

One-Pot, High-Yield Synthesis of 5-Fold Twinned Pd Nanowires and Nanorods

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One-dimensional metal nanostructures such as nanowires and nanorods have been attracting much research attention owing to their various potential applications deriving from their unique optical, electronic, magnetic, catalytic, and sensing properties.^{1,2} Metal nanowires and nanorods have been extensively prepared by different techniques,¹ such as chemical vapor deposition,³ lithography,⁴ template-directed fabrication,^{5,6} and micelle-/surfactant-assisted electrochemical or chemical synthesis.^{2,7,8} With these techniques, significant progress has been made recently in the synthesis of Ag and Au nanowires and nanorods.^{8,9} In contrast to Ag and Au, the fabrication of well-defined one-dimensional Pd nanostructures remains a great challenge.⁹ Currently, prepared Pd nanowires are either polycrystalline or networked.^{6,10} While freestanding single-crystalline or twinned Pd nanowires have not been synthesized, limited success has been achieved in the synthesis of Pd nanorods.¹¹

We report here a facile high-yield synthetic strategy to uniform Pd nanowires and nanorods with a high aspect ratio. As-prepared one-dimensional Pd nanostructures have a 5-fold twinned structure. To the best of our knowledge, it is the first time that twinned Pd nanowires and nanorods with a high aspect ratio have been prepared. The kinetics studies revealed that the Pd nanowires transform into nanorods with a smaller aspect ratio and finally to multiply twinned particles upon increasing the reaction time.

The Pd nanowires were hydrothermally prepared by reduction of palladium(II) chloride at 200 °C for 2 h in a Teflon-lined stainless-steel autoclave with a capacity of 20 mL using poly(vinylpyrrolidone) (PVP) as the reductant in the presence of sodium iodide (see Supporting Information for details). This synthetic method is highlighted by its simplicity and high-yield production of extra-long Pd nanowires with a uniform diameter.

The representative TEM images of the as-made Pd nanowires are shown in Figure 1. As the dominant form, the long nanowires have a uniform diameter of 9.0 ± 1.0 nm along their entire length, which is in the range of micrometers and can be up to $3 \mu\text{m}$. It is also indicated that the produced Pd nanowires are highly flexible (Figure 1d). The existence of twinned boundaries is revealed in every examined Pd nanowire with no exception. Throughout each whole twin domain, two types of lattice fringes with interplanar spacings of 0.228 and 0.194 nm, ascribed to $\{111\}$ and $\{200\}$ planes of fcc Pd, are clearly observed in a typical high resolution TEM (HRTEM) image (Figure 1e), suggesting the $\langle 110 \rangle$ growth direction of Pd nanowires. Selected-area electron diffraction patterns were recorded on individual nanowires to identify the twinned structure within the nanowires. As illustrated in Figure 1f, the electron diffraction patterns display the superposition of two sets of patterns belonging to the $\langle 110 \rangle$ and $\langle 111 \rangle$ zone diffraction of an fcc structure. Together with HRTEM, the diffraction patterns suggest that the as-prepared Pd nanowires are likely of 5-fold twinned structure bound by five $\{100\}$ side surfaces along the $\langle 110 \rangle$ direction. Such a feature is common among one-dimensional metal nanostructures.

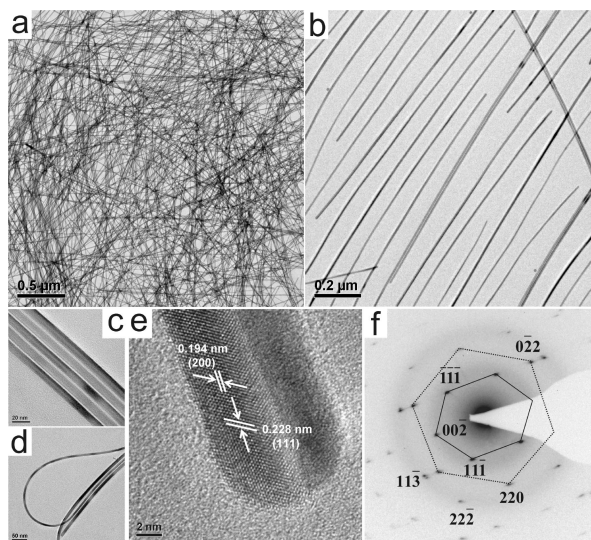


Figure 1. Long Pd nanowires made in 2-h reactions. (a–d) Representative TEM images of as-prepared Pd nanowires. (e and f) HRTEM image and selected-area-electron diffraction patterns of individual nanowires.

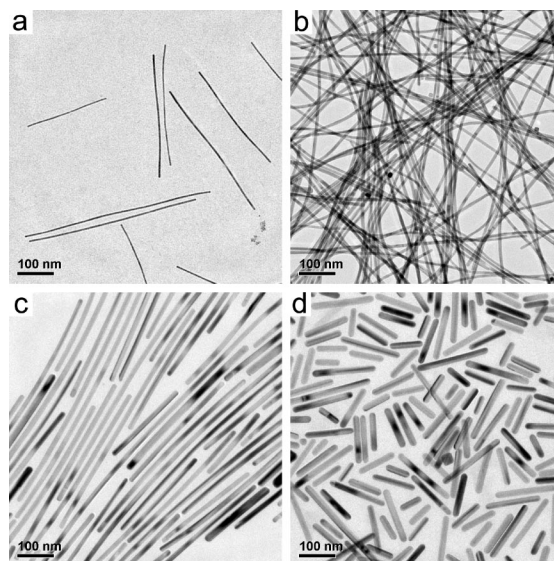


Figure 2. Representative TEM images of the one-dimensional Pd nanostructures produced in (a) 1.5-, (b) 2.0-, (c) 4.0-, (d) 8-h reactions.

As illustrated in Figure 2, a significant morphological evolution of the Pd nanostructures with the reaction time was observed in our syntheses. The nanowires produced in 1.5-h reactions had a diameter of 5 nm. Their length was in the range of submicrometers, significantly shorter than those obtained in 2-h reactions. Increasing the reaction time from 2 to 4 h led to shortening the length of the nanowires from

2.0 to 0.6 μm on average. The diameter of the nanowires was enlarged from 9 to 15 nm. As a result, the average aspect ratio of the nanowires decreased from approximately 220 to 40. Such a diameter and length change process continued when the reaction time was further prolonged. At the end of 8 h, the nanowires essentially transformed into nanorods with a uniform diameter of 19 nm. The aspect ratio of the rods was reduced to ~ 6 . When the reaction time was further increased to 24 h, most nanorods became multiply twinned nanoparticles with a size of ~ 57 nm (Figure S1).

Although the Pd nanostructures experienced a morphological change from nanowires to nanorods, and then to nanoparticles as the reaction time increased, it should be noted that the multiply twinned structure was maintained throughout the transformation process. The preferential growth of twinned nanostructures in our syntheses is mainly because of their capability to offer fast growth kinetics. Many previous reports have evidenced the preferential binding halide to the $\{100\}$ facets of various metals, which inhibits the growth of $\{100\}$.^{7b,12} With this prohibition, two preferential structures are single-crystalline nanocubes/nanobars fully enclosed by $\{100\}$ facets and nanorods with 5-fold twinned structure. The growth rate of twinned nanorods would be significantly faster than that of nanocubes due to the existence of non- $\{100\}$ facets (Figure 1e) at the tips of twinned nanorods. Such an expectation was confirmed by the observation that the minor byproduct (i.e., nanocubes) revealed in the 2-h reactions was smaller in size (12 nm) and also in a relatively small quantity. After the depletion of metal precursors, the growth of nanorods stops and their ripening occurs. Considering that $\{100\}$ facets are not thermodynamically favorable, the twinned nanorods should be ripened in such a way that the portion of $\{100\}$ facets is lessened, which satisfactorily explains the morphological transformation events from long nanowires to short nanorods and finally to multiply twinned particles. The formation mechanism of nanorods reported here might provide an alternative to fabricate nanorods which are mostly prepared through direct growth from nanoparticulate seeds.²

The coordinated use of both PVP and I^- is critical to the formation of the Pd one-dimensional nanostructures reported here. PVP plays dual roles as both reductant and surface protecting agent. As suggested by Xia and co-workers, the reducibility of PVP is attributed to the presence of the hydroxyl groups at the ends of PVP molecules.¹² Our experiments have found that control over the concentration of PVP is important to obtain Pd nanowires. Halving the PVP concentration led to the formation of Pd nanoparticles with mixed morphologies including cubes, bars, triangles, tetrahedra, and also irregular particles (Figure S2). Doubling the PVP concentration yielded spheres and short nanorods with an aspect ratio less than 2. In addition to the use of an appropriate PVP concentration, the presence of I^- is crucial. In the absence of I^- , the reactions produced networked Pd nanowires together with a small amount of nanoparticles with the size between 30 and 50 nm (Figure S3). The networked Pd nanowires consisted of interconnected Pd nanoparticles and were significantly different from the uniform nanowires prepared in the reactions where I^- was present.

Due to the structural anisotropy, as-prepared one-dimensional Pd nanostructures exhibit chemically distinguishable reactivities on their tips and sides. The galvanic replacement reaction between Pd nanowires produced from 4-h reactions and HAuCl_4 was selected to demonstrate their reactivity difference (Figure 3). If not separated from the reaction media, the sides of the nanowires were tightly bound with PVP and Au nanoparticles formed on the tips of the nanowires. However, if the nanowires were separated and purified, the sides (i.e., $\{100\}$ facets) of the nanowires became accessible so that Au nanoparticles grew on the sides.

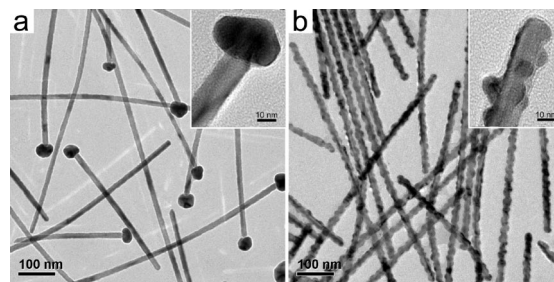


Figure 3. TEM images of Au–Pd nanostructures obtained by reacting Pd nanowires, before (a) and after (b) being separated from reaction media, with HAuCl_4 . The Pd nanowires are produced from 4-h reactions.

In conclusion, Pd nanowires and nanorods with uniform diameters were successfully prepared in the presence of PVP and I^- . The structural anisotropy endows the one-dimensional Pd nanostructures with different chemical reactivities on their tips and sides. These one-dimensional nanostructures potentially hold promise as building blocks for functional materials and devices.

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Supporting Information Available: Experimental details and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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