Anodic aluminum oxide template synthesis
The anodic aluminum oxide (AAO) template with a large number of nanochannels was prepared on an aluminum substrate by its anodic oxidation. Before the anodic oxidation, aluminum substrate (purity > 99.99%) was electropolished using 10 wt% HClO₄, 83% ethanol and 7% water mixed solvents at 20 V, 5 °C for 10 min. The anodic oxidation was performed in 1.8 wt% oxalic acid at 80 V, 10 °C, and the resulting pores were widened by a chemical etching. The etching was carried out by immersing the anodically oxidized substrate in 5 wt% phosphoric acid at 30 °C for 30 min. The depth of the nanochannels was controlled within a range from 250 nm to 750 nm by changing the anodic oxidation time from 50 s to 90 s. The diameter of the resulting nanochannels is 70 nm, and the number of the nanorods per square centimeter is about $8 \times 10^9$.

Electrochemical cell employed for cyclic voltammetry measurements
A schematic of the electrochemical cell employed for the cyclic voltammetry measurements is shown in Fig. S1. The cell is constituted of Pyrex glass having a dual structure. The outer vessel is a water jacket directly connected to a temperature-controlled bath to maintain the temperature of the electrolyte solution in the inner vessel at 25 °C. To fabricate the working electrode from the carbon film, only an array side of each carbon film was in contact with the electrolyte solution through a circular hole of a silicone gasket (inner diameter: 6 mm), and a current collector (a Pt plate) was attached to the backside of the carbon film. Thus the apparent surface area of the working electrode is always identical (0.28 mm²), regardless of the samples (the carbon films and a Pt plate).

![Fig. S1 Electrochemical cell for cyclic voltammetry measurements](image-url)
**Cyclic voltammetric behavior of Ac-Ni**

In addition to the redox peaks of ferri/ferro hexacyanide ions, a pair of undefined peaks was observed at the voltage around 0.7 V in Fig. 7e. These peaks can be ascribed to the redox reactions of nickel-containing compounds eluted from Ni metals, since these peaks were observed in another experiment using a pure Ni plate as a working electrode. Pinholes, such as broken nanorods would be the reason why such peaks were observed, but such broken ones were rarely found by the SEM observation. In addition, $\Delta E_p$ was far larger for CVD-Ni than the case with the Ni plate (for example, $\Delta E_p$ was 162 mV for CVD-Ni, and was 80 mV for the Ni plate at the sweeping rate of 100 mVs$^{-1}$), suggesting that the surface of CVD-PVC is less active than the Ni plate. These facts indicate that the electrochemical reactions mainly occurred on the surface of the carbon covering the Ni core.