One pod synthesis of single-crystal silver nanowires for selective detection of Pb(II)

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With tannin as both reducing and stabilising agents, high yield single-crystalline silver (Ag) nanowires were synthesised in a simple solution system at 45–55°C. No additional capping or co-reduction agent was required. The length of the Ag nanowires could be up to several tens of micrometres and the average diameter was 50 nm. By adjusting the temperature and pH values of the reaction system, nanoparticles were obtained as the main product. The tannin protected Ag nanowires could be used for the detection of Pb(II) ions with high sensitivity and selectivity and the detection limit could be as low as 10^{-8} M. This detection assay is more practical in application because of its green and low cost preparation and longer storage time at ambient conditions.

1. Introduction: One-dimensional (1D) nanostructures of noble metals are of considerable interest due to their different or superior electrical, optical, and chemical properties as compared to the bulk counterparts [1–3]. Among all metal nanomaterials, silver (Ag) nanowires have interesting electrical and optical properties that can be used in a variety of applications, including transparent electrodes [4, 5], motion sensors [6], biomolecular sensing [7], photonic structures that can launch optical signals at a scale without optical refraction limits [8], plasmonic antennae for surface-enhanced Raman scattering (SERS) [9], and fluorescence enhancement of a dye molecule approximated to an Ag nanowires surface [10]. Therefore, many methods have been devoted to the synthesis of 1D Ag nanomaterials, e.g. electrochemical technique [11], hydrothermal method [12], porous materials template [13], polyol process [14], UV-photoirradiation route [15], and vapour-phase synthesis [16]. Among all the methods, the solution-phase chemical synthesis should be one most promising route to the preparation of Ag nanowires in terms of cost, yield, and simplicity. Moreover, with growing concern on the biological and environmental impact of nanomaterials, it is urgent to find methods creating non-toxic, 'green' nanoparticles. Hence, there is a need to develop clean, non-toxic and environmentally friendly methods for the synthesis of Ag nanowires.

In this Letter, we describe a green protocol for large-scale fabrication of Ag nanowires by using tannin, a polyphenolic plant extract, as both reducing and stabilising agent. Furthermore, the as-prepared Ag nanowires are single-crystalline structure. Compared with most of Ag nanowires obtained by solution-phase methods, which adopt penta-twinned structure [17–19], Ag nanowires with single-crystalline nature are rarely reported. Mohanty *et al.* [16] synthesised single-crystalline Ag nanowires by a vapour-phase method. Pan's group prepared single-crystalline Ag nanowires through a solution process [20]. However, the yield of Ag nanowires in both above two methods was low and was estimated to be 5–10%. The yield of single-crystalline Ag nanowires in this work can be as high as 90%. By modulating reaction conditions, Ag nanoparticles can be obtained. The formation mechanism of single-crystalline Ag nanowires is also discussed. The procedure in this work requires only simple reagents and equipment, can be carried out under aerobic conditions, and does not demand seeding protocols or ultra-fine control over the temperature and pressure. Finally, these nanowires can be used for Pb^{2+} detection with higher sensitivity and selectivity over other metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Ba^{2+}, Hg^{2+}), which is based on the localised surface plasmon resonance (LSPR) effect of Ag nanowires. As far as we know, this is the first application of Ag nanowires for detection of Pb^{2+} and the detection limit could be as low as 10^{-8} M. For the preparation is green and low cost, the detection of Pb^{2+} by Ag nanowires is more practical.

2. Experimental section

2.1. Preparation of Ag nanowires: In a typical procedure, equal volumes of 5 mM $AgNO_3$ solution and 5 mM tannin solution were freshly prepared, respectively. After the mixture of the two solutions, the reaction system was put into a 50°C thermostatic water bath immediately without vibration. The reaction lasted for 2 h. During this stage, the reacting solutions became bright yellow initially, indicating the appearance of Ag nanoparticles, and then turned into suspension with yellowish precipitates eventually. Finally, the precipitates were isolated by centrifugal separation at 2500 rmp for 10 min, which were then rinsed several times with water, and the supernatant was discarded every step. Through these treatments, nanoparticles in the product were washed away. At last, the pure nanowires were suspended in 5 ml water for later use.

2.2. Detection of Pb^{2+} with Ag nanowires: The detection of Pb^{2+} in aqueous solution was performed at room temperature. Stock solutions (1×10^{-4} M) of the aqueous salts of Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Ba^{2+}, and Hg^{2+} were prepared to investigate their interference in Pb^{2+} detection. Pb^{2+} aqueous solutions with different concentration were also prepared. For detection, 100 μl of Ag nanowires was added to the above salts solutions (5 ml). The absorption spectra of the resulting solutions were measured with UV–vis spectrophotometer.

2.3. Characterisation of Ag nanowires: UV–vis absorption spectra were recorded with an Agilent VARIAN Cary-50 UV–vis spectrophotometer, using 1 cm path length quartz cuvettes for measurements. The morphology was observed with a HITACHI H-7500 transmission electron microscope (TEM) and HITACHI S-4800 field-emission scanning electron microscope (SEM). High-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) were characterised by a JEOL JEM-3010 electron microscope operated at an acceleration voltage of 300 kV.

3. Results and discussions: Fig. 1*a* presents a representative low-magnification TEM image of the Ag product obtained by the typical experiment, which apparently consists of a large quantity of uniform nanowires up to several tens of micrometres in length.
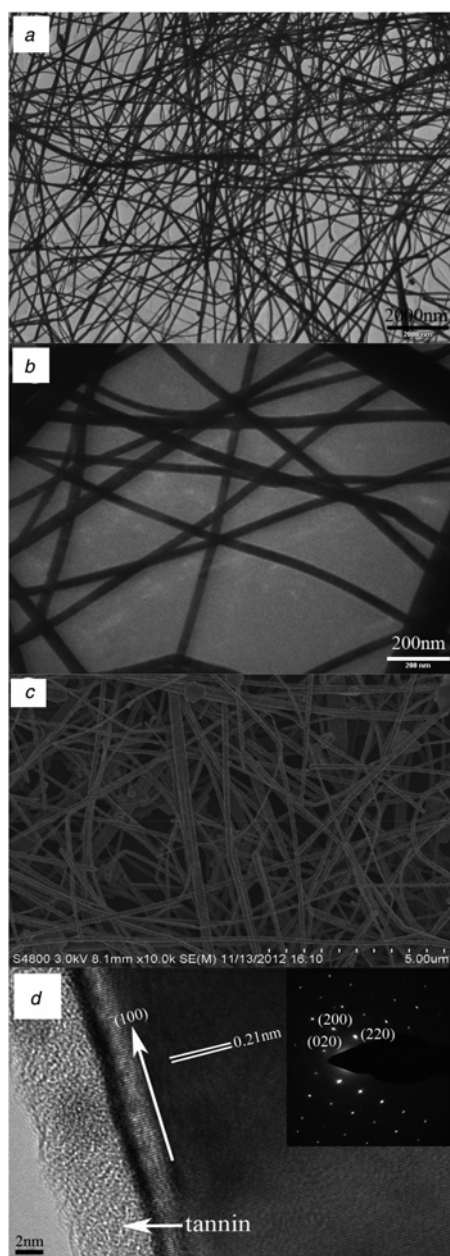
Fig. 1 *TEM images of silver nanowires with different magnification (a and b). SEM image of Ag nanowires (c). HRTEM and SAED images of a single Ag nanowire (d)*

Fig. 2 *IR spectra of pure tannin and Ag nanowires (a, the right ordinate belongs to Ag nanowires). TEM image of Ag nanowires with nanocubes on them (b)*

Fig. 1*b* shows the morphology of the sample with higher magnification and the average diameter of these nanowires is about 50 nm. A typical SEM image is shown in Fig. 1*c*, which further confirms the high yield of the Ag nanowires. Fig. 1*d* shows an HRTEM image of one nanowire with clear lattice fringes, which reveal the single-crystalline nature of the nanowire. The lattice spacing is measured to be 0.21 nm, agreeing well with that of (100) planes of face-centred cubic (fcc) Ag. This also shows that nanowires grow along the [100] crystallographic direction [21]. The corresponding SAED pattern is shown as an insert of Fig. 1*d*, which displays a set of dot patterns revealing the single-crystalline nature. And the SAED pattern corresponds to the [100] crystallographic zone axis of fcc Ag, which further confirms the [100] growth direction. Similar phenomena have been reported in cubic Ag nanobars [22] and Ag nanowires [20].

Tannin is the most indispensable parameter to the [100] direction growth of one dimensional Ag nanostructure. It is well-known that
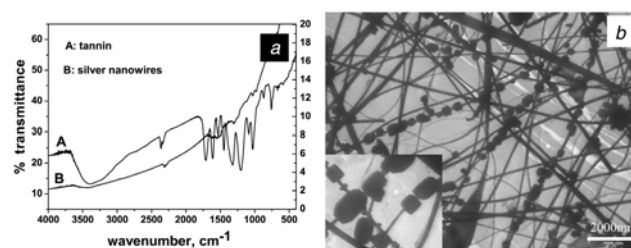
tannin is a naturally occurring plant polyphenol, which has been used as a mild reducing agent in the fabrication of Au or Ag nanomaterials through the oxidisation of its hydroxyl groups [23]. The selective adsorption on special crystal faces of tannin molecules causes the anisotropic growth of Ag nanowires along [100] direction. This speculation can be confirmed by HRTEM investigation as shown in Fig. 1*d*, in which an organic layer can be clearly found on the surface of Ag nanowires as indicated by arrows. In support of this hypothesis, IR spectra of pure tannin and Ag nanowires are provided in Fig. 2*a*. For only trace tannin being adsorbed on the surface of Ag nanowires, the corresponding IR spectrum peak intensity is weak. There is a marked difference in the hydroxyl region. Pure tannin shows a broad peak in the region of 3300–3500 cm^{-1}, due to phenolic –OH groups. However, extremely weakened peaks are observed after the growth of Ag nanowires, thus indicating that the hydroxyl groups are involved in the formation of the Ag nanowires [23]. There are six equivalent (100) faces in fcc Ag, it is deduced that tannin molecules adsorb selectively on four (100) faces. As a result, the two naked opposite (100) faces become growth point and one-dimensional nanowire comes into being at last. At the same time, the growth of given (100) faces may suppress the growth of all the other neighbouring faces. Evidence to prove the adsorption of tannin on four opposite (100) faces is the formation of occasional nanocubes in the product as shown in Fig. 2*b*. It can be seen that the nanocubes are linked by nanowires on one pair of opposite (100) faces. In addition, tannin can form stable complexes with silver ions [23, 24]. The complex between tannin and Ag ion slows down the reducing reaction rate, which is favourable to one dimensional anisotropic growth [25]. Of course, it is still an interesting topic that why the tannin molecules adsorb only one pair of opposite faces but another two pair of faces, which need more deeply work.

Tannin is a kind of acid reducing reagent (the pH value of the typical synthesis system in this work is about 3), so the pH value of solution will affect its reducing ability. The alkaline condition is in favour of the increase of its reducing ability, so Ag nanoparticles were synthesised by tannic acid in alkaline aqueous solution because of fast nucleation [26]. In this work, NaOH solution (0.1 M) was used to increase the pH value of the system. Fig. 3*a* shows the product obtained at a pH value of 9, we can only see many nanoparticles with occasion nanoplates. When the pH value decreased to 7, few of nanowires could be found as shown in Fig. 3*b*. Further decreasing the pH value to 5, as presented in Fig. 3*c*, the ratio of nanowires increased, but nanoparticles were still the main product. To investigate the situation of pH value less than 3, 0.1 M nitric acid was adopted. When 1 ml acid was added to the reaction system (pH = 2), the yield of the total product apparently decreased. TEM investigation indicated that nanoparticles were the main product and few of nanowires could be discovered (Fig. 3*d*). When further increasing the amount of acid to 5 ml (pH = 1.5), nanoparticles became the only product (Fig. 3*e*) and the total yield further decreased. The decrease of

yield should be attributed to the decrease of the reducing ability of tannin at the acid condition.

Temperature is another vital factor for the formation of Ag nanowires. When the reaction temperature was in the range of 45–55°C, nanowires were the main product and the yield was up to 90% (the yield was estimated by counting the number of nanowires and nanoparticles in the product before centrifugal separation). Only nanoparticles with a size of 50–100 nm were obtained when the temperature was increased to 70°C (Fig. 4b). Further elevating the temperature to 90°C, nanoparticles were still the absolute
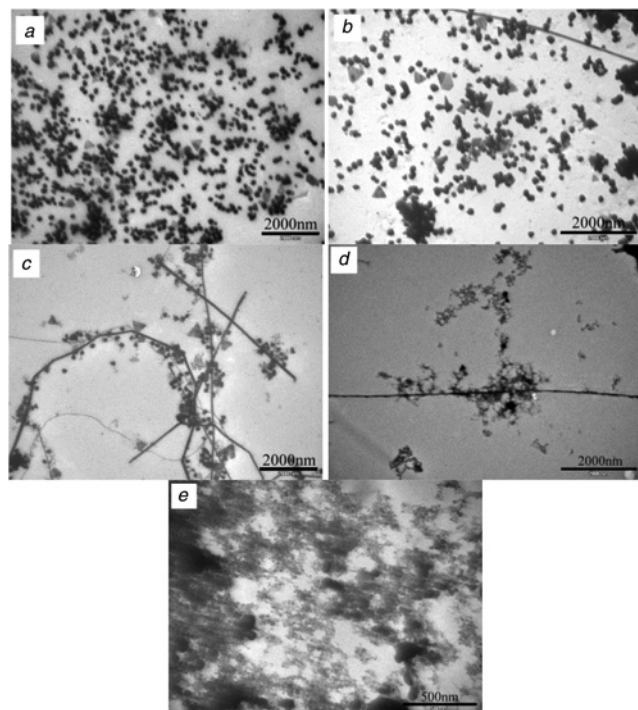

Fig. 3 *TEM images of Ag nanostructures obtained with different pH values*
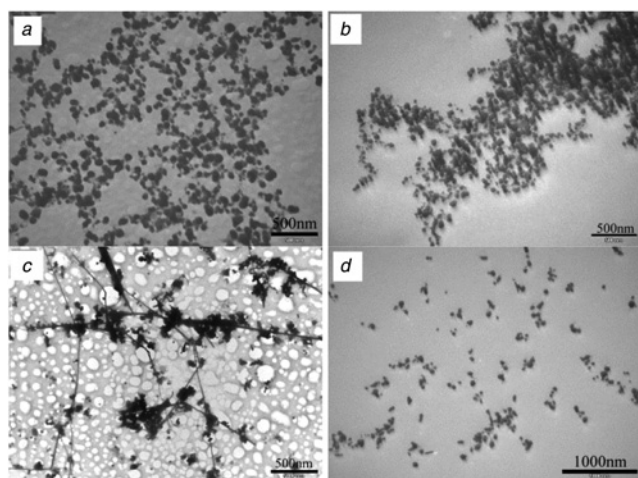*a* 9
b 7
c 5
d 2
e 1.5

Fig. 4 *TEM images of Ag nanostructures obtained at different temperatures*
a 90°C
b 70°C
c 25°C
d 13°C

product as shown in Fig. 4a. When the temperature was decreased to 25°C, nanoparticles were the majority in the product and coexisted with a few nanowires (Fig. 4c). Nanoparticles became the absolute product when the temperature was further decreased to 13°C (Fig. 4d). Generally, a lower temperature would make the reaction rate slow down. According to the above discuss that slow reaction rate is favourable to anisotropic growth, nanowires but the nanoparticles should be the major product at a lower temperature. However, as indicated in Figs. 4c and d, the lower the temperature was, the fewer the Ag nanowires were. This is an interesting phenomenon. At lower temperature, the reaction rate is low, but the directional arrangement of tannin molecules on (100) faces is not favourable, because there is not enough driving energy provided. So only nanoparticles form at last and tannin molecules wrap around the nanoparticles. With the increasing of temperature, more and more energy is provided for driving the tannin molecules to adsorb on specials surfaces. As a result, more and more Ag nanowires occur in the final product and become the majority at a temperature of 50°C or so. On the other hand, at the higher reaction temperature, such as 90 and 70°C, the reaction rate is higher, and tannin has no enough time to adsorb on special faces. Furthermore, the Brownian motion is intensified and aggregation between nuclei is speeded up. Consequently, newly formed nuclei have no enough time to arrange directionally on special (100) faces. Therefore, although the ability of directional adsorption for tannin molecules is enhanced by increasing temperature, nanoparticles are still the only product at a higher temperature. To balance the two opposite temperature effects, a suitable temperature (50 ± 5°C) is necessary for nanowires with higher yield.

Pb(II) is a persistent environmental contaminant with high toxicity, which can cause damage to kidney, liver, and nervous system and pose severe effects on human health [27, 28]. For these reasons, the measurement of Pb^{2+} is becoming more common and imperative in chemical, environmental, clinical and toxicology fields. Various methods are available for the determination of Pb^{2+} in aqueous samples. Recently, a technique based on the LSPR absorption of Au or Ag nanoparticles has been developed for heavy metal detection [29–31]. It is known that there is a stronger complexation between tannin and Pb^{2+}. So the as-obtained Ag nanowires were used to detect Pb^{2+} and high sensitivity and selectivity were obtained. Fig. 5a shows the UV–vis spectra of Ag nanowires sensing detection of Pb^{2+} ions with different concentrations. With increasing Pb^{2+} ions concentration from 10^{-8} to 10^{-3} M, respectively, it is found that the intensity of the maximum absorption peak of Ag nanowires centred at around 470 nm lowers gradually. The detections of Pb^{2+} ions with a concentration of 10^{-9} and 10^{-10} M are shown in Fig. 5b. It can be seen that there is no obvious change of Ag nanowires absorption peak. The above experimental results demonstrate that the Pb(II) detection limit of the Ag nanowires is 10^{-8} M. The detection limits of Ag nanowires with different storage time were also investigated. The results indicated that Ag nanowires stored in water for one year could still detect 10^{-8} M Pb^{2+} ions without an obvious change of maximum absorption peak position. For real life applications, in environmental samples, there can be several impurities due to the presence of other heavy metal ions. To understand whether our assay is selective to Pb(II), we have also performed experiments on our assay response to the addition of other metal ions. Fig. 5c shows the response of our Ag nanowires based probe in the presence of various alkaline and transition metal ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Ba^{2+}, Hg^{2+}) at the level of 10^{-4} M concentration. The data clearly shows that our tannin protected Ag nanowire probe is highly selective to the detection of Pb(II) ions.

A number of studies for the detection of Pb^{2+} based on noble metal nanomaterials have been reported, some of them are summarised and compared with the present work as listed in Table 1. In most of the detections, quantum dots or smaller nanoparticles
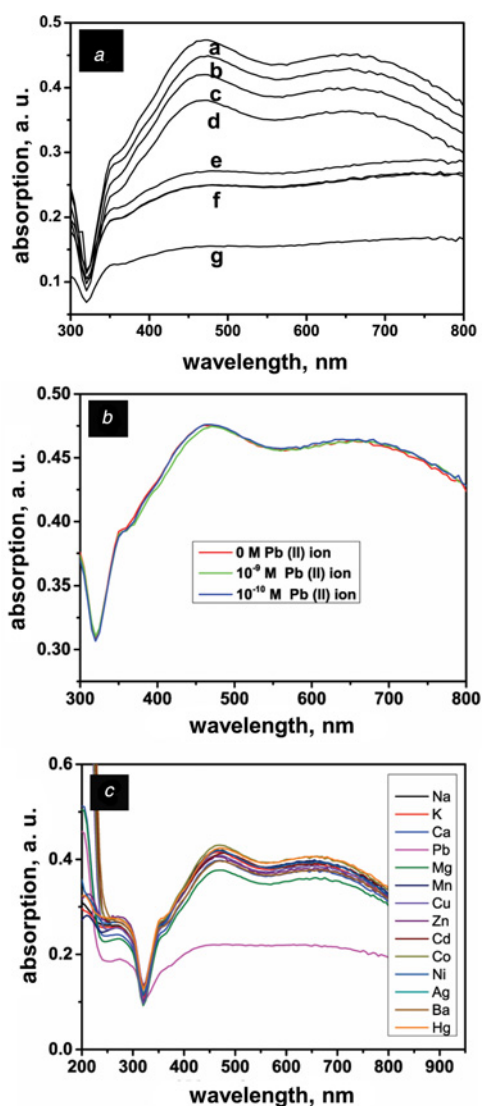
Fig. 5 *UV–vis spectra showing the sensing detection of Pb (II) ions using silver nanowires: a: 0 M; b: 1×10^{-8} M; c: 1×10^{-7} M; d: 1×10^{-6} M, e: 1×10^{-5} M; f: 1×10^{-4} M; g: 1×10^{-3} M (a) as well as 1×10^{-9} M and 1×10^{-10} M (b). Plot showing selectivity of the tannin protected silver nanowire probe (c)*

Table 1 Comparison of the detection limit for Pb^{2+} using noble metal nanomaterials

Detection techniques	Noble metal nanoparticles	Detection limit	Ref.
Fluorometry	Ag nanoparticles	200 ppq	[32]
Fluorometry	Au nanoparticles/graphene	10 nM	[30]
Fluorometry	Au nanodots	2 nM	[33]
Colourimetry	Ag nanoparticles	0.1 μM	[34]
Mass spectrometry	Au nanoparticles	0.5 nM	[35]
LSPR[a] sensor	Au nanoislands	0.01 ppb	[31]
LSPR	Ag nanowires	0.1 nM	this work

[a]Localised surface plasmon resonance.

were adopted and nanowires were used very rarely. Generally, the preparation of quantum dots or small nanoparticles is higher cost. Especially, Au nanoparticles are very expensive. Moreover, many of them could not be stored for a long time and need to be synthesised freshly. Relatively, the Ag nanowires reported here can be reliably and reproducibly synthesised with low cost and could be stored for a longer time at ambient conditions. Also, the synthesis of nanowires is biocompatible. Therefore, although the detection limit of Ag nanowires in the present work is not the lowest, this strategy sill presents a number attractive analytical features, such as simple and green synthesis, low cost, longer storage time as well as relatively low detection limit, which make them more practical.

4. Conclusion: In summary, single-crystalline Ag nanowires with high yield can be synthesised by an extremely simple solution method with the assistance of tannin. The preparing system was composed only of water, tannin and $AgNO_3$. The optimal temperature was in the range of 45–55°C, which is a very mild condition in the synthesis of single-crystal Ag nanowires. In addition, nanoparticles could also be obtained with the change of temperature and pH value. The tannin stabilised Ag nanowires can be used to the detection of Pb(II) ions with high sensitivity and selectivity. For the preparation is green, simple and low cost, the detection by Ag nanowires is more practical in biology application.

6 References

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