Hierarchical Top-Porous/Bottom-Tubular TiO$_2$ Nanostructures
Decorated with Pd Nanoparticles for Efficient Photoelectrocatalytic Decomposition of Synergistic Pollutants

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Figure S1. XRD pattern of TiO$_2$ NTs annealed at 450 °C for 1h.

Figure S1 shows XRD pattern of TiO$_2$ NTs annealed at 450 °C for 1h. The peaks located at 25.4°, 37.1°, 38.0°, 48.1°, 54.1°, 55.0°, and 68.9° can be indexed to (101), (103), (004), (200), (105), (211), and (116) crystal planes of anatase TiO$_2$. The strong preferential orientation of (101) is observed. The Ti crystal peaks are denoted as star symbol. The Pd/TiO$_2$ NTs show the same XRD pattern as TiO$_2$ NTs (not shown here) and no typical diffraction peaks of Pd were observed.
which could be ascribed to the overlap of the characteristic peak of Pd (111) at 40.1° with the strong (101) peak of Ti at 40.2°.

**Figure S2.** (a) EDX spectrum of Pd/TiO$_2$ NTs; EDX elemental mapping of (b) Ti, (c) Pd, (d) O, (e) N, and (f) F on the top surface.

EDX and elemental mapping analysis were carried out to examine the chemical compositions and the spatial distributions of elements of Pd/TiO$_2$ NTs surface. As illustrated in Figure S2a, besides Ti, O, and Pd, N and F were also detected at significant levels. The content of Pd is around 1.05 atom % on the surface of Pd/TiO$_2$ NTs. The Pd and Ti show similar elemental mappings (Figure S2b and c), which implies a uniform distribution of Pd nanoparticles on the TiO$_2$ NTs surface. The existence of N and F are ascribed to titanium's interaction with NH$_4$F electrolyte during the anodization process although the status of N and F, whether doped into TiO$_2$ lattice or simply present as adsorbed species, could not be determined by the EDX analysis.