Supporting Information

Preparation and characterization of conducting mixed-valence 9,9'-dimethyl-3,3'-bicarbazyl rectangular nanowires

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LDI-TOFMS measurement. The nanowire sample was soaked in extrapure water, and dispersed into the water by sonication for 1 minute. The test sample was obtained by dropping the dispersed solution on the LDI sample plate, then drying. Figure S1 shows the LDI-TOFMS spectrum (linear mode) of the test sample. The spectrum indicated a signal at m/z = 359.894. This value coincided with the molecular weight (360.458) of **1**.

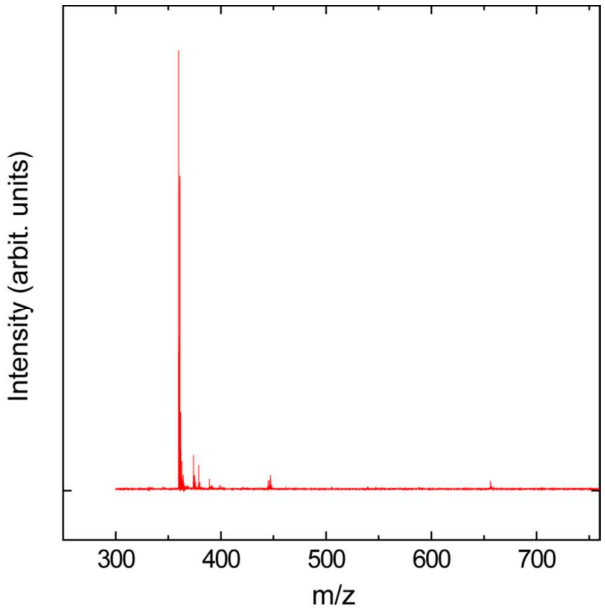

Fig. S1 LDI-TOFMS spectrum of the nanowire sample.

ESR measurement. The ESR measurement was carried out using a powder sample of the nanowire (Fig. S2). The sample was prepared by the typical conditions described in the text. ESR spectrum was recorded by a JEOL JES-TE200 spectrometer. The g factor value was determined using MnO as an external standard (g = 2.0058). Despite the use of a tiny amount of the nanowire sample, an extremely large signal with a g-value of 2.00329 was observed. This g value falls under the category of organic radicals. Additionally, a large peak-to-peak line width suggests that the radical species are delocalized in a large π-conjugation system and coupled with many nuclei. These results clearly demonstrate the presence of radical species, i.e., 9,9'-dimethyl-3,3'-bicarbazylium (**2**).

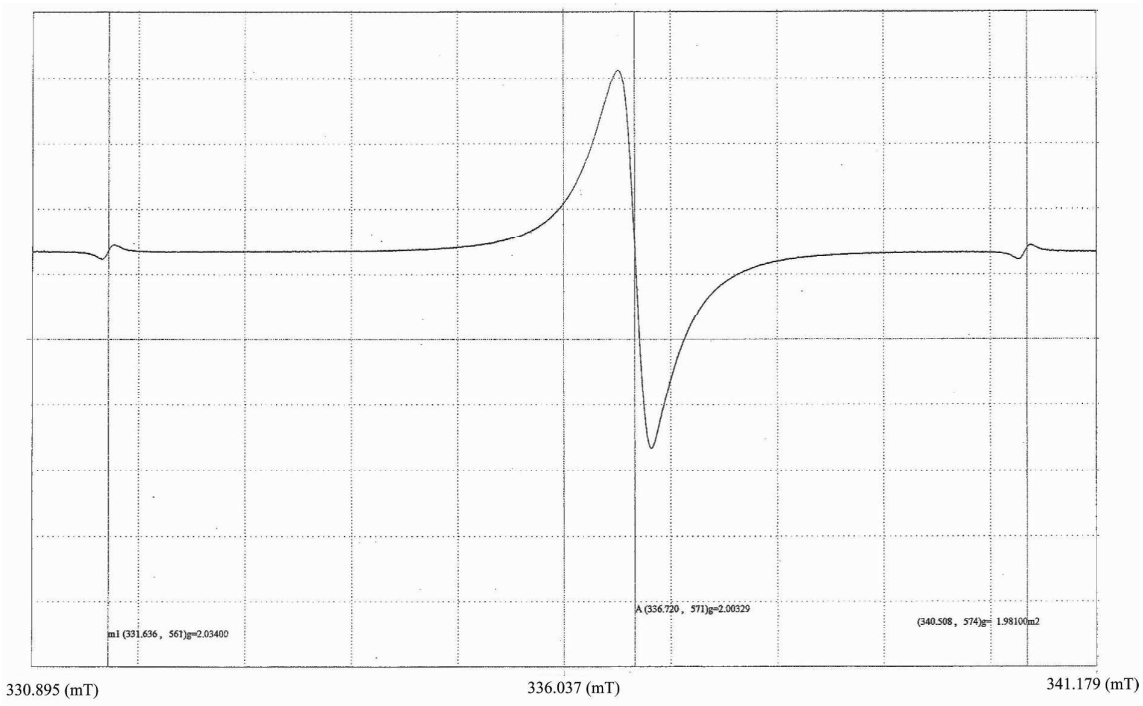

Fig. S2 ESR spectrum of the nanowire.

XPS measurement. Figure S3 shows the XPS spectrum of the Cl 2p region of the nanowire sample. The spectrum was recorded by a ULVAC-PHI PHI Quantera SXM spectrometer. The absolute binding energy scale in the XPS was determined by setting the C 1s signal to 284.6 eV. A signal corresponding to Cl of the perchlorate anion was observed at 209.1 eV.[S1]

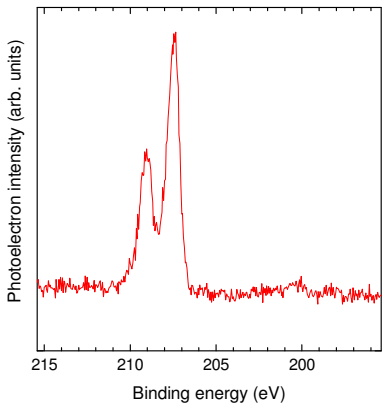

Fig. S3 Cl 2p XPS spectrum of the nanowire.

Effect of solvent. The oxidation of 9-methylcarbazole by $Fe(ClO_4)_3$ was carried out in various solvents under a nitrogen atmosphere at 0°C as described in the text, and the shapes of their deposits were examined. As solvents, methanol, acetonitrile, and ethanol were used. Figure S4 shows the SEM images of the deposits obtained using methanol (a), ethanol (b), and acetonitrile (c). When methanol and acetonitrile were used, nanowire structures were obtained. On the other hand, when ethanol was used, irregular-shaped conglomerates were obtained by the chemical oxidation.

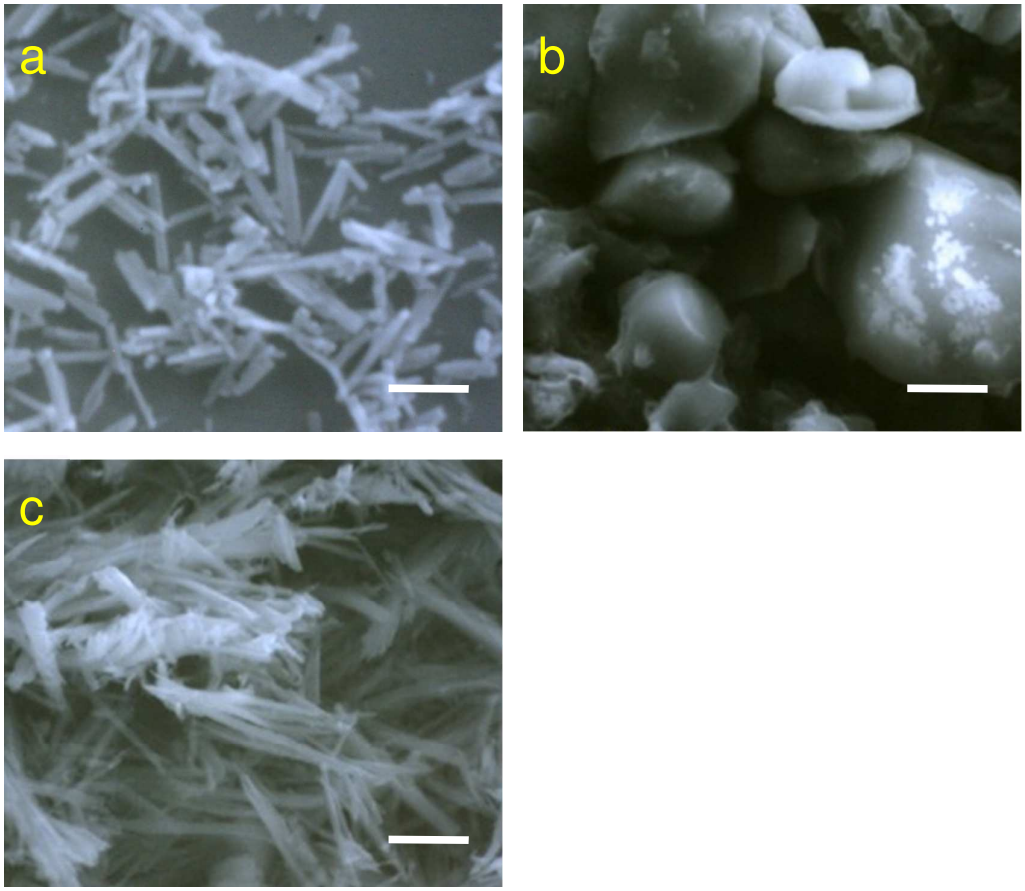

Fig. S4 SEM images of the product prepared by the addition of 0.071 M $Fe(ClO_4)_3$ solution (20 ml) to 0.050 M 9-methylcarbazole solution (20 ml) at 0 ^oC: a; methanol; b, ethanol; c, acetonitrile. Scale bars: 5 μm.

Effect of solvent mixing ratio. The oxidation of 9-methylcarbazole by $Fe(ClO_4)_3$ was carried out in methanol/acetonitrile mixtures under a nitrogen atmosphere at 0^oC as described in the text, and the shapes of their deposits were examined. Figure S5 shows the SEM images of the deposits obtained using methanol/acetonitrile mixtures with the volume ratio of 5/1 (a), 4/1 (b), 3/1 (c), 2/1 (d), 1/1 (e), 1/2 (f), and 1/3 (g). Table S1 summarizes the average diameter, average length, and aspect ratio of the nanowire prepared in each solvent mixture. The highest aspect ratio was obtained for the mixing ratio of 3/1.

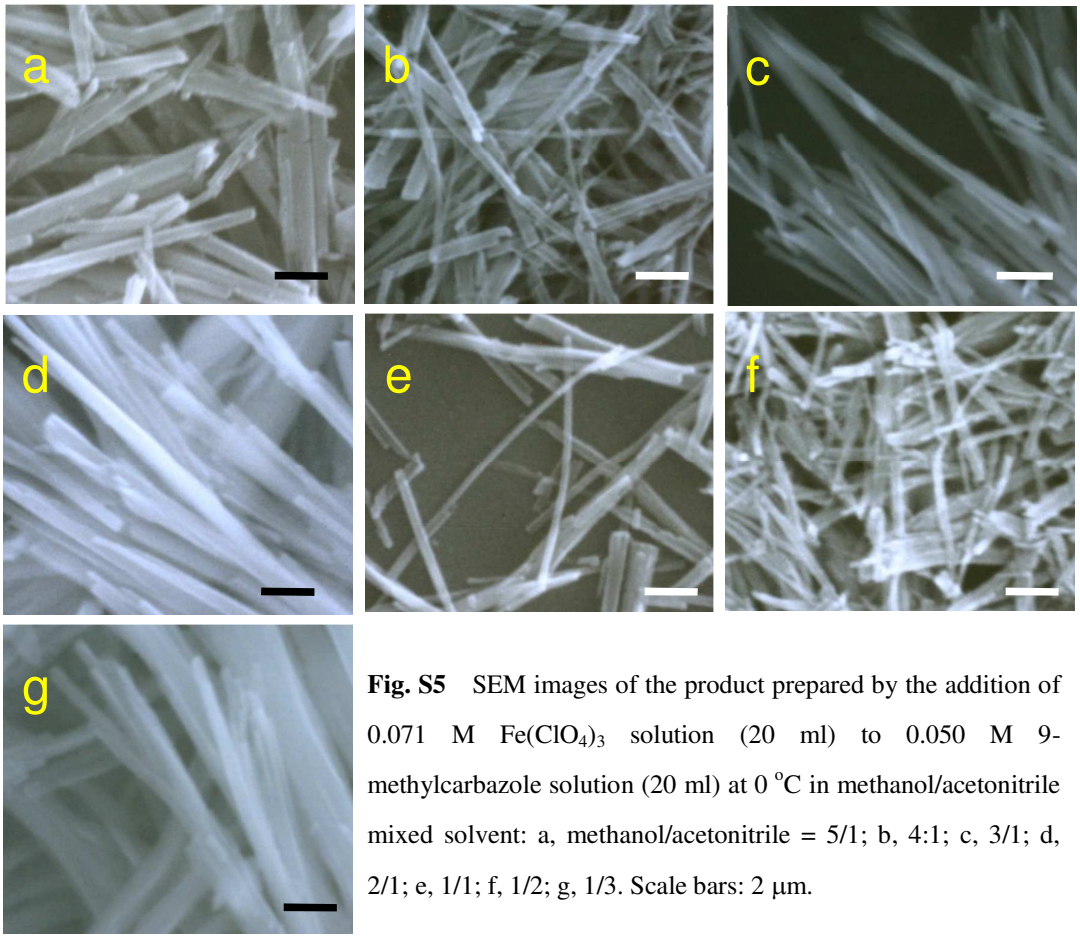

Fig. S5 SEM images of the product prepared by the addition of 0.071 M $Fe(ClO_4)_3$ solution (20 ml) to 0.050 M 9-methylcarbazole solution (20 ml) at 0 ^oC in methanol/acetonitrile mixed solvent: a, methanol/acetonitrile = 5/1; b, 4:1; c, 3/1; d, 2/1; e, 1/1; f, 1/2; g, 1/3. Scale bars: 2 μm.

Table S1 The dependence of nanowire diameter and length on the methanol/acetonitrile mixing ratio

Methanol:acetonitrile vol. ratio	Average diameter (nm)	Average length (μm)
5 : 1	567	8.93
4 : 1	546	13.2
3 : 1	397	16.8
2 : 1	566	13.5
1 : 1	523	14.6
1 : 2	471	15.0
1 : 3	465	14.4

Effect of concentration ratio. The nanowire was prepared by varying the concentration ratio of 9-methylcarbazole and $Fe(ClO_4)_3$. The synthesis was carried out by the addition of 20 ml of 0.0071 M (a), 0.036 M (b), 0.071 M (c), 0.14 M (d), and 0.29 M $Fe(ClO_4)_3$ solutions (e) to 20 ml of a 0.050 M 9-methylcarbazole solution in methanol/acetonitrile (3/1 vol ratio) mixtures at 0^oC under a nitrogen atmosphere, and the shapes of their deposits were examined. Figure S6 shows the SEM images of the

obtained nanowires. Table S2 summarizes the average diameter, average length, and aspect ratio of the nanowires prepared in each solvent mixture. The highest aspect ratio was obtained for the concentration ratio of $Fe(ClO_4)_3$/9-methylcarbazole = 1.4.

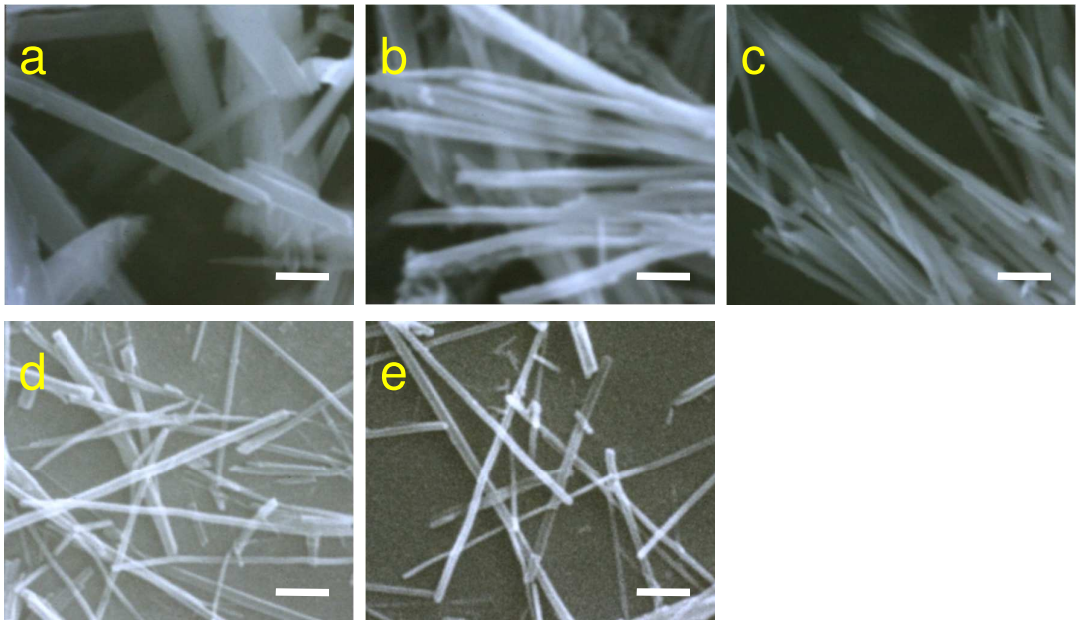

Fig. S6 SEM images of the product prepared by the addition of 20 ml of 0.0071 M (a), 0.036 M (b), 0.071 M (c), 0.14 M (d), and 0.29 M $Fe(ClO_4)_3$ solution (e) to 0.050 M 9-methylcarbazole solution (20 ml) at 0 ^{o}C in methanol/acetonitrile mixed solvent (vol. ratio = 3/1). Scale bars: 2 μm.

Table S2 The dependence of nanowire diameter and length on the concentration ratio of $Fe(ClO_4)_3$ and 9-methylcarbazole (the concentration of the latter was kept constant at 0.050 M)

Concentration ratio	Average diameter (nm)	Average length (μm)
0.14	743	17.4
0.72	632	12.9
1.4	397	16.8
2.8	425	16.7
5.8	439	14.6

Effect of reaction temperature. The nanowire was prepared by varying the reaction temperature. The synthesis was carried out by the addition of a 0.071 M $Fe(ClO_4)_3$ solution (20 ml) to a 0.050 M 9-methylcarbazole solution (20 ml) in a methanol/acetonitrile (3/1 vol ratio) mixture under a nitrogen atmosphere, and the shapes of their deposits were examined. Figure S7 shows the SEM images of the nanowires prepared at 0^{o}C (a), 22^{o}C (b), 40^{o}C (c) and 60^{o}C (e). Table S3 summarizes the average diameter,

average length, and aspect ratio of the nanowires prepared at the various temperatures. The highest aspect ratio was obtained at 0°C.

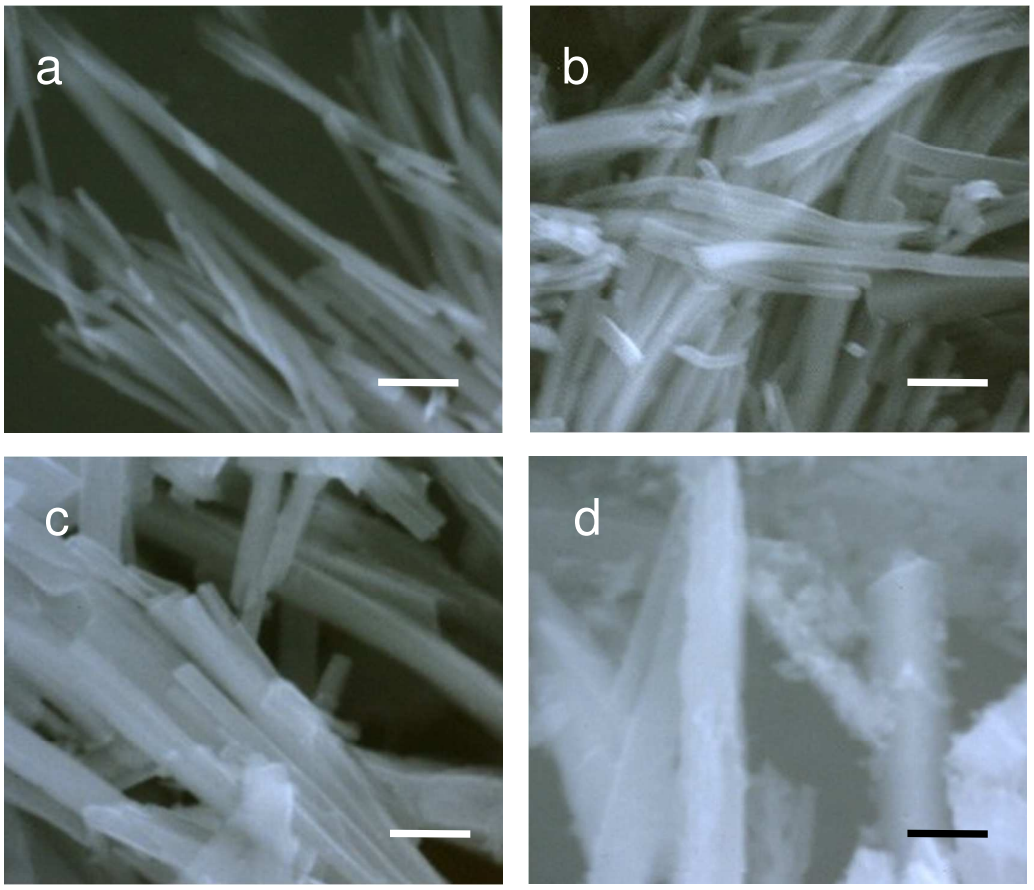

Fig. S7 SEM images of the nanowires prepared by the addition of 0.071 M $Fe(ClO_4)_3$ solution (20 ml) to 0.050 M 9-methylcarbazole solution (20 ml) at 0°C (a), 22°C (b), 40°C (c) and 60°C (e). Scale bars: 2 μm.

Table S3 The dependence of nanowire diameter and length on the reaction temperature

Reaction temperature (°C)	Average diameter (nm)	Average length (μm)
0	397	16.8
22	607	17.2
40	889	12.7
60	1520	15.6

Electro-oxidation of nanowires. The controlled-potential electro-oxidation of the nanowires was carried out. The test samples were cast on an indium-tin-oxide (ITO) coated glass plate from a nanowire dispersion which was prepared by adding the nanowire (5 mg) to 1 ml CH_3OH. After that, the samples were dried in a vacuum at 80°C for 30 min. The electrochemical properties of the test samples were examined in an

acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate. A two-compartment type electrolytic cell was used in which a main compartment and a sub-compartment were separated by a G4 glass filter. A working electrode (test sample on the ITO plate) and a counter electrode (Pt plate) were placed in the main compartment. On the other hand, a KCl agar bridge connected to a reference electrode (saturated calomel electrode, SCE) was placed in the sub-compartment.

Figure S8 shows the scanning micrographs (SEM) of the test samples treated at 1.00 V (parts a, b, and c) and 1.17 V (parts d, e, and f). The electrolysis time, *t*, was 5 min (a and d), 10 min (b and e), and 30 min

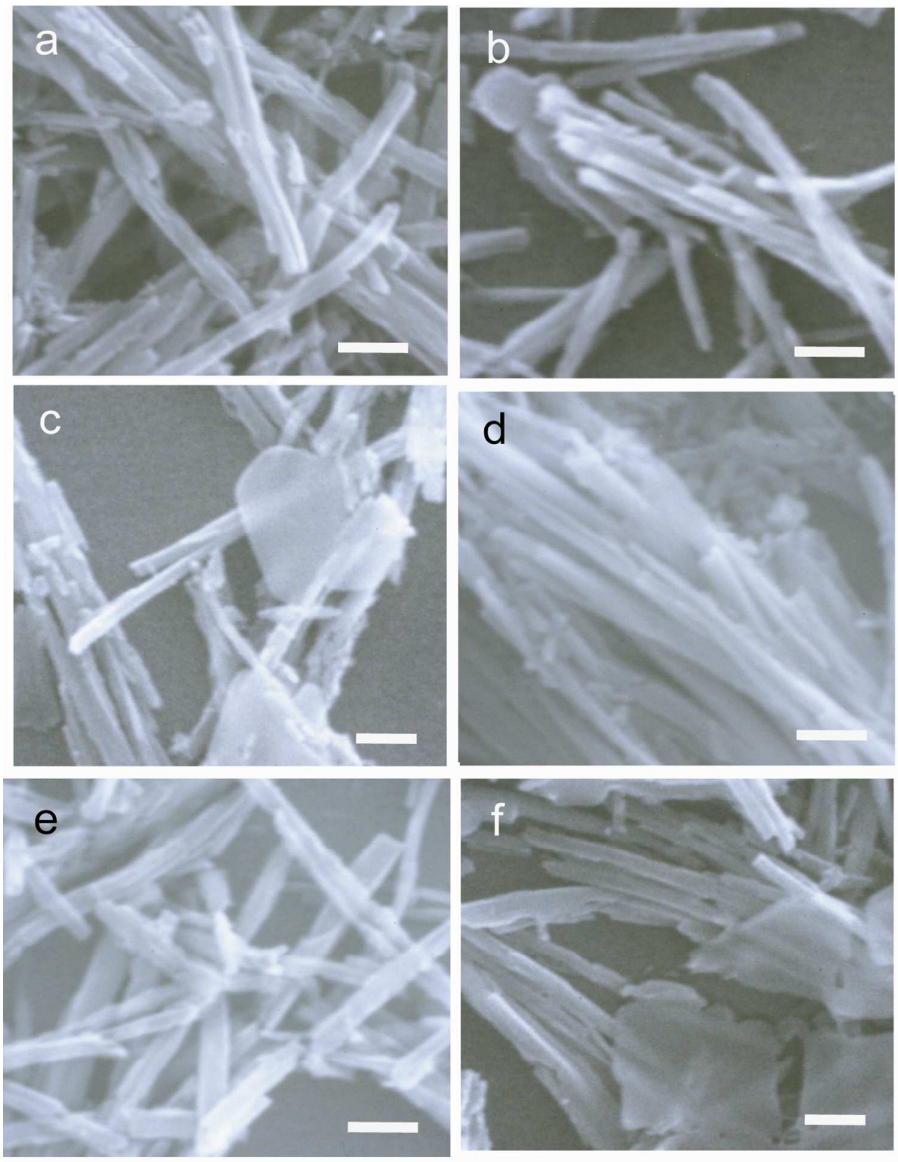

Fig. S8 SEM images of the nanowires supported on an indium-tin-oxide coated glass plate. The nanowires were subjected to controlled-potential electrolysis at 1.00 V (a, b, and c) and 1.17 V vs SCE (d, e, and f). Electrolysis time: a and d, 5 min; b and e, 10 min; a and f, 30 min. Charge amount passing through the sample: a, 1.66×10^{-4} S/cm^2; b, 2.70×10^{-4} S/cm^2; c, 1.50×10^{-3} S/cm^2; d, 1.21×10^{-3} S/cm^2; e, 3.39×10^{-3} S/cm^2; f, 1.07×10^{-2} S/cm^2. Scale bars: 2 μm.

(c and f). The amount of electricity passing through the test sample, Q, was shown in the figure caption. At an applied potential of 1.00 V, the nanowire structure was not altered by the electrolysis for t = 5 (Q = 1.66×10^{-4} C/cm^2) and 10 min (Q = 1.66×10^{-4} C/cm^2). However, prolonged electrolysis (t = 30 min, Q = 1.50×10^{-3} C/cm^2) disrupted the nanowire and a sheet structure was observed. A similar tendency was observed for the electrolysis at 1.17 V, however, the extent to which the nanowires were disrupted appears to be larger than that at 1.00 V. Such disruption and transformation of the nanowires may be caused by the conversion of **1** to **2** by the electro-oxidation and the subsequent additional doping of ClO_4^-.

Electrical measurement. Part a in Fig. S9 shows the electrical measurement configuration (two-terminal configuration)[S2] for the bottom-contacted nanowire device. The nanowire was prepared under the typical conditions, and was mechanically transferred onto prepatterned Pd microelectrodes of 50-nm thick and 3-μm gap on an oxidized silicon chip substrate. The sample was installed in a probe station and

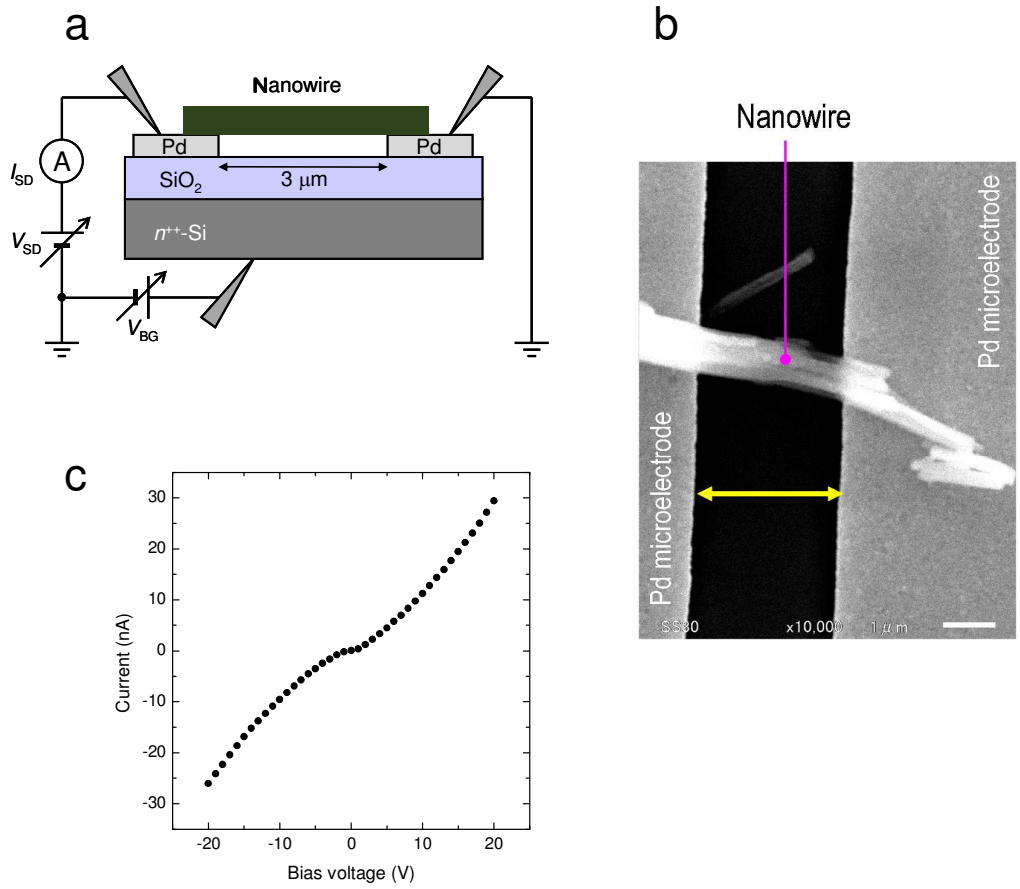

Fig. S9 a) Schematic of a bottom-contact nanowire device. b) SEM image of the device. Scale bar: 1 μm. c) current-voltage (I_{SD}-V_{SD}) characteristic of the nanowires in the dark..

the source-drain current (I_{SD}) was measured by applying a source-drain voltage (V_{SD}) and a back gate voltage (V_{BG}). Part b shows the SEM image of the bottom-contacted device. Part c shows the current-voltage (I_{SD}-V_{SD}) characteristic of the device shown in part b measured in a two-terminal configuration. An almost linear I_{SD}-V_{SD} response was obtained, with a corresponding conductivity of approximately 3.0×10^{-5} S/cm. Note that the conductivity value represents a lower bound since it involves the contributions from the contact resistances between the nanowire and the source electrode and between the nanowire and the drain electrode. Therefore, the electric conductivity value was lower than that of the polycarbazole film (10^{-4} ~ 10^{-3} S/cm)[S3,S4] prepared by electropolymerization.

References

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