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Direct solution synthesis of Pd nanowire networks and their application in surface-enhanced Raman scattering

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Abstract

Highly branched Pd 2D nanowire networks are prepared by a template- and surfactant-free method in an ethylene glycol (EG)–dimethyl sulfoxide (DMSO) mixture under mild conditions. Pd nanowire networks with lengths ranging from hundreds of nanometers to several micrometers and branches with uniform diameters of ~ 8 nm are grown. The most likely formation mechanism is also proposed. The as-produced Pd nanowire networks exhibit high surface-enhanced Raman scattering activity for 4-mercaptopyridine probe molecules with 5.0×10^{-8} M concentration.

1. Introduction

Network structure fabricated with nanoparticles, nanowires or nanotubes as the building blocks and their growth process have been actively investigated not only because of their interesting intrinsic properties arisen from low dimensionality and quantum effects, but also because of their capability for direct nanosystem integration, which is expected to have applications in the generation of nanoscale electronic and optic-electronics devices. Many experimental routes including vapor phase deposition [1–3], templated electro-deposition [4], hydrogen/oxygen plasma methods [5] and solution-phase methods based on capping reagents have been successfully used to organize networks of metals or semiconductors, such as T-Se, Pt, In_2O_3 , Ga_2O_3 , Cu, Au, etc [6–9].

Much attention has been focused on palladium because studying palladium nanostructures is both theoretically interesting and practically important. Palladium nanoparticles play an important role in many industrial applications. For instance, Pd NPs have shown high catalytic activity in the reduction of automobile pollutants and facilitate organic reactions [10–12]. It also has an application in gas sensors [13], owing to its specific sensitivity towards hydrogen. For these reasons, much effort has been devoted to the production of Pd nanostructures with monodispersed sizes and well-defined morphologies [14–20]. However, most of the research has

focused on the monodispersed nanoparticles and only a few papers have reported the synthesis of Pd nanowire arrays or networks [21–26]. The assembly of metallic Pd nanowires is still at the edge of success, partly because of the difficulty of synthesizing Pd nanowires with high aspect ratio in large numbers. Similar to common metal nanostructures, the intrinsic properties of Pd nanostructures can be tailored by controlling their sizes, shapes, compositions, crystallinities and crystal structures. Designing a simple method to fabricate NPs into various types of metallic Pd with novel shapes is urgently needed to exploit the peculiar properties and unique applications of Pd nanostructures.

Here, highly branched Pd 2D nanowire networks in an ethylene glycol (EG)–dimethyl sulfoxide (DMSO) mixture were successfully synthesized under mild conditions. It is worth pointing out that, without any surface modifying reagent, the Pd nanowire networks can be achieved by a simple solution route. The length of as-grown Pd nanowire networks ranges from hundreds of nanometers to several micrometers and the branches of as-grown Pd nanowire networks have uniform diameters of ~ 8 nm. The growth mechanism of the as-produced crystals is also discussed in this paper, which opens up a new possibility to control the shape of anisotropic nanostructures. Using 4-mercaptopyridine (4-Mpy) as a probe molecule, the Pd nanowire networks exhibit high surface-enhanced Raman scattering (SERS) activity.

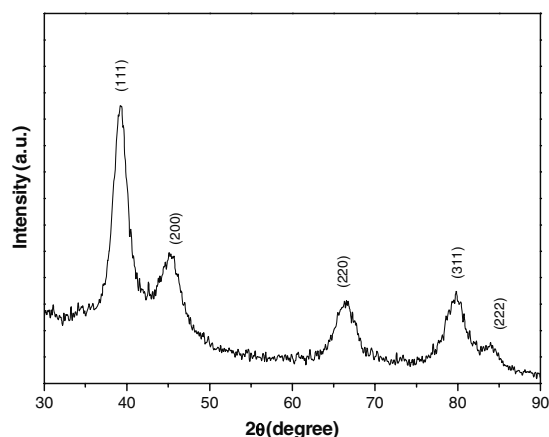


Figure 1. XRD pattern of the as-prepared linear Pd NPs assemblies.

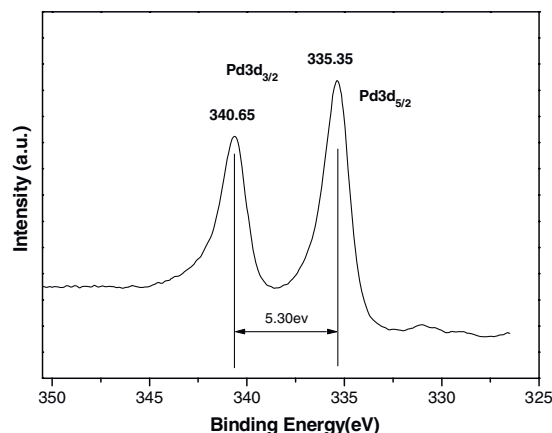


Figure 2. XPS spectra of the Pd nanowire networks.

2. Experimental details

All chemicals were analytical reagents without further purification. In a typical synthesis, 0.0224 g $\text{Pd}(\text{CH}_3\text{CO})_2$ (Aldrich) was introduced into 2 ml of dimethyl sulfoxide (DMSO) and 23 ml of ethylene glycol (EG) in a three-necked flask equipped with a reflux condenser and a magnetic Teflon-coated stirrer at room temperature. The reaction mixture was slowly heated to 120 °C and held in air for 3 h. After being cooled down to room temperature, the products were centrifuged, washed with distilled water and then with ethanol for several times to remove any excess EG and DMSO and finally dried in vacuum at 60 °C.

The as-obtained samples were then characterized by a Rigaku Dmax2200 diffractometer equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54180 \text{ \AA}$) for the structural determination. The valence states of Pd nanostructures were examined by x-ray photoelectron spectroscopy (XPS). The XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W $\text{Al K}\alpha$ radiation. Further microstructural analyses were performed using a high-resolution transmission electron microscope (TEM, JEOL 2100F). TEM samples were prepared by dispersing the as-prepared powder in alcohol with ultrasonic treatment, dropping it onto a holey carbon film supported on a copper grid and drying the dropped sample in air.

SERS substrates were fabricated by drop-casting 6 μl of the Pd nanowire network ethanol solution onto an Si wafer and drying completely under vacuum. The dry films were immersed in a 5 mM aqueous solution of 4-mercaptopyridine (4-MPy) for 1 h in order to absorb enough probe molecules. The substrate was then taken out, rinsed with deionized water to remove any unabsorbed 4-MPy molecules and dried with a stream of air. Raman spectra were recorded with a JY LabRAM HR800 UV confocal micro-Raman spectrometer. The He–Ne laser (632.8 nm) was used as a source of excitation. The laser radiation is focused on the sample by means of a 50 $\times$ microscope objective. The signal acquisition time was 200 s. In our experiments, the maximal laser power delivered to the sample was 5 mW.

3. Results and discussions

3.1. Structural analysis and chemical state investigation

A representative XRD pattern of the as-synthesized products is shown in figure 1. All of the diffraction peaks can be assigned to {111}, {200}, {220} and {311} planes of face-centered cubic (fcc) palladium (JCPDS card no. 87-0461). No impurity phases are detected, indicating the formation of pure and highly crystallized Pd.

A high-resolution scan of XPS over the range 325–360 eV was performed to ascertain the chemical state of the as-obtained Pd. The binding energies obtained in XPS analysis were corrected for specimen charging by referring the C_{1s} peak to 284.60 eV. As depicted in figure 2, the binding energies of 335.35 and 340.65 eV correspond to Pd ($3d_{5/2}$) and Pd ($3d_{3/2}$), respectively. The binding energy values of the samples are similar to the data reported for metallic Pd in the literature [27–29], which confirms that pure metallic Pd was obtained because no peak around 336 eV corresponding to Pd (II) species is detected.

3.2. Morphological investigations of Pd nanowire networks

Typical TEM and HREM images of Pd nanostructures are shown in figure 3. As shown in figure 3(a), though the nanowire networks are often overlapped, folded or twisted, they are generally well dispersed through observation. The products are highly interconnected with branches and formed into two-dimensional (2D) nanowire networks. The length of the networks reaches hundreds of nanometers and the branches have an average diameter of 8 nm.

To study the growth direction and microstructure of the branches, a typical ‘T’ nanowire junction taken from the nanowire networks (indicated by a rectangle in figure 3(a)) is further investigated by HRTEM. As shown in figure 3(b), the orientations of the atomic lattice fringes are varied along the junctions. Both of the fringe spacings are determined to be 0.23 nm, which is close to the (200) lattice spacing of bulk palladium. This indicates the Pd nanowire networks are assembled by numerous particles and they prefer to orient themselves with similar crystallographic facets, which

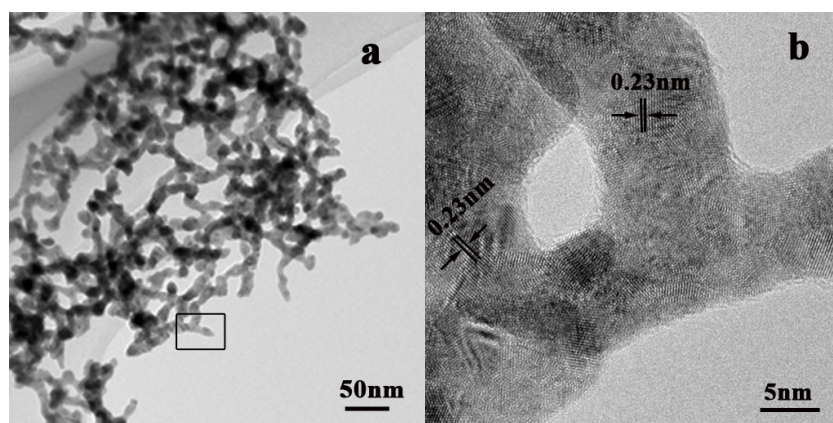


Figure 3. TEM image (a) of as-produced Pd nanowire networks and HRTEM images (b) of ‘T’ junctions, which were indicated by a rectangle in (a).

is similar to the previous reports of Taratula *et al* [30]. These findings provide direct evidence that Pd polycrystalline nanowires are formed by tightly fused nanoparticles.

For the accurate understanding of the growth mechanism of as-prepared Pd network structures, it is necessary to investigate the morphologies of intermediates. The morphological evolution of Pd nanowire networks is studied by TEM, as shown in figure 4.

3.3. Intermediate process in the formation of Pd nanowire networks

Figure 4 shows typical TEM images of Pd nanostructures obtained at different reaction times. It can be seen that, in the initial stage of the reaction, small monodispersed particles are formed. These particles are irregular in shape and their sizes vary on the scales of 2–5 nm (figure 4(a)). It is interesting to find that some of these particles are accumulating to form zonal aggregation. As the reaction proceeds, these particles appear to show more tendencies to zonal aggregation and after 5 min no monodispersed particles can be seen. As shown in figure 4(b), all the nanoparticles have self-assembled in a pearl-strip fashion. It should be pointed out that at this moment the pear-strip NP assemblies are composed of independent nanoparticles. These independent nanoparticles gradually coalesce into nanowires. Meanwhile some of the nanowires connect with each other, forming extensive nanowire networks. As indicated by arrows in figure 4(c), a short nanowire composed of independent nanoparticles is connecting with the nanowire. More details of the connection are revealed in the enlarged TEM image in figure 4(d). In the left part, all nanoparticles have coalesced into nanowires, where the formed nanowires are very coarse on the surface. In the right part, meanwhile the nanoparticles still appear apart from each other. After 15 min, no individual particles can be observed, which suggests that all the particles have coalesced into nanowires. These nanowires connect with each other to form a network structure (figure 4(e)) and the surfaces of the nanowires become slicker. Eventually, 2D nanowire networks extending over a surface area of several square micrometers with relative smooth surface are obtained

(figure 4(f)). This intermediate course provides powerful evidence for the formation mechanism of nanowire networks.

3.4. Growth mechanism for the Pd nanowire networks

Based on the experimental results, we believe the nanoparticle coalescence mechanism is the most likely mechanism for the formation of Pd nanowire networks. Figure 5 shows the schematic representation of the most likely formation process of Pd nanowire networks. Three main stages are included:

- (1) Palladium acetate was dissolved in DMSO and formed $[\text{Pd}(\text{DMSO})_2]^{2+}$ and then transformed to Pd nanoparticles by the reduction reaction [31]. The initial Pd nanoparticles anisotropically grow and assemble in a pearl-strip fashion by electrostatic interactions or steric effects [32–34].
- (2) The linear assembled nanoparticles gradually collided, joined with each other and then formed branched nanowires.
- (3) The nanowires contacted at their terminals and coalesced into longer nanowires, eventually forming 2D nanowire networks by Ostwald ripening.

Other similar nanoparticle coalescence mechanisms have been brought forward to explain the AuCu and Au nanowire network formation processes [32–35]. In these reports, the boiling point of the solvent, the interaction between solvent and nanoparticles or liquid interfaces in biphasic mixtures significantly contribute to the morphology formation, which is also similar to our results. In our system, the DMSO plays an important role in the growth of the nanowires and branches.

To investigate the effect of DMSO on the nanowire network formation, controlled experiments with different proportions of DMSO in the mixed solvent were carried out. As shown in figure 6(a), in the absence of DMSO, only monodispersed Pd nanoparticles were obtained. With DMSO in the range of 5%–60% in the mixed solvent, the final products keep the similar morphology of the nanowire networks and the diameters are all about 8 nm (figure 6(b)). When the DMSO is increased to 80%, the diameters increased to 15 nm and the surfaces of the nanowire are rougher than those shown in

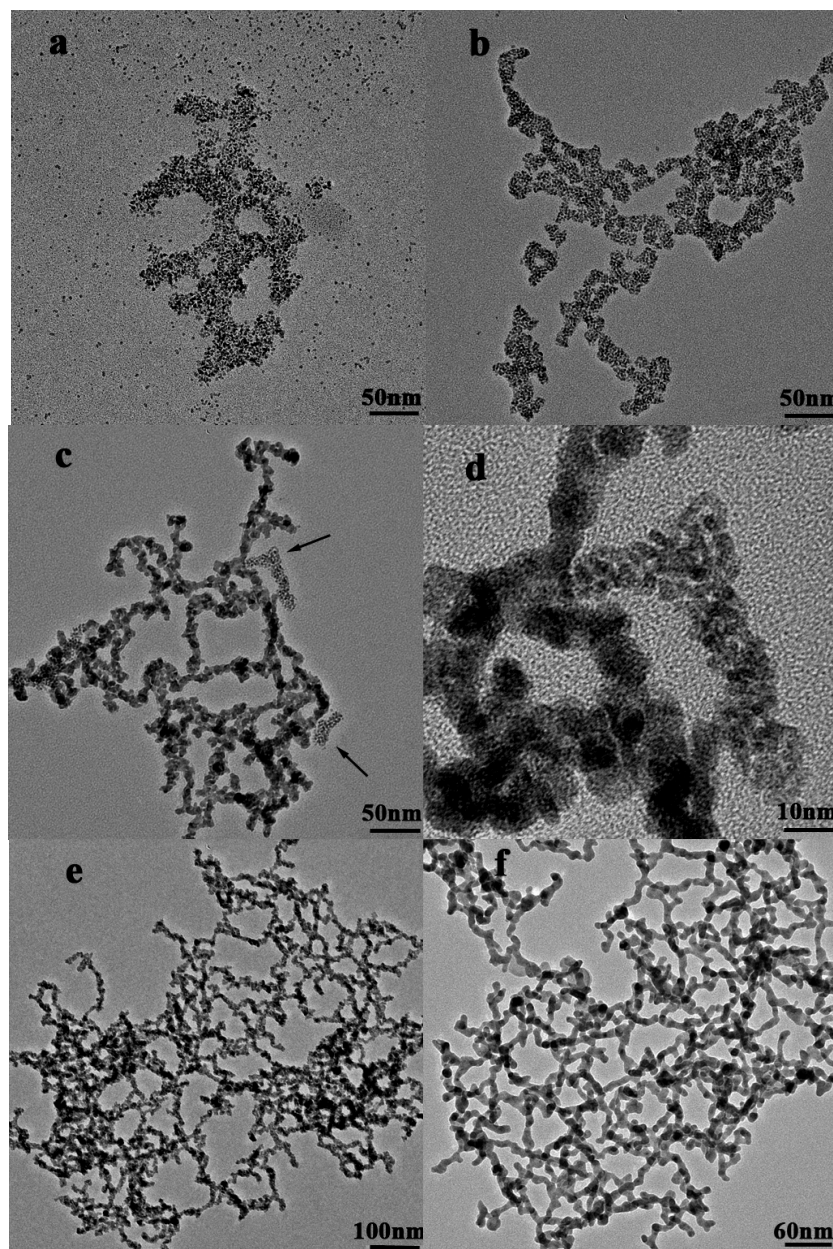


Figure 4. TEM images showing the shape evolution of Pd nanowire networks. (a) Reaction time of 2 min; (b) reaction time of 5 min; (c) and (d) reaction time of 10 min; (e) reaction time of 15 min; (f) reaction time of 3 h.

figure 6(b). When DMSO increased to 90%, the diameter of the nanowires increased to about 30 nm. More interesting is that single nanoparticles can be recognized distinctly and all of them remain in a linear assembly forming nanowire network shapes.

The same tendency was reported very recently in CdTe nanowire growth [36]. In this report, with the DMSO concentration in the mixture increasing, the diameters of the resulting nanowires increase. DMSO in the NW growth solution inhibits the formation of pearl-necklace assemblies, which explains the cessation of NW formation for the solutions with DMSO proportions greater than 60%. However, in our system this is different. When DMSO is greater than 90%, nanoparticles still assemble into a nanowire network. How

does this work? We suggest that a soft template limits the nanoparticle assembly style. What acts as the template? Our system is surfactant-free; the only possible source is the solvent. This may be caused by the special chemical and physical properties of DMSO. It is well known that DMSO is one of the most widely used solvents with an extensive dissolving power [37, 38]. Also, it is a highly associated liquid and the dimethyl sulfoxide molecules can connect with each other by hydrogen bonds and form networks. This network provide a pathway or serves as a soft template for nanoparticle coalescence and nanowire networks.

Surface properties of as-prepared Pd nanowire networks are studied by FTIR after vigorous washing and sonication in deionized water and ethanol for three times. As shown

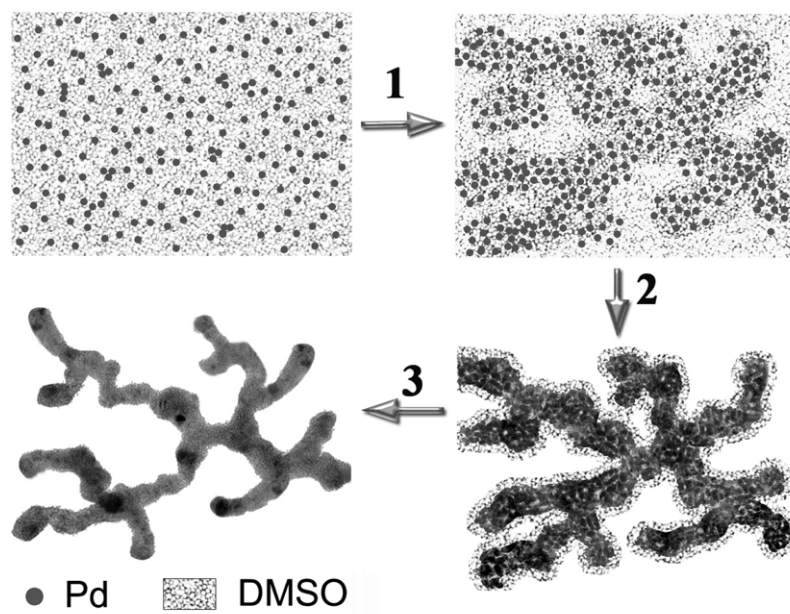


Figure 5. Schematic illustration of the formation process of the Pd nanowire network.

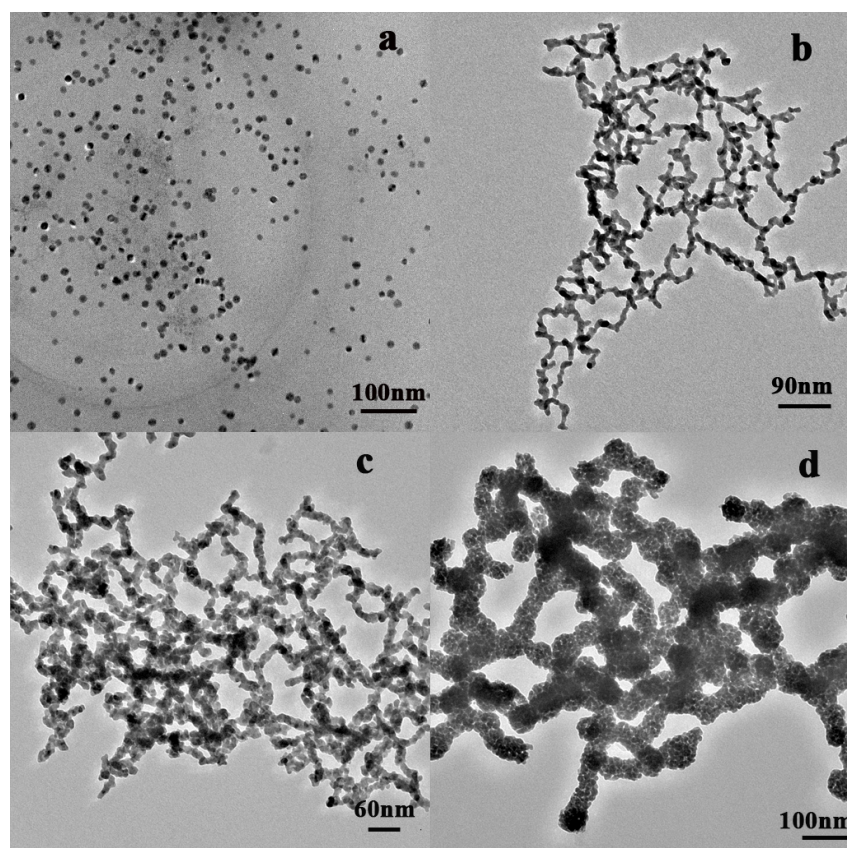


Figure 6. TEM images of Pd nanostructure in different solvents. (a) Monodispersed nanoparticles obtained in EG; (b) 5–60% DMSO in mixture; (c) 80% DMSO in mixture; (d) 90% DMSO in mixture. All the proportions of DMSO are by volume ratio and all the reaction times are 3 h.

in figure 7, the band at 669 cm^{-1} can be assigned to C–S stretching frequencies. The CH_3 rocking mode and CH_3 asymmetric deformation mode are observed at 1020 and

1390 cm^{-1} , respectively. The band of S–O stretching at 1116 cm^{-1} is higher than in the free ligand, which indicates the DMSO is coordinated with Pd through the sulfur atom [39, 40].

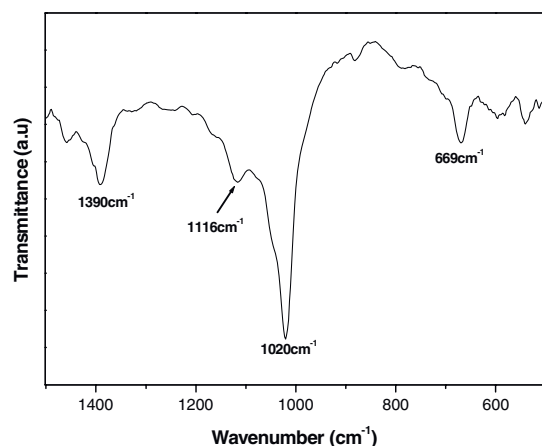


Figure 7. FTIR spectra obtained from Pd nanowire networks.

The FTIR results confirm the presence of DMSO on the Pd nanowire network surfaces. The exact role of DMSO in forming nanowire networks should be further investigated in our future work.

3.5. SERS activity of Pd nanowire networks

Surface-enhanced Raman scattering (SERS) is a powerful tool for optical detection and spectroscopy of single molecules adsorbed on certain metallic substrates, which were worked through an electrochemical surface roughening procedure or composed by well-defined nanostructured materials. As well as the three noble metals Au, Ag and Cu researched initially, some transition metals also showed an excellent enhancement factor for organic adsorbates, such as Pt, Ru, Rh, Pd, Fe, Co, Ni and their alloys. These evolutions will extend further the applications of SERS. Xia and his coworkers reported Pd cubes and hollow boxes exhibited extraordinary high SERS activity [41, 42]. To the best of our knowledge, it is not reported until now that Pd nanowire networks are used as SERS-active materials.

4-MPy was chosen as the probe molecule owing to its clear vibrational features reported by many researchers [43–46]. Here, SERS activity of Pd nanowire networks was examined. To illustrate the limit of detection for this system, we prepared aqueous solutions ranging from 5.0×10^{-3} M to 5.0×10^{-8} M, Raman spectra of 4-MPy enhanced by the Pd nanowire networks/Si substrate were obtained (shown in figure 8). As shown in figures 8(c)–(f), the SERS substrates give well-resolved Raman spectra of all 4-MPy solutions, which show some enhanced Raman peaks with similar Raman shifts and different intensities. Obviously, the smaller the concentration of 4-MPy solutions (from figures 8(f) to (c)), the lower the intensity of the typical Raman scattering bands. Even though the signal-to-noise ratio of the spectrum at concentration 5.0×10^{-8} M is extremely poor, the typical vibrational modes of 4-Mpy could still be observed in part at this concentration. By optimizing the acquisition time and the number of accumulations, we can obtain relative higher quality spectra (as shown in figure A.1). So the detection limit of the Pd nanowire networks for 4-MPy is as little as 5×10^{-8} M.

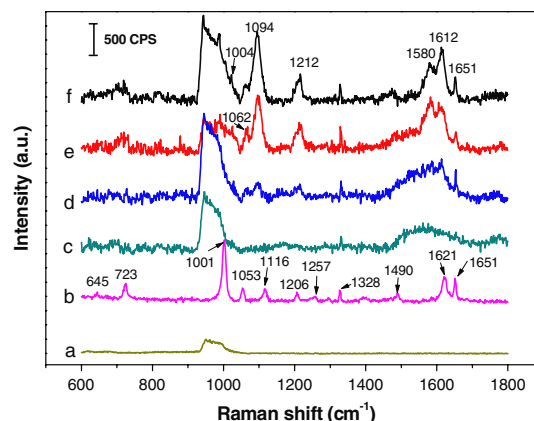


Figure 8. SERS spectra of bare Si substrate (a) and 4-mercaptopyridine (4-MPy) with different concentrations: (b) 0.5 M 4-MPy solution; (c) 5.0×10^{-8} M 4-MPy adsorbed on Pd nanowire network/Si substrate; (d) 5.0×10^{-7} M 4-MPy adsorbed on Pd nanowire network/Si substrate; (e) 5.0×10^{-6} M 4-MPy adsorbed on Pd nanowire network/Si substrate; (f) 5.0×10^{-3} M 4-MPy adsorbed on Pd nanowire network/Si substrate.

(This figure is in colour only in the electronic version)

The bands from 915 cm^{-1} to 1000 cm^{-1} in figures 8(c)–(f) can be assigned to vibrations of the Si wafer under Pd samples (refer to figure 8(a)). In general, SERS mainly comes about as a combination of two effects, electromagnetic (EM) enhancement and chemical enhancement. For noble metals, the former is the primary factor [42]. The EM enhancement associated with large local fields is caused by surface plasmon resonance. As described in the structure and morphological analysis, all the crystal faces in the fcc crystal structure can be exposed in as-grown Pd nanowire network samples. In particular, the {220} and {311} with high Miller index or with high free energies [47] easily locate at edges, corners, protuberances, etc. They can act as ‘hot sites’ for surface plasma resonance, as well as chemical absorption.

The Raman frequencies in the SERS spectra, as well as in the normal Raman spectra of solid 4-MPy [52] and 0.5 M aqueous solution (shown in figure 7(b)), are listed in table 1. One can discover that some natural vibrational modes of 4-MPy solid were obviously enhanced and others were hardly visible after being adsorbed on Pd nanowire network/silica substrate. Also the enhanced Raman peaks are not consistent absolutely with those of the molecules in the aqueous solution. The intense peaks at 1094, 1212, 1580 and 1612 cm^{-1} in figures 8(c)–(f) can be assigned to the $\nu(\text{ring breathing})/\nu(\text{C-S})$, $\beta(\text{C-H})$, $\nu(\text{C-C})$ and $\nu(\text{C-C})$, which all belong to the in-plane vibrational modes of the 4-MPy molecule. In addition, there are two weak shoulder peaks near 1004 and 1062 cm^{-1} . Except for $\beta(\text{C-H})$, all of the peaks shifted in the low frequency direction relative to the normal Raman spectra of 4-MPy solution. According to the previous report, 4-MPy is adsorbed on the metal surface by virtue of the sulfur atom in the thiol group so that the plane of the pyridine ring is perpendicular to the substrate surface [48–50]. These shifts are possibly associated with a chemical interaction between metal atom and probe molecule.

Table 1. Raman frequencies (cm^{-1}) and assignments of the main bands of 4-MPy in figure 7.

Raman frequency	SERS of the 4-MPy molecules adsorbed on Pd nanowire network/Si substrate					Raman frequency	Assignments [48]
	0.5 M solution	5.0×10^{-3} M	5.0×10^{-6} M	5.0×10^{-7} M	5.0×10^{-8} M		
645	—	—	—	—	—	647	$\beta(\text{C}-\text{C}-\text{C})$
723	—	—	—	—	—	721	$\beta(\text{C}-\text{C})/\nu(\text{C}-\text{S})$
1001	1004	1004	—	—	—	990	$\nu(\text{C}=\text{C})$ ring
1053	1062	1062	1062	—	—	1045	$\beta(\text{C}-\text{H})$
1116	1094	1094	1094	—	—	1106	$\nu(\text{ring breathing})/\nu(\text{C}-\text{S})$
1206	1212	1212	1212	—	—	1200	$\beta(\text{C}-\text{H})$
1328	1328	1328	1328	—	1328	—	—
1490	1475	1480	—	—	—	1478	$\nu(\text{C}=\text{C}/\text{C}=\text{N})$
—	1580	1580	1580	—	—	1604	$\nu(\text{C}-\text{C})$
1621	1612	1612	1612	—	—	1617	$\nu(\text{C}-\text{C})$
1651	1651	1651	1651	—	1651	—	$\nu(\text{O}-\text{H})$

In the spectral differences between the normal Raman spectra of 4-MPy solid and its solution, the bands at 990, 1045 and 1200 cm^{-1} shifted to higher wavenumber positions at 1001, 1053 and 1206 cm^{-1} in the solution spectrum, respectively. This is associated with the loss of intermolecular hydrogen bonding between the molecules in solution [51]. We suppose that the blueshift of the $\beta(\text{C}-\text{H})$ mentioned above is possibly derived from this change.

It should be mentioned that all the data were repeated at least three times at an arbitrary spot and all of them can show obvious Raman signals of 4-MPy. The as-prepared Pd nanowire network/silica system is a stable SERS-active substrate, which has the advantages of easy preparation, high stability, good reproducibility and high sensitivity. Thus, it is reasonable to expect that the as-obtained Pd nanowire networks have a bright future in their applications.

4. Conclusions

In this paper, we first report Pd nanowire networks can be obtained with a free surface modified reagent by a simple solution route. A nanoparticle coalescence mechanism was proposed to illuminate Pd nanowire network growth progress. By fine adjustment of the DMSO concentration in the mixed solvent, a series of nanowire networks with different diameters from 8 to 30 nm can be achieved. The solvent DMSO plays a decisive role in the synthesis mechanism. It not only acts as the solvent, but also as a soft template to control the product's morphology. The as-prepared Pd nanowire networks are stable SERS-active materials. Its detection limit to 4-MPy touches to 10^{-8} order. This kind of SERS substrate composed of as-grown nanostructures has the advantages of ease of preparation, high stability, good reproducibility and high sensitivity. Thus, it is reasonable to expect that the as-obtained Pd nanowire networks have a bright future in their applications.

Acknowledgments

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Appendix

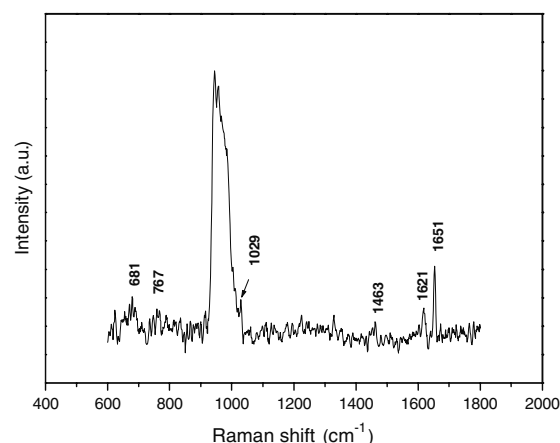


Figure A.1. SERS spectra of 4-mercaptopyridine at 5.0×10^{-8} M. The acquisition time is 300 s, twice.

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