusively studied hereafter (Figure S6 in SI).

In order to avoid the fluctuant contribution of free AgNWs in ethanol and reduce that of the ethanol solvent itself, SERS experiments were carried out under 561nm evanescent light excitation (Figures S7, S8, and further details in SI). PVP and MUA signatures can then be distinguished by identifying specific Raman fingerprints of these species (Figure S9 and TableS1 in the SI). Two marker bands are selected, namely the C<C=>O stretching vibration centered at 1766cm^{-1} for PVP and the C-S stretching vibration centered at 630cm^{-1} for MUA. The wavenumber of the C<C=>O mode of PVP can be assigned to the PVP bound to the surface of AgNWs when it ranges between 1750 and 1769cm^{-1} .^[31--33] In contrast, free PVP molecules exhibit a C<C=>O stretching vibration centered at 1776cm^{-1} due to the increased force constant of the C<C=>O bond. The wavenumber of the C-S stretching vibration of MUA nicely matches the value expected for the *Gauche* conformation of the molecule adsorbed on a silver surface.^[34,35] Finally, in order to take into account possible intensity variations between SERS spectra, the 885cm^{-1} band of ethanol, assigned to skeletal CCO stretching or CH₃ rocking vibrations,^[36--37] was chosen as the internal reference. Even though the bulk Raman signal of ethanol is very weak in regions void of AgNWs under

evanescent field excitation, it can be detected easily in little stacks of AgNWs probably due to its SERS enhancement (Figure S9 in SI).

The PVP-MUA substitution mechanism proceeds in two main steps. For $t < \tau_{\text{PVP}} \approx 40\text{min}$, PVP molecules are replaced by their MUA counterparts as reflected by the intensity decay of the $I_{\text{PVP}}/I_{\text{EtOH}}$ ratio which nullifies for $t > \tau_{\text{PVP}}$, congruent with the disappearance of the 1766cm^{-1} bound-PVP C=C=O band and the emergence of the 1776cm^{-1} free-PVP C=C=O band (Figure 3A). This 40min duration is in agreement with the time necessary to replace PVP by cysteamine and methoxy-terminated polyethylene glycol thiol.^[31] Parallel to the extinction of the C=C=O band at 1766cm^{-1} , the C-S marker band at 630cm^{-1} grows (Figure 3B). For $\tau_{\text{PVP}} < t < \tau_{\text{MUA}} \approx 90\text{min}$, the intensity of this latter band continues to increase (Figure 3C), which suggests that more C-S bonds are in the near-field of AgNWs. This derives from the ability of MUA molecules to adsorb on silver by forming COO-Ag or S-Ag bonds.^[34] This competition between the two anchor terminal sites of MUA molecules leads to a partial covering of AgNWs through strong Ag-S bonds for $t < \tau_{\text{PVP}}$. For $t > \tau_{\text{PVP}}$, MUA molecules tend to adopt the more stable orientation by breaking COO-Ag bonds to create S-Ag bonds until τ_{MUA} is reached. This process is slower than the MUA functionalization of bare silver electrodes which is almost complete within 60min, which suggests the existence of a retardation effect induced by the necessary removal of PVP molecules.^[34] Note that it was not possible to follow the intensity change of the COO-Ag Raman band expected at 1394cm^{-1} owing to the unfortunate overlap with the Raman band assigned to ethanol CH₂ wagging vibrations (Figure S9 and Table S1 in SI).^[34,37] Finally, for $t > \tau_{\text{MUA}}$, all the AgNWs are covered with MUA molecules adsorbed via Ag-S bonds.

This two-step mechanism of the PVP-MUA substitution presents a peculiar dependence as a function of the MUA concentration. For 500 μM and 100 μM MUA solutions, τ_{PVP} and τ_{MUA} are not affected, but each step appears globally slower at the lower 100 μM

concentration. Concerning the PVP desorption after injection of a 500 μ M MUA solution, the intensity ratio $I_{\text{PVP}}/I_{\text{EtOH}}$ falls down quickly within 6min and reaches a plateau ($I_{\text{PVP}}/I_{\text{EtOH}} \approx 0.15$) before vanishing at τ_{PVP} . In contrast, for a 100 μ M MUA solution, the initial decrease lasts 12min and the plateau occurs at higher intensity ratio ($I_{\text{PVP}}/I_{\text{EtOH}} \approx 0.60$). Regarding the C-S bond formation, the $I_{\text{MUA}}/I_{\text{EtOH}}$ ratio increases gradually for a 500 μ M MUA solution while, after a short initial surge, it stabilizes at $I_{\text{MUA}}/I_{\text{EtOH}} = 0.19$ after 40min before pursuing its rise for a 100 μ M MUA solution. This atypical behavior is related to the reduction of the molecular accessibility of *hot spot* regions with respect to isolated sections of AgNWs, which first react with MUA molecules. For large excess MUA concentration (500 μ M), most *hot spot* regions can be simultaneously functionalized. However, at lower MUA concentration (100 μ M), the PVP-MUA substitution slows down due to the steric hindrance and leads to an intermediate plateau associated with the existence of an incubation time before triggering the PVP-MUA substitution (for $t < \tau_{\text{PVP}}$) and the MUA reorientation (for $\tau_{\text{PVP}} < t < \tau_{\text{MUA}}$) mechanisms in *hot spot* regions.

Passivating a AgNW network with MUA significantly improves their stability. As was determined here, by simple submersing AgNWs in a solution of MUA, the molecule fully covers the nanowire surface and this likely acts as a barrier against corrosion (Figure S10 in SI). In addition to being simple, cheap and non-toxic, this passivation layer does not lower the transparency of the AgNW networks nor interfere with its intrinsic conductivity or mechanical flexibility. Therefore, it constitutes a promising, commercially viable passivation approach.

Conclusion

In brief, we have demonstrated that the surface of PVP-coated AgNWs, produced in 1,2-propanediol, can be easily passivated by MUA. The PVP-MUA substitution proceeds in two steps: (i) a first anchoring of the MUA on the metal surface via Ag-OOC and Ag-S

bonds, and (ii) the reorganization of the MUA molecules to form only Ag-S bonds. Finally, the promising chemical stability of MUA-coated AgNWs compared to PVP-coated ones opens up exciting possibilities for electro-optical devices that have yet to be explored.

Experimental Section

Materials: Silver nitrate (AgNO_3 , 99.999%), Ethylene Glycol (J.T. Baker); propylene glycol (Aldrich); Poly(vinylpyrrolidone) MW $\approx$ 55k (Aldrich); H_2O (milliQ water); ethanol 96%; acetone; 11-mercaptoundecanoic acid 98% (Aldrich); H_2O_2 and nitric acid (Thermofisher) were used as received without any further purification.

Synthesis and surface modification of PVP-coated Ag nanowires: The shape-controlled silver nanocrystals were prepared by a modified polyol method.^[18] In a typical process, 6mL of AgNO_3 solution (0.1M in 1,2-propanediol) and 8.6mL of PVP solution (concentration in monomer of 0.21M in polyol) was successively added to a volume of 8.6mL of 1,2-propanediol in a round bottom flask. After properly mixing the reactant, 70 μL of NaCl solution (0.1M polyol) were added dropwise to the solution and after 5minutes under vigorous stirring, the mixture was heated up to 140°C under reflux and mild agitation (1hour). The obtained AgNWs were washed with acetone and water to remove excess polyol and PVP via centrifugation. The AgNWs suspension was subsequently transferred from water to absolute ethanol thanks to five consecutives ten-minute centrifugation cycles at 6000rpm. By using such experimental conditions, AgNWs exhibit a mean diameter of $35 \pm 6\text{nm}$. The aspect ratio of the elongated nanostructures can be tuned by adding nitric acid (0.22M) in the solution as recently patented.^[18] A pre-addition of a small amount of HNO_3 in the reaction medium increases the diameter of the nanowires from 35nm to 175nm (no HNO_3 pre-added (AgNWs diameter: 35nm), 0.05ml HNO_3 added (45nm), 0.06ml (62nm), 0.08ml (75nm), 0.1ml (92nm), 0.15ml (135nm), 0.5ml (175nm)).

For the surface modification process in solution, a fresh MUA solution of 50mM in absolute ethanol was prepared. The AgNW suspension was diluted in EtOH to reach a Ag concentration of 5mM, and a volume of MUA corresponding to a molar ratio Ag:MUA of 1:4 was added to the nanowire suspension. The mixture was incubated at room temperature overnight under mild agitation, washed twice by a ten-minute centrifugation at 6000rpm and redispersed in the same volume of EtOH as before. The surface passivation could also be performed on AgNWs deposited on a glass substrate by dipping the substrate in a solution of MUA. 50 μ l of Ag NWs suspension (6mg.ml⁻¹) was deposited on glass substrates (24 $\times$ 32mm) using a wire-wound metering rod (Meyer rod coating). The substrates were then immersed in an ethanolic solution of MUA (18mM) for 1hour.

Stability of Ag nanowires: The chemical stability of the Ag nanowires in solution against an oxidizing environment was evaluated by monitoring changes in the optical properties of a colloidal suspension incubated with H₂O₂ (Figure S2 in SI). 100 μ l of H₂O₂ (1M) was introduced in 5ml of a colloidal suspension of AgNWs coated with PVP or MUA. In a separate experiment, the stability of the metallic nanowires in air was evaluated by conductivity measurements. Conductive AgNW networks were rod-coated on glass substrates. All samples were exposed to lab air at ambient conditions (23 $\pm$ 2°C and a relative humidity of 70 $\pm$ 4%). Four point probe measurements were periodically taken over during a time interval of 4months (Figure S10).

Sample preparation for SERS measurements: SERS experiments on AgNWs immersed in ethanol were carried out using home-made glass liquid cells following a three-step procedure. A 20 μ L volume of concentrated ethanolic solution of PVP-coated AgNWs (5mM) was first dried into the cell to allow for the formation of localized AgNW stacks. A 20 μ L volume of ethanol was then slowly added in order to avoid the complete dispersion of stacks. A few microliters of an ethanolic solution of MUA was finally injected to reach the desired (500 μ M or 100 μ M) MUA concentration into the cell and start the PVP-MUA substitution.

Electron microscopy characterization: Transmission electron microscopy (TEM) was performed with a JEOL 2200FS and a JEOL 2100F microscope operating at 200kV. Samples were prepared by depositing one drop of the colloidal dispersion on a carbon-coated copper grid. The scanning electron microscopy images (SEM) were collected on a JEOL 6700-FEG instrument.

Elemental analysis and surface characterization: Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) measurements were performed, using a Varian 720-ES spectrometer, to determine metal nanoparticle concentrations. Samples were prepared in plastic Falcon tubes, where a known volume of colloidal dispersions ($>0.5\text{mgL}^{-1}$) was attacked by aqua regia. All experiments were repeated 5 times.

Optical characterization on colloidal solutions: The absorption spectra of the colloidal suspensions were recorded in the range of 300--1300nm with a UV-3600 Shimadzu UV-Vis-NIR spectrophotometer by using a 1cm optical-path-length quartz cells.

X-ray Photoelectron Spectroscopy: XPS measurements were performed on a Thermo Fisher Scientific K-Alpha spectrometer with a monochromated Al K α source (1486.6eV). The x-ray spot size was 200 μm and charge compensation was used on insulating samples. The spectrometer was calibrated with monocrystalline gold and silver foils (binding energies of 84.0eV for Au 4f $_{7/2}$ and 368.25eV for Ag 3d $_{5/2}$). Surveys were acquired at a 200eV pass energy and the high resolution spectra were acquired with a pass energy of 40eV. ThermoScientific Avantage software was used for fitting and quantification (Scofield table).

Single nano-object optical spectroscopy: The instrument allowing for the realization of colocalized TIR SERS and DFRSM measurements has been described in detail elsewhere^[24,25] (FigureS7) and in the Supporting Information. Note that measured DFRSM spectra have been corrected to account for the frequency-dependent response of the spectrometer and they have been normalized with respect to the intensity of the incoming light in the investigated 400--800nm spectral range. Furthermore, all the TIR-SERS experiments were carried out above the critical angle $\alpha_c \approx 63.8^\circ$

in ethanol, and more precisely at $\alpha_i \approx 66.9^\circ$ corresponding to a penetration depth $\delta_{\text{ethanol}} \approx 200\text{nm}$. However, as the propagation depth in silver is typically 10 fold lower than in neat ethanol,^[35] the genuine δ_{exp} value is expected to be lower than 100nm upon excitation of little stacks of AgNWs immersed in ethanol.

Simulation framework: The optical properties of the various nanostructures deposited on a glass substrate were analysed using a three-dimensional finite-difference time-domain software (FDTD Solutions, from Lumerical Solutions, Inc.) (Ref: Lumerical Solutions, Inc. “Innovative Photonic Design Tools,” <https://www.lumerical.com/>.) The geometry of the structures is a pentagonal silver nanowire considered as infinitely long in the Y-direction and with a distance h (Figure S4) between the base deposited on the glass substrate and the opposite vertex varying from 45 to 62, 75, 92, 135 and 175nm. The nanowires are covered by a thin dielectric layer of PVP (5nm) to mimic the experimental situation. The dielectric properties of the various components are a dispersion-less dielectric permittivity of 2.338 (2.151) for PVP (glass), together with the permittivity of silver from the software database as described by Palik (0--2 μm).^[38] The simulation space was constructed using perfectly matched layers (PMLs) along the X- and Z-axes. The excitation of the structure was performed by using a broadband 2fs pulse centred at 687THz, with a bandwidth of 625THz, launched along the horizontal X-axis (Figure S3) and polarized along Z. Owing to the implementation of a Total Field Scattered Field formulation, the absorption, scattering and extinction cross-sections of the various nanostructures were obtained in a first step. In a second step, the electric field amplitude profiles were obtained for various resonance modes of interest as well as the amplitude profile corresponding to the used experimental excitation wavelength, fixed at 561nm.

Supporting Information

Supporting Information is available from the Wiley Online Library.

Acknowledgements

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References

1. T. Sanniccolo, M. Lagrange, A. Cabos, C. Celle, J.P. Simonato, D. Bellet, *Small* **2016**, *44*, 6052--6075.
2. K. Zilberberg, T. Riedl, *J. Mater. Chem. A* **2016**, *4*, 1448-14508.
3. J. Jiu, K. Suganuma, *ACS Appl. Mater. Interfaces*, **2016** *6*, 1733-1751.
4. D. Langley, G. Giusti, C. Mayousse, C. Celle, D. Bellet, J.P. Simonato, *Nanotech.* **2013**, *24*, 452001-452010.
5. Y. Wei, S. Chen, X. Yuan, P. Wang, L. Liu, *Adv. Funct. Mater.* **2016**, *26*, 5078-5085.
6. Y. Xia, K. Gilroy, H. Peng, X. Xia, *Angew. Chem. Int. Ed.* **2017**, *56*, 60-95.
7. R. Costi, A.E. Saunders, U. Banin, *Angew. Chem. Int. Ed.* **2010**, *49*, 4878-4897.
8. J.L. Elechiguerra, L. Larios-Lopez, C. Lui, D. Garcia-Gutierrez, A. Camacho-Bragada, M.J. Yacaman, *Chem. Mater.* **2005**, *17*, 6042-6052.
9. Y. Kalachyova, D. Mares, V. Jerabek, P. Ulbrich, L. Lapcak, V. Svorcik, O. Lyutakov, *Sens. Actuators A* **2017**, *19*, 14761-14769.
10. C. Mayousse, C. Celle, A. Fraczekiewicz, J.P. Simonato, *Nanoscale* **2015**, *7*, 2107-2115.
11. M. Yeh, P. Chen, Y. Yang, G. Chen, H. Chen, *ACS Appl. Mater. Interf.* **2017**, *12*, 10788-10787.
12. D.G. Lee, D. Lee, J.S. Yoo, S. Lee, H.S. Jung, *Nano Convergence* **2016**, *3*, 20-27.

13. A.T. Pham, X.Q. Nguyen, D.H. Tran, V. NgocPhan, T.T. Duong, D.C. Nguyen, *Nanotechnology* **2016**, 27, 335202-335209.
14. F.S.F. Morgenstern, D. Kadra, S. Massip, *Appl. Phys. Lett.* **2011**, 99, 18, 221111-211114.
15. G.S. Liu, J.S. Qiu, D.H. Xu, *ACS Appl. Mater. Interfaces* **2017**, 9, 15130-15138.
16. R. Chen, S.R. Das, C. Jeong, M.R. Khan, D.B. Janes, M.A. Alam, *Adv. Funct. Mater.* **2013**, 23, 5150-5158.
17. J. Idier, W. Neri, C. Labrugère, I. Ly, P. Poulin, R. Backov, *Nanotechnology* **2016**, 27, 105705-105712.
18. M. Plissonneau, L. d'Alençon, T. Lemercier, M. Tréguer-Delapierre, *European Patent*, 17306072.4--1103 **2017**.
19. G. Deignan, I.A. Goldthorpe, *RSC Adv.* **2017**, 7, 35590--35597.
20. J. Jiu, J. Wang, T. Sugahara, S. Nagao, M. Nogi, H. Koga, K. Suganuma, M. Hara, E. Nakazawa, H. Ushida, *RSC Adv.* **2015**, 5, 27657--27664.
21. B. Diroll, K.M. Weigandt, D. Jishkariani, M. Cargnello, R. Murphy, L. Hough, C. Murray, B. Donnio, *Nano Lett.* **2015**, 15, 12, 8008—8012.
22. P. Mulvaney, *Langmuir* **1996**, 12, 3, 788--800.
23. W.A. Murray, W.L. Barnes, *Adv. Mater.* **2007**, 19, 3771.
24. D. Talaga, M. Comesaña-Hermo, S. Ravaine, R.A.L. Vallée, S. Bonhommeau, *J. Opt.* **2015**, 17, 114006.
25. N. Vilar-Vidal, S. Bonhommeau, D. Talaga, S. Ravaine, *New J. Chem.* **2016**, 40, 7299--7302.
26. M. Song, A. Bouhelier, P. Bramant, J. Sharma, E. Dujardin, D. Zhang, G. Colas-des-Francis, *ACS Nano* **2011**, 7, 5874--5880.

27. D. Cialla, A. März, R. Böhme, F. Theil, K. Weber, M. Schmitt, J. Popp, *Anal. Bioanal. Chem.* **2012**, *403*, 27—54.
28. C.L. Du, Y.M. You, T. Chen, Y. Zhu, H. Hu, D.N. Shi, H.Y. Chen, Z.X. Shen, *Plasmonics* **2011**, *6*, 761—766.
29. M. Chen, I.Y. Phang, M.R. Lee, J.K.W. Yang, X.Y. Ling, *Langmuir* **2013**, *29*, 7061--7069.
30. C.H. Moran, M. Rycenga, Q. Zhang, Y. Xia, *J. Phys. Chem. C* **2011**, *115*, 21852--21857.
31. M.A. Mahmoud, C.E. Tabor, M.A. El-Sayed, *J. Phys. Chem. C* **2009**, *113*, 5493--5501.
32. Y. Gao, P. Jiang, D.F. Liu, H.J. Yuan, X.Q. Yan, Z.P. Zhou, J.X. Wang, L. Song, L.F. Liu, W.Y. Zhou, G. Wang, C.Y. Wang, S.S. Xie, *J. Phys. Chem. B* **2004**, *108*, 12877--12881.
33. C. Ma, J.M. Harris, *Langmuir* **2012**, *28*, 2628—2636.
34. M.K. Bryant, J.E. Pemberton, *J. Am. Chem. Soc.* **1991**, *113*, 3629--3637.
35. W.L. Barnes, A. Dereux, T.W. Ebbesen, *Nature* **2003**, *424*, 824--830.
36. F. Li, Z. Men, S. Li, Z. Li, C. Sun, *Spectrochim. Acta Part A* **2018**, *189*, 621—624.
37. G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd edition, John Wiley & Sons Ltd., Chichester, New York, Weinheim, Toronto, Brisbane, Singapore, **2001**.
38. E.D. Palik, *Handbook of Optical Constants of Solids*, Academic, San Diego, **1985**.

Figure 1. TEM and SEM images of the uniform Ag nanowires produced in 1,2-propanediol (scale bar of the SEM image : 100 nm; HRTEM image of nanowire tip).

Figure 2. (A) DFRSM spectra associated with 6 single PVP-coated AgNWs with different heights h ranging from 45 to 175 nm. B) Corresponding FDTD-calculated Rayleigh scattering spectra. C) Topographic tapping mode AFM image of a 45 nm-high PVP-coated AgNW deposited on a glass slide (scale bar : 200 nm). D) Corresponding DFRSM image (scale bar : 1 μ m). E) Calculated electric field magnitude (under 561 nm irradiation) around a 45 nm-high NW for the plasmon mode showing a band maximum at 525 nm.)

Figure 3. A) B) SERS spectra of AgNWs in 100 μM MUA solution recorded at different times under 561 nm excitation (black solid lines). Bands centered at 1766 cm^{-1} (red solid lines), 1776 cm^{-1} (red dashed line) and 630 cm^{-1} (blue solid line) are assigned to the bound-PVP C=O mode, the free-PVP C=O mode and the bound-MUA (CS)_G mode. Peaks at different wave-numbers are indicated with blue dashed lines. C) Normalized intensity ratio of the bound-PVP C=O band (red curves with squared symbols) and the MUA (CS)_G band (blue curves with rounded symbols) with the ethanol internal reference band at 885 cm^{-1} as a function of time, for 500 μM (closed symbols) and 100 μM (open symbols) MUA solutions. Solid lines are guides for the eye.