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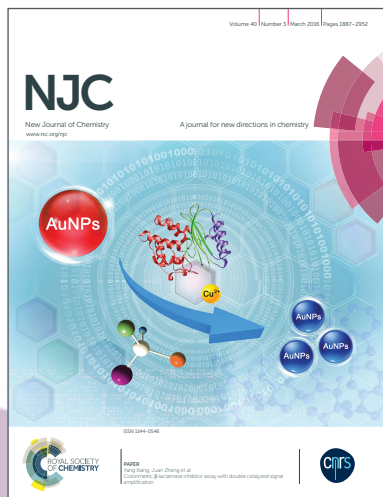
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ARTICLE

Practical mediated-assembly synthesis of silver nanowires using commercial *Camellia sinensis* extracts and their antibacterial properties

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Camellia sinensis is a well-known plant used for health purposes due to its high phenolic compound content and antioxidant properties. For the first time, an infusion of green tea has allowed the growth and stabilization of silver nanowires (AgNWs). Two commercial types of green tea leafs, were used for the practical synthesis of AgNWs at low temperature. The use of low concentrations of polyvinylpyrrolidone (PVP) as directing agent was successful for obtaining nanobar/nanorod assemblies forming 2-fold to 10-fold nanowires. FESEM, HRTEM and HAADF microscopies helped identify ~ 50 nm diameters in the large ~ 1.3-micron nanowires. The antibacterial properties of the AgNWs were investigated against *Escherichia coli*, and *Staphylococcus aureus*. The AgNWs morphology may damage the cell wall, accelerating the cellular stress that produce fatal inactivation of the infectiosus microorganism. This work provides a green approach to the aqueous biosynthesis of AgNWs with promising antibacterial properties.

Introduction

Silver nanostructures have been important in several scientific fields such as electronics, physics, chemistry, catalysis, photoelectrochemistry, biology and medicine[1] due to their optical, mechanical, electromagnetic, catalytic and biochemical properties.[1-3] In electronics, silver nanowires (AgNWs) are desirable materials that present mechanical flexibility, which means that cannot be deformed, foldable and compressed while preserving their optical and electronic characteristics.[2] In addition to medical and environmental applications, the nanostructure presents low or none toxicity.[4] Silver nanoparticles display potential antimicrobial effects against infectious microorganisms such as marine algae, pathogenic microorganisms such as fungi and bacteria; they also help semiconductors enhance their catalytic activity.[2,5-7] Silver has interesting electrical or conductivity properties, so the one-dimensional nanostructures (nanorods or nanowires) are remarkable for study because of the enhanced latter characteristics.[8] The main characteristic of nanowires is the relationship between a large surface and the volume ratio, which means that silver nanostructures exhibit size and shape-dependent properties.

The synthesis of AgNWs has been widely dominated by chemical or physical methods that give well-shaped AgNWs, however, detrimental harmfulness, and expensive reagents or extravagant equipment are required.[2,9-10] Sun et al. obtained AgNWs of 50 μm in length and 30-40 nm in diameter using ethylene glycol, polyvinylpyrrolidone (PVP) and $PtCl_2$ nanoparticles as seeds for growing the AgNWs at 160°C.[8] Ma and Zhan[11] reported the polyol synthesis of 1-D microstructures with 3-14 μm in length and 80-323 nm in diameter in the presence of halogens and PVP at ~160 °C. Jiang et al.[12] grew Ag nanowire arrays on a Si wafer with a diameter of 100 nm and 80 μm in length at room temperature, using cetyltrimethylammonium bromide (CTAB) and (3-aminopropyl)triethoxysilane to mediate the growth of the arrays; the surfactants were easy to be removed by washing with ethanol. Other oriented growths of AgNWs need the use of inorganic templates such as polymers, aluminium oxide or/and specialized equipment like e-beam lithography, pulsed electrodeposition, etc.[13-14] A diversity of synthesis methods has been reported for the synthesis of silver nanoparticles (AgNPs); noteworthy examples include: i) physical methods like laser ablation, gamma irradiation, electron irradiation, etc.;[15-16] ii) chemical methods such as chemical reduction, photochemical methods, microwave processing;[17-18] and iii) biological synthesis that is the approach to attain eco-friendly routes.[19-20]

Alternative routes trying to find an eco-friendly method have been focused on the use of organisms. Among these organisms, plants seem to be the best candidates.[21] Plant extracts have been the most used for the synthesis of silver and gold nanostructures.[19] This green approach avoids the use of toxic chemicals and is cost-effective because it does not require high temperatures and/or pressures for the AgNWs synthesis. Different nanostructure morphologies have been

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reported using plant extracts like silver-15-nm-sphere-like and gold triangles of 50-350 nm using an *Aloe vera* extract as high content of reducing biomolecules such as reducing agent.[22] The *Cassia angustifolia* extract yielded spherical AgNPs of 9-31 nm in diameter by its sennoside components, which served as both reducing and capping agents.[23] Jeeva et al.[24] obtained triangular AgNPs by boiled *Caesalpinia coriaria* and when the extract was centrifuged, triangular, hexagonal and spherical AgNPs were found. Overall, the most reported natural biomolecule extract for the synthesis of metallic nanoparticles is *Camellia sinensis* (green tea) due to its epigallocatechin, epigallocatechin-3-gallate (EGCG), epicatechin and epicatechin-3-gallate.[25-26] For instance, Vilchis-Nestor et al. synthesized gold and AgNPs, after Loo et al., Bhaumik et al. and Jia et al. reported mainly spherical AgNPs with 4, 33-86 and 100 nm in diameter, respectively.[27-30] The specific role played by EGCG was reported by Hussain and Khan who established that the –OH groups present in the molecule are responsible for the AgNP stabilization. The AgNPs were coated with an organic skim of about 4 nm. The capping agents could possibly be originated from leaf extracts of tea, hydroxyflavones and catechins.[31]

Few reports dealing with the growth by green synthesis of AgNWs and nanorods have been reported. Lin et al. obtained nanowires by using a *Cassia fistula* extract with 50-60 nm in diameter and ~ 10 μm in length in 48 h; so, the studies show the possible formation mechanisms of AgNWs from linear aggregation of spherical nanoparticles, where with longer exposure times, the nanowires are longer.[32] Jacob et al. reported the synthesis at room temperature of silver nanorods by using a *Coscinium fenestratum* extract. AgNWs of 28-68 nm in diameter on average were achieved which presented good cytotoxic activity against Hep-2 cells.[33] Insights regarding that *Camellia sinensis* can produce nanostructures different from quasi-spheres such as a few hexagonal shapes and nanorods were reported by Jia et al.[30]

The present research work reports on well-characterized AgNWs by using two commercial green tea extracts (Mexican and Korean) that act as reducing and capping agents. A possible growth mechanism underlying the eco-friendly synthesis of the nanowires was proposed based on the information given by the images obtained by means of the HRTEM, HAADF, FESEM and UV-vis spectroscopy techniques; the evaluation of their growth inhibitory effects on gram-positive and gram-negative bacteria is also reported.

Experimental Section

Reagents and bacterium strain

All the chemical reagents were analytical grade. AgNO$_3$ (99.5% of purity) was purchased from Merck; two commercial green teas were used: Mexican Tea (Royal Tea, Mexico) and Korean Tea (Baseong green tea). Polyvinylpyrrolidone (PVP) of 40000 MW by Sigma Aldrich and 2-propanol (99.93% of purity,

BAKER, ®ACS) were also used. Tripticasein soy broth (TSB) was purchased from Becton Dickinson, Mexico. The bacterium strains were *Staphylococcus aureus* ATCC 25923 and *Escherichia coli* ATCC 25922, which were provided by the "Centro de Investigación y Estudios Avanzados en Salud Animal".

Preparation of the extract and synthesis of silver nanowires and nanoparticles

One gram of green tea leafs was added to 100 mL of deionized boiling water (~ 98°C). After 10 min boiling, the infusion was filtered with a cellulose Whatman grade 1 filter. A fresh infusion was prepared for each kind of commercial tea. The synthesis of AgNWs was carried out with 1 mL of previously prepared infusion and with a 0.001M solution of AgNO$_3$. Both solutions were mixed at a volume ratio of 1:20 (infusion: AgNO$_3$). AgNO$_3$ was added dropwise to the infusion together with 0.003, 0.006 or 0.012 g of PVP, respectively; then, the resultant solution was stirred magnetically at ~ 45 °C until confirming the complete dissolution. Afterwards, the solution was aged under dark conditions for 30 days at room temperature. The evolution was monitored with aliquots using a UV-vis spectrophotometer Agilent Cary 5000. For the synthesis of the silver nanoparticles (AgNPs), identical conditions were used that for the AgNW synthesis, but without adding PVP.

Characterization

UV-vis spectroscopy (Cary 5000 UV-vis-NIR, Agilent Technologies) was used to monitor the evolution of the eco-friendly synthesis and the surface plasmon resonance of the as obtained silver nanostructures over time. Scanning electron (FIB DUAL BEAM FEI HELIOS 600 NANOLAB) and transmission electron (HRTEM FEI TECNAI F30 STWIN G2) microscopies were used to establish the morphology; the sample was washed several times with deionized water and 2-propanol by centrifugation cycles at 10000 rpm for 10 min and sonication for 20 min. The AgNWs were suspended in 2-propanol and one drop was placed on an aluminium support for SEM and a cupper grid for TEM until evaporation.

Antibacterial assays

The AgNWs were evaluated as bactericide agents of *S. aureus* and *E. coli* with the method for the determination of minimum inhibitory concentration (MIC).[34] A 96-well microplate with 2-fold dilution of AgNWs was used. The growth of *E. coli* and *S. aureus* was carried out in TSB overnight. Aliquots were taken of this culture and adjusted at 5x10^6 colony formed unit (CFU)/mL.[34] 100 μL of bacterial solution was added to each well and mixed with the AgNWs, and it was incubated at 37 °C for 24 h. The optical density was measured at a wavelength of 600 nm (Epoch, Biotek, Winooski, Vermont, USA). Finally, the plate was inoculated after 24 h at 37 °C and counted after incubation. The experiment was performed in triplicate. To verify the Ag concentration in the experiments, inductively

coupled plasma optical emission spectroscopy (ICP-OES) with a 730-ES spectrometer from Varian Inc. was used. It was determined as 6.5 and 25.8 mg/L, respectively.

Results and discussion

Insights from the UV-vis spectra

Fig. 1a-b shows the UV-vis spectra of the AgNWs synthetized with Mexican (M), and Korean (K) green tea infusions as a function of time. The spectra show two bands, at ~ 350 nm and at ~460 nm, which indicate the reduction of the silver nitrate colloids to AgNPs nanostructures. The presence of the bands is directly related to the coexistence of nanobar/nanorod assemblies forming AgNWs and quasi spherical AgNPs.[2,35] The band at ~460 nm shifts from 500 nm, and broadens, the effects denotes the formation of one-dimensional silver nanostructures, which is attributed to the surface plasmon oscillation along the long-axis of the nanowires.[8] The surface plasmon resonance (SPR) depends indirectly on the nanostructure morphology due to the resonance plane and symmetry.[2,35] As the size of fold nanowires increases the band SPR broadens and shifts to lower wavelength, after 30 days of maturation both absorption bands looks more intense due to the mediated-assembly synthesis of AgNWs.
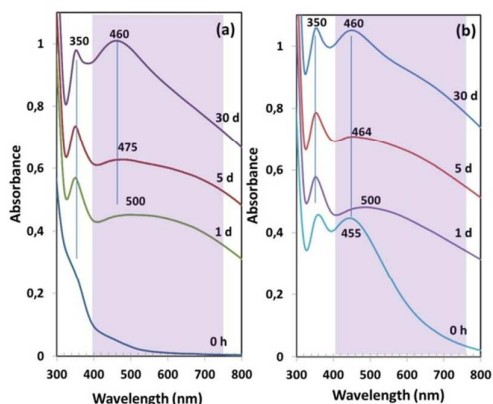

Fig. 1 UV-vis spectra of the synthesis of AgNWs with (a) Mexican green tea and (b) Korean green tea.

Notably, the intensity of 460 nm band is increased and broader as a function of the synthesis time for the AgNWs made using the tea extract; the intensity of the band at 350 nm seems to slowly increase after 30 days due to the broad band at 460 nm. The band a 350 nm is also attributed to the SPR of closer spherical AgNPs. After one day, a new small band appeared at 500 nm due to the length of the grown nanowires, attributed to the transverse plasmon mode of rod/bar-shaped silver nanostructures. The band increase the intensity to centered a 460 nm in 30 days.[9] In the case of the synthesis with K tea, the

band at 450 nm increased and slightly became more intense in contrast with the M tea synthesis; the band at 351 nm remained practically constant after one day.

Lin et al. obtained short AgNW band absorption after 12 h at 360 nm, while Jacob et al. reported an intense band at 620 nm attributed to nanorods; in both cases, the band at ~420 nm corresponds to nanoparticles with diameters of 20-50 nm; the difference between the wavelength and band width is the length of the nanostructures.[32-33] The presence of the SPR bands at 350, 380 and 410 nm corresponds to uniform nanowires of 35 nm in diameter and 50 micron in length that were synthesized by the polyol process directed by PVP.[2,9]

The M and K tea extracts could reduce the colloidal dispersions of silver nitrate in aqueous PVP medium; under these conditions, an assortment of mainly long fold silver nanowires and AgNPs adsorbed on AgNWs surface were achieved.
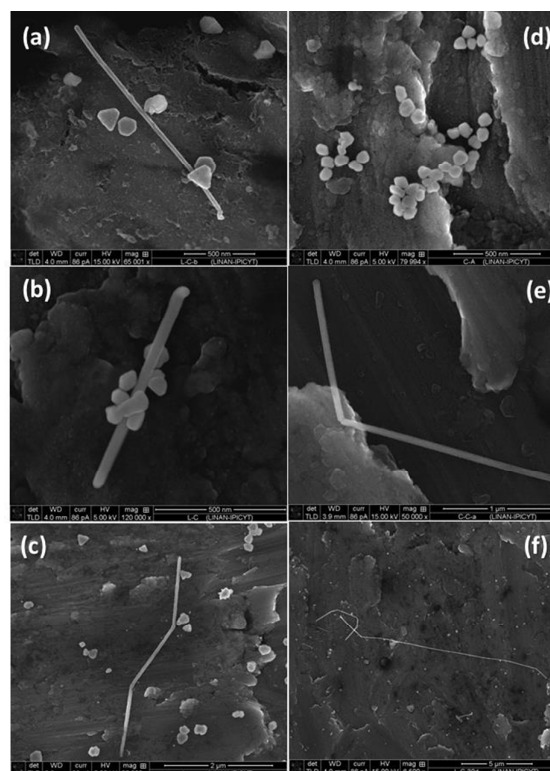

Fig. 2 FESEM images for the AgNWs (a-c) using 0.003 g of PVP with M tea, (d) silver nanowires without using PVP as nanowire formation directing agent with K tea (e) using 0.003 g of PVP with K tea and (f) a large AgNW using 0.003 g of PVP with M tea.

The FESEM images, Fig. 2a-f, show the AgNWs formed by both teas. An important characteristic is the presence of small

nanoparticles on and at the end of the nanowires; triangular and hexagonal nanoplates are found alone in the AgNWs, notably in the synthesis with the M tea; additionally, some irregular AgNPs were found, which some were adsorbed on the AgNW surface, Fig. 2a-c. If PVP was not used in the synthesis, the predominant morphology was that of quasi-spheres together with some irregular and triangular AgNPs, Fig. 2d.

Fig. 2c shows a long AgNW of around 4 μm, which consists of three straight nanorods that are zigzag-like, Fig. 2e a 2-fold AgNW of ~ 5 μm and in Fig. 2f a large AgNW of ~ 15 μm as it was reported by Chen et al.[10] who obtained similar nanostructures using ethylene glycol as reducing agent in the presence of PVP and nanoscale gold seeds.

The straight, 2-fold NWs and 3-fold AgNWs have 51 nm in diameter and 0.9 μm in length in the case of the AgNWs obtained with the Mexican infusion and 61 nm in diameter and 1, 4 μm in length for the South-Korean infusion, Fig. 3a-b, on average. The color of the solution varied from transparent at the start of the biosynthesis reaction to yellowish-brown, becoming gradually dark until getting a lighter brown tone due to the 0.003 g of PVP incorporated.
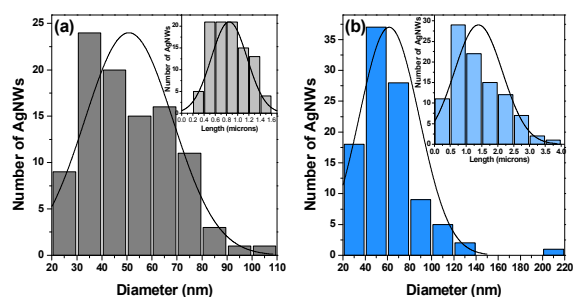

Fig. 3 Size histogram of AgNWs (a) using the Mexican tea extract and (b) using the Korean tea extract.

The morphology and dimensions of the as-synthesized AgNWs strongly depend on the incorporation of PVP and the nature of the green tea extract. For further understanding of the growth way, TEM characterization was carried out focusing on the synthesis with the Mexican infusion.
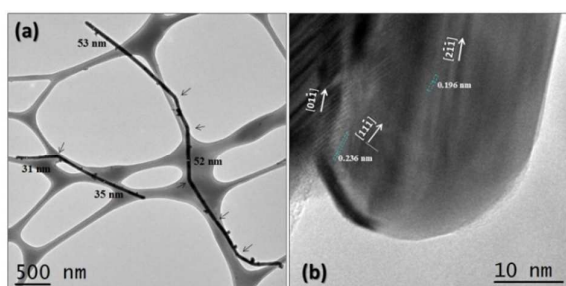

Fig. 4 Selected TEM images of the straight morphology of the 2-fold assembly.

The images obtained by TEM are shown in Fig. 4, which clearly confirm the nanowire morphology and the straight and 2-fold assembly of the AgNWs. The arrows show the zigzag-like angles or joints that link two nanorods, Fig. 4a. The AgNWs shown in the Fig. 4a are 2-fold nanowires with lengths about 4 and 2 μm and with connecting angles above 120°. In Fig. 4b, the selected HRTEM image for the end of an AgNW shows the fringe lattices for the (111) of 0.239 nm and (200) planes of 0.196 nm. In previous studies reported in the literature, authors have suggested the growth of AgNWs as bicrystals twinned parallel at {111} planes that support our green synthesis by directed-PVP. It is clearly observed that the well-resolved fringe spacing agrees with the PDF card 00-004-0783 of face-centered-cubic silver phase.

The HRTEM analysis of the connecting junction of nanowires obtained with the Mexican green tea infusion was performed in order to understand the self-assembly mode, Fig. 5a-f. These materials tend to grow as twinned particles at {111} planes due to the PVP protection of [211] and [011] growth directions. Fig. 5a-b shows the end-to-end straight assembly of a two silver nanorods of ~ 42 nm in diameter and Fig. 5b shows a 2-fold nanowire, which has a zigzag angle of ~ 120°. The connecting joint clearly shows that either the straight or zigzag array is probably achieved by linking two straight nanorods. In Fig. 5c-d, it is inferred that AgNPs of ~ 30 nm are attracted to each other by the Ostwald ripening process, which leads to grow as the well reported multiply twinned nanoparticles (MTPs) with a decahedral shape due to the selective adsorption of PVP on the {100} and {111} facets forming straight-like nanowires. However, when a hexagonal silver particle is involved in the growth process, a zigzag connecting junction is probably generated. Some AgNPs of ~ 30 nm can be observed adsorbed along the wires, which may be segregated during the reduction-nucleation-adsorption-growth-branching-growth process. The growth of a new straight nanorod at the end of a pre-grown silver nanorod seems difficult according to the image shown in Fig. 5d, which features oval AgNPs adsorbed next to the end of a pre-grown nanorod, which may be due to the organic tea compounds adsorbed along the wire; if the formation of a new straight nanorod happens, this fact also opens the possibility of a three-way-growth-chain-like-silver- assembly network. Many TEM and HRTEM images were checked without finding this kind of AgNP network, only some irregular AgNPs of ~ 30 nm. It can be supposed that when AgNPs are involved during the formation of a connecting junction, a zigzag connection is favored. Selected HAADF images, Fig. 5e-f, show that the nanorods folded as nanowires are growing from smaller AgNPs, where some AgNPs are also clearly appreciated on the surface of the nanowires.
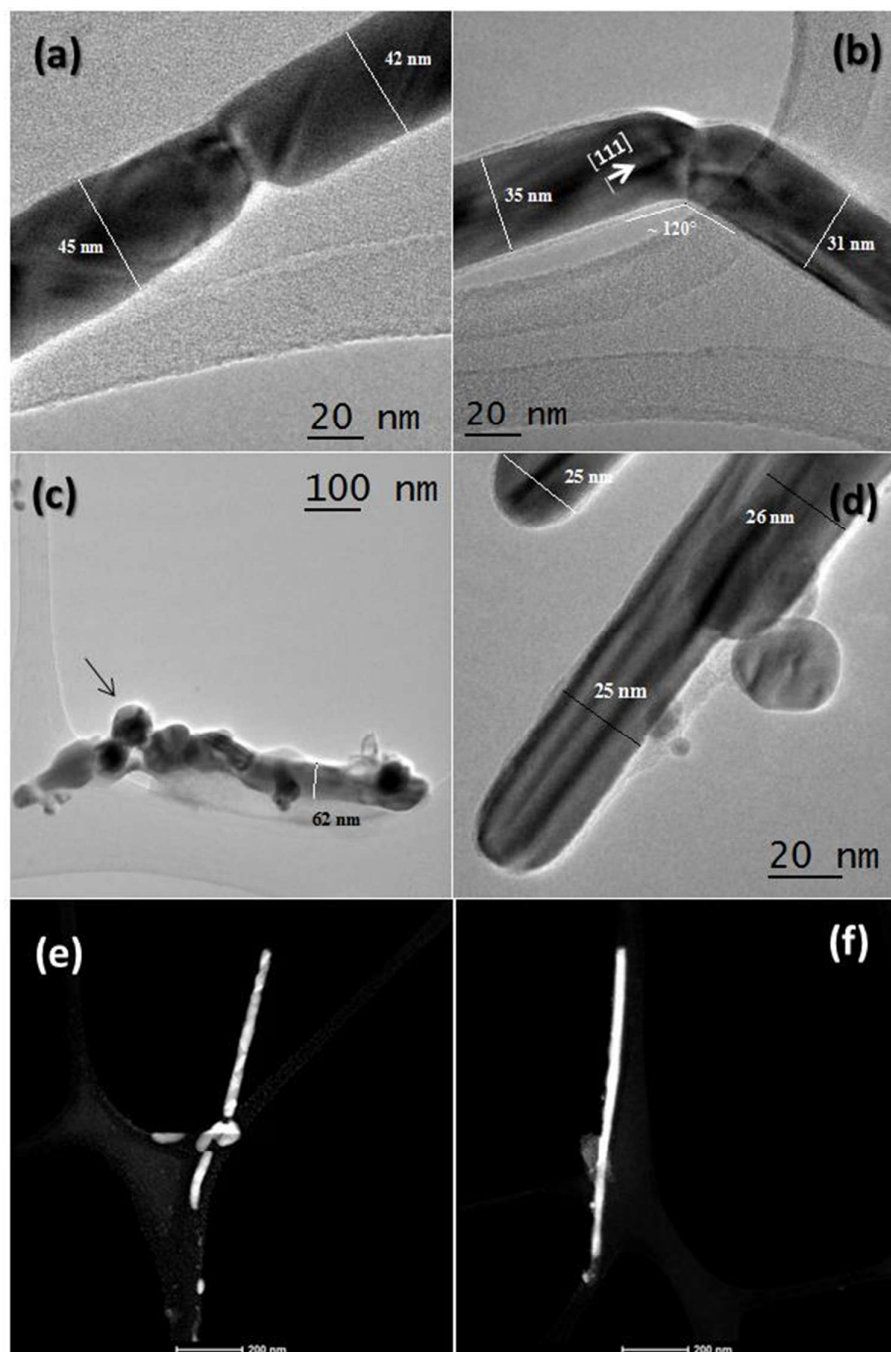
Fig. 5 HRTEM images of AgNWs obtained with Mexican tea (a), end-to-end straight silver nanorod assembly, (b) 2-fold AgNW assembly, (c-d) the assemblage ripening process, (e-f) selected HAADF images showing the formation of AgNWs for smaller AgNPs.
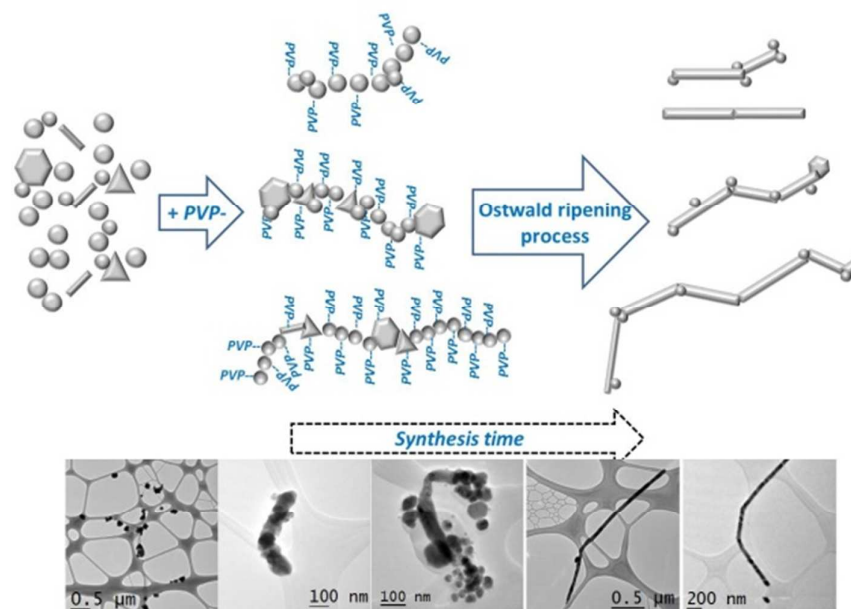
Scheme 1 shows a representative scheme of growing folded nanowires. Fig. 6 shows histograms of the end-to-end connecting manner of the nanorod distribution. There are structures from simple to 10-fold-nanowire-chain-like-silver-nanorod assembly. Mainly long straight-like and 2-fold nanowires are favored. The reducing agents from *C. sinensis* extract reduce Ag$^+$ and lead to the formation of metallic AgNWs assemblies, nanowires originated from silver oxides seeds, metallic silver state is mainly on the surface of the AgNWs.

The addition of PVP to direct the formation of AgNWs was useful to obtain AgNWs. For the first time, it was demonstrated that the *C. sinensis* extract is capable of producing AgNWs similar to those reported with chemical synthesis. The bacteriostatic activity of the green AgNWs was evaluated in the inhibition of *E. coli* and *S. aureus* as infectious microorganisms.

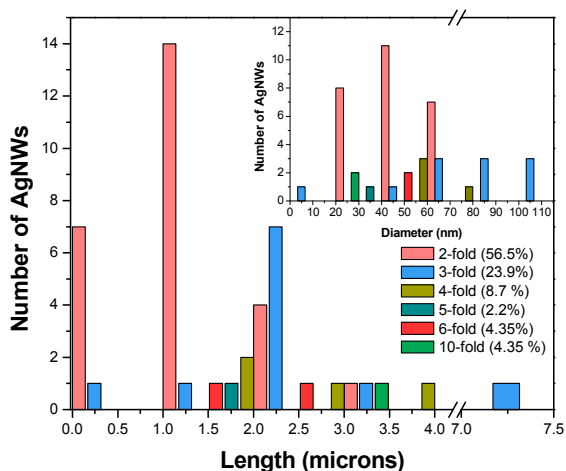Scheme 1 Representative scheme of the AgNW fold assembly.

Fig. 6 Histograms of the end-to-end manner of connecting the nanorod distribution

Antibacterial assays

Fig. 7 shows the response of gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacteria to the cytotoxic AgNWs and AgNPs after 24 h of exposure. Two concentrations were evaluated for the determination of the minimum inhibitory concentration: 6.25 and 25.8 mg/mL. *E. coli* seems to be more vulnerable to both silver morphologies. The AgNWs achieved more inhibition for *S. aureus* in contrast with the AgNPs notably at 25.8 mg/mL. *E. coli* presented more resistance for the bacteriostatic inhibition; 25.8 mg/mL of AgNWs were necessary to achieve a considerable *E. coli* inhibition. Prior to membrane damage a peptidoglycan layer became wide as a defence of *E. coli*.; for this bacteria the morphology of AgNWs was no crucial for causes death of *E coli* or accelerating the cell growth inhibition by damaging the capsule and cytoplasmic membrane.

The dissimilar response to the cytotoxic inhibition of gram-negative bacteria contrasted with the gram-positive bacteria was previously reported and attributed to the kind of membrane cell.[36] In gram-positive bacteria, the membrane is composed of polysaccharides that can produce a biofilm that is used as a defense mechanism when bacteria are stressed, while the gram-negative bacteria present inner and outer peptidoglycan membranes.[36] The biofilm serve as a protective barrier that also can immobilizes silver nanostructures, gram positive peptidoglycan is around 30 through 100 nm thick and contains many layers. AgNPs are smaller that AgNWs and be covered by peptidoglycan film more easily than AgNWs. The results show that silver cytotoxicity seems to relatively increase for *S. aureus* when AgNWs are used, which is maybe due to the sharp morphology that allows more contact with the cell, even damaging the cell-wall rather than an

internalized process that was reported for spherical AgNPs.[37-38] However, a low concentration of AgNWs seems to be effective for both microorganisms. So, the possible effects of the AgNW cytotoxicity can be oxidative stress induction, protein dysfunction and membrane damage due to the detrimental toxicity of the AgNWs. Even if the total annihilation was not reached, our results are similar to those shown in previous reports, and with a lower concentration than the one reported previously.[39-40] For the mediated-assembly synthesis of silver nanowires, is only required a commercial green tea, together with a low molar concentration of PVP. The practical method synthesis stands a soft conditions and friendly route for get silver nanostructures.

Conclusions

A practical approach to the green synthesis of a zigzag-like AgNWs assembly was demonstrated using green tea extracts and a low concentration of PVP as agent-wire director at 45°C. The synthesis assisted with only PVP is an approach to the green methodology using two commercial green tea extracts. Mexican tea achieved more homogenous AgNWs and presented important antibacterial activity against *E. coli* and *S. aureus.*

The AgNW cytotoxicity seems to be effective mostly to *S. aureus* due to the detrimental effect of the 1-D morphology. Further studies with different concentrations are needed to accomplish the annihilation of bacteria and understand the main mechanism of the AgNW cytotoxicity.
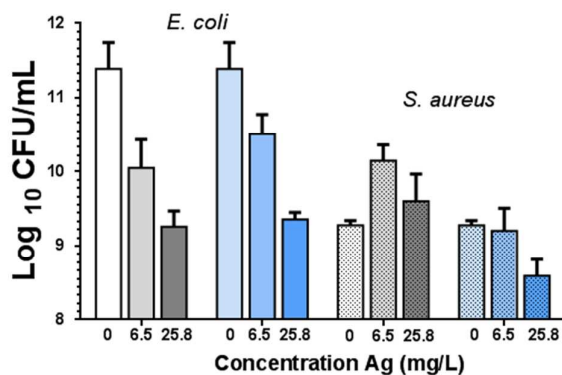

Fig. 7. Survival of *E. coli* ATCC 25922 and *S. aureus* ATCC 25923 after 24 h of exposure to AgNWs; Grey (AgNPs) and Blue (AgNWs).

Acknowledgements

References

1 W. Chen, L. Zheng, M. Wang, Y. Chi, G. Chen, *Anal. Chem.,* 2013, **85**, 9655-9663.
2 T. Cheng, Y. Z. Zhang, W. Y. Lai, Y. Chen, W. J. Zeng, W. Huang, *J. Mater. Chem. C,* 2014, **2**, 10369.
3 Y. Zhang, J. Xia, Y. Liu, L. Qiang, L. Zhu, *Environ. Sci. Technol.,* 2016, **50**, 13283-13290.
4 A. López-Serrano, R. Muñoz, J. Sanz, C. Cámara, *Anal. Methods.,* 2014, **6**, 38.
5 F. Martínez-Gutiérrez, E. P. Thi, J. M. Silverman, C. Camargo de Oliveira, S. L. Svensson, A. Vanden, E. Morales-Sánchez, N. E. Reiner, E. C. Gaynor, E. L. G. Pryzdial, E. M. Conway, E. Orrantia, F. Ruiz, Y. Av-Gay, H. Bach, *Nanomedicine: Nanotechnology, Biology, and Medicine*, 2012, **8**, 328-336.
6 V. Rodríguez-González, R. B. Domínguez-Espíndola, S. Casas-Flores, O. A. Patrón-Soberano, R. Camposeco-Solis, and S.-W. Lee, *ACS Appl. Mater. Interfaces*, 2016, **8**, 31625–31637.
7 S. Obregón, S. W. Lee, V. Rodríguez-González, *Materials Letters*, 2016, **173**, 174-177.
8 Y. Sun, B. Gates, B. Mayers, Y. Xia, *Nano Lett*., 2002, **2**, 165-168.
9 Y. Su, B. Mayers, T. Herricks, Y. Xia, *Nano Lett.*, 2003, **3**, 955-960.
10 D. Chen, L. Gao, *J. Cryst. Growth*, 2004, **264**, 216-222.
11 J. Ma, M. Zhan, *RSC Adv.*, 2014, **4**, 21060.
12 C. Jiang, S. Liu, X. Chen, S. Yu, *Cryst. Eng. Comm.*, 2014, **16**, 8646.
13 J. Xu, G. Cheng, R. Zheng, *Applied Surface Science.*, 2010, **256**, 5006-5010.
14 S. Liu, J. B. H. Tok, Z. Bao, *Nano Lett.*, 2005, **5**, 1071-1076.
15 F. Mafuné, J. Kohno, Y. Takeda, T. Kondow, *J. Phys. Chem. B,* 2000, **104**, 9111-9117.
16 K. A. Bogle, S. D. Dhole, V. N. Bhoraskar, *Nanotechnology,* 2006, **17**, 3204-3208.
17 M. N. Nadagouda, T. F. Speth, R. S. Varma, *Acc. Chem. Res.*, 2011, **44**, 469-478.
18 B. Tang, L. Sun, J. Li, M. Zhang, X. Wang, *Chem. Eng. J.*, 2015, **260**, 99-106.
19 A. K. Mittal, Y. Chisti, U. C. Banerjee, *Biotechnol. Adv.*, 2013, **31**, 346-356.
20 R. Rajan, K. Chandran, S. L. Harper, S. Yun, P. T. Kalaichelvan, *Ind. Crops Prod.*, 2015, **70**, 356-373.
21 I. M. Chung, I. Park, K. Seung-Hyun, M. Thiruvengadam, G. Rajakumar, *Nanoscale Res. Lett.*, 2016, **11**, 40.
22 S. P. Chandran, M. Chaudhary, R. Pasricha, A. Ahmad, M. Sastry, *Biotechnol. Prog.*, 2006, **22**, 577-583.
23 T. P. Amaladhas, S. Sivagami, T. A. Devi, A. Ananthi, S. P. Velammal, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 2012, **3**, 045006.
24 K. Jeeva, M. Thiyagarajan, V. Elangovan, N. Geetha, P. Venkatachalam, *Ind. Crops Prod.*, 2014, **52**, 714-720.
25 C. Anesini, G. E. Ferraro, R. Filip, *J. Agric. Food Chem.*, 2008, **56**, 9225-9229.
26 R. L. Prior, X. Wu, K. Schaich, *J. Agric. Food Chem.*, 2005, **53**, 4290-4302.
27 A. R. Vilchis-Nestor, V. Sánchez-Mendieta, M. A. Camacho-López, R. M. Gómez-Espinosa, M. A. Camacho-López, J. A. Arenas-Alatorre, *Mater. Lett.*, 2008, **62**, 3103-3105.
28 Y. Y. Loo, B. W. Chieng, M. Nishibuchi, S. Radu, *Int. J. Nanomed.*, 2012, **7**, 4263-4267.
29 J. Bhaumik, N. S. Thakur, P. K. Aili, A. Ghanghoriya, A. K Mittal, U. C. Banerjee, *ACS Biomater. Sci. Eng.*, 2015, **1**, 382-392.
30 J. L. Jia, H. H. Xu, D. Q. Li, W. H. Ye, W. J. Liu, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.*, 2015, **45**, 941-946.
31 S. Hussain, Z. Khan, *Bioprocess Biosyst. Eng.*, 2014, **37**, 1221-1231.

32 L. Lin, W. Wang, J. Huang, Q. Li, D. Sun, X. Yang, H. Wang, N. He, Y. Wang, *Chem. Eng. J.*, 2010, **162**, 852-858.

33 S. J. P. Jacob, H. Mohammed, K. Murali, M. Kamarudeen, *Colloids Surf., B,* 2012, **98**, 7-11.

34 Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria That Grow Aerobically; Approved Standard—Ninth Edition. *CLSI document M07-A9*. Wayne, PA: Clinical and Laboratory Standards Institute 2012.

35 C. X. Kan, J. J. Zhu, X. G. Zhu, *J. Phys. D: Appl. Phys.*, 2008, **41**, 155304.

36 Q. L. Feng, J. Wu, G. Q. Chen, F. Z. Cui, T. N. Kim, J. O. Kim, *J. Biomed. Mater. Res.*, 2000, 52, 662-668.

37 I. Sondi, B. Salopek-Sondi, *J. Colloid Interface Sci.*, 2004, **275**, 177–182

38 A. Patrón-Soberano, B. P. Núñez-Luna, S. Casas-Flores, A. De las Peñas, R. B. Domínguez-Espíndola, V. Rodríguez-González, Photochem. Photobiol. Sci., 2017, 16, 854-860.

39 J. R. Morones, J. L. Elechiguerra, A. Camacho, K. Holt, J. B. Kouri, J. Tapia-Ramírez, M. J. Yacaman, *Nanotechnology*, 2005, **16**, 2346-2353.

40 M. Lv, S. Su, Y. He, Q. Huang, W. Hu, D. Li, C. Fan, S. T. Lee, *Adv. Mater.*, 2010, **22**, 5463-5467.