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Synthesis and Self-assembly of Partially Sulfonated Poly(arylene ether sulfone)s and Their Role in Formation of Cu_2S Nanowires

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Supporting Information

MATERIALS AND METHODS

General. All chemicals were purchased from Sigma-Aldrich and used without further purification, except toluene, dimethyl sulfoxide (DMSO), and sulfolane were distilled under reduced pressure before use. Purchased sulfur purified by sublimation has 100 mesh particle size. Dialysis membrane (Spectra/Por ® 7, cutoff: 1kD) was purchased from Spectrum Laboratories, and used without further purification. Formvar/carbon coated TEM Cu grids were purchased from Electron Microscopy Sciences, and used without treatment. Cu foil was immersed in a 4 M HCl aqueous solution for 15 min and subsequently in deionized water, followed by cleaning in an ultrasonic bath using absolute ethanol for 10 min. The cleaned Cu foil was left to dry in air. <100> p-type and n-type Si wafers polished on one side were purchased from Wafer Biz Inc. Square pieces of Si wafer (ca. 1 cm × 1 cm) were washed with methanol and acetone to remove surface impurities, and then dried under a nitrogen flow prior to use. HF treated Si wafer of no oxide layer was prepared by cleaning in freshly prepared buffered oxide etch solution (6 parts of 40% ammonium fluoride and 1 part of 49% hydrogen fluoride aqueous solution) for 3 min, then thoroughly rinsed with deionized water. Piranha-treated Si wafer was prepared by cleaning in freshly prepared piranha solution (30% hydrogen peroxide and 70% concentrated sulfuric acid) for 30 min, then thoroughly rinsed with deionized water. HF-treated and piranha-treated Si wafers were prepared freshly prior to use. HMDS treated glass was prepared by immersing in hexamethyldisilazane at 70 ^{o}C for 24 h, then thoroughly rinsed with hexane. Graphene/Cu foil was provided by Prof. Hee-Tae Jung (KAIST), and detailed synthetic procedure was presented elsewhere.[1] Other substrates were used without pre-cleaning process.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Fourier Transform AC 400 spectrometer. Chemical shift of NMR was reported in part per million (ppm) using residual proton resonance of solvent as internal reference. Gel permeation chromatography (GPC) traces were obtained with Younglin 9200 equipped with UV detector (set at 270 nm) and packing column (Shodex, GF-HQ columns) using *N*, *N*-dimethyl formamide (DMF) containing 50 mmol of lithium bromide and 50 mmol of phosphoric acid as an eluent at 40 ^{o}C. The number and weight-average molecular weights of the polymers were calculated relative to linear polystyrene standards. Dynamic light scattering (DLS) measurements were performed on a 90Plus/BI-MAS particle size analyzer (Brookhaven Instruments Corp.) at wavelength of 658 nm. The scattering angle used for the measurements was 90 ^{o}. UV/vis absorption experiments were performed on a OPTIZEN POP (Mecasys Co., Ltd) spectrometer. All samples for DLS and UV/vis experiments were filtered through a 0.45 μm syringe filter before characterization. Field-emission scanning electron microscopy (FE-SEM) study was conducted using a Nova 230 FE-SEM or a Magellan 400 FE-SEM without gold sputtering. Field-emission transmission electron microscopy (FE-TEM) study was performed on a Tecnai G2 F30 FE-TEM (300 kV) or a Tecnai F20 FE-TEM (200 kV). XPS is configured with a monochromated Al K (1486.8 eV) 300 W X-ray source with an ultrahigh vacuum ($<10^{-10}$ Torr). The takeoff angle was fixed at 45^{o}, and all spectra were calibrated using the hydrocarbon C(1s) peak (284.5 eV).

4-Fluoro-4’-hydroxydiphenyl sulfone potassium salt (1). 4-Fluoro-4’-hydroxydiphenyl sulfone potassium salt was prepared from 4-fluoro-4’-hydroxydiphenyl sulfone according to the literature procedure.[2-4]

3'-Potassium sulfonated-4-fluoro-4'-hydroxydiphenyl sulfone potassium salt (2). 1 (10.0 g, 39.64 mmol) was dissolved in sulfuric acid (100 mL) in a one-necked flask equipped with a condenser. The solution was heated to 100 ^{o}C for 12 h, and then poured into saturated KCl solution (800 mL) to salt out a white precipitants identified as 3'-potassium sulfonated-4-fluoro-

4'-hydroxydiphenyl sulfone. After cooling to room temperature, filtered precipitants was dried *in vacuo* for 12 h to remove water. To remove residual KCl salt, precipitants dissolved in DMSO was precipitated into isopropanol (800 mL) after passing through paper filtration. After drying *in vacuo* for 12 h, percentage of 3'-potassium sulfonated-4-fluoro-4'-hydroxydiphenyl sulfone was calculated from ^{1}H NMR spectrum. Then, 1.00 equivalent of potassium hydroxide was added to the aqueous solution of 3'-potassium sulfonated-4-fluoro-4'-hydroxydiphenyl sulfone. The mixture was stirred at room temperature for additional hours. The homogeneous solution was azeotropically distilled with the addition of ethanol. After dried *in vacuo*, product was recryatallized from methanol to give white product (2.89 g) (yield 17.8%). ^{1}H NMR (DMSO- d_6, 400 MHz, ppm): 7.81 (d, 1H, J = 2.9 Hz), 7.78 (m, 2H), 7.33 (t, 2H, J = 8.9 Hz), 7.24 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.9 Hz), 6.09 (d, 1H, J = 9.0 Hz). ^{13}C NMR (DMSO- d_6, 100 MHz, ppm): 172.96, 163.56 (d, J = 248.5 Hz), 141.61 (d, J = 2.7 Hz), 133.74, 129.79, 129.00, 128.77 (d, J = 9.3 Hz), 122.12, 116.21 (d, J = 22.5 Hz), 113.072. Anal. Calcd for $C_{12}H_7FK_2O_6S_2$: C, 35.28; H, 1.73; F, 4.65; K, 19.14; O, 23.50; S, 15.70. Found: C, 34.46; H, 1.93; S, 14.02.

Polymerization. A dried Schlenk flask charged with monomer **1**, **2**, and 18-crown-6 (1 eq to potassium groups of monomers) was dried *in vacuo* for 6 h at 50 °C. The feed ratio of two monomers was varied to control the incorporation ratio of sulfonated groups. Sulfolane (10 wt% to monomer contents) was added to a flask *via* gas-tight syringe under dry nitrogen atmosphere. The mixture was degassed three times by “freeze-pump-thaw” cycles. Then, the reaction mixture was heated for 120 h at 160 °C. After polymerization, the reaction mixture was cooled to room temperature and precipitated into 2 M KCl solution. The precipitated polymer was filtered, and reprecipitated into 2 M KCl solution after dissolving in DMF to remove 18-crown-6. To remove residual KCl salt, polymer solution of DMF after paper-filtration was precipitated into diethyl ether. Then, the solid was filtered off and dried *in vacuo* to give white powder product of **P15-K**, **P25-K**, and **P36-K**.

Growth of Cu_2S nanowires on various substrates. Polymer aqueous solutions were prepared by dissolving synthesized **P*n*-K** (SO_3K form) in DMF (10 wt%), which were dialyzed in deionized water for 1 day, and the final concentration was adjusted to 2 wt% by adding more water. 0.2 M $CuCl_2$ solution or 0.5 M H_2SO_4 solution was used instead of deionized water to change counter cation of polymer from K^+ into Cu^{2+} (**P*n*-Cu**) or H^+ (**P*n*-H**), respectively. When copper source, *e.g.* TEM Cu grid, Cu foil, or copper cation of **P*n*-Cu**, was given, Cu_2S nanowires were grown on solid substrates (Si wafers or carbonious substrates) dipped in a polymer aqueous solution containing small amounts of elemental sulfur at room temperature. When polymer aqueous solutions were prepared by dialysis, external addition of elemental sulfur was not required, because a little amount of sulfide contaminants in dialysis-pack was captured by polymeric micelles in the process of dialysis. Except for dialysis, direct dissolution of **P*n*-K_{ND}** in deionized water (5 mg/ 0.4 mL) by heating succeeded in growing Cu_2S nanowires only when aqueous solution of elemental sulfur was added (0.1 mL). Sulfur aqueous solution was prepared by heat and sonication of sublimed sulfur agent in deionized water for 2 hr.

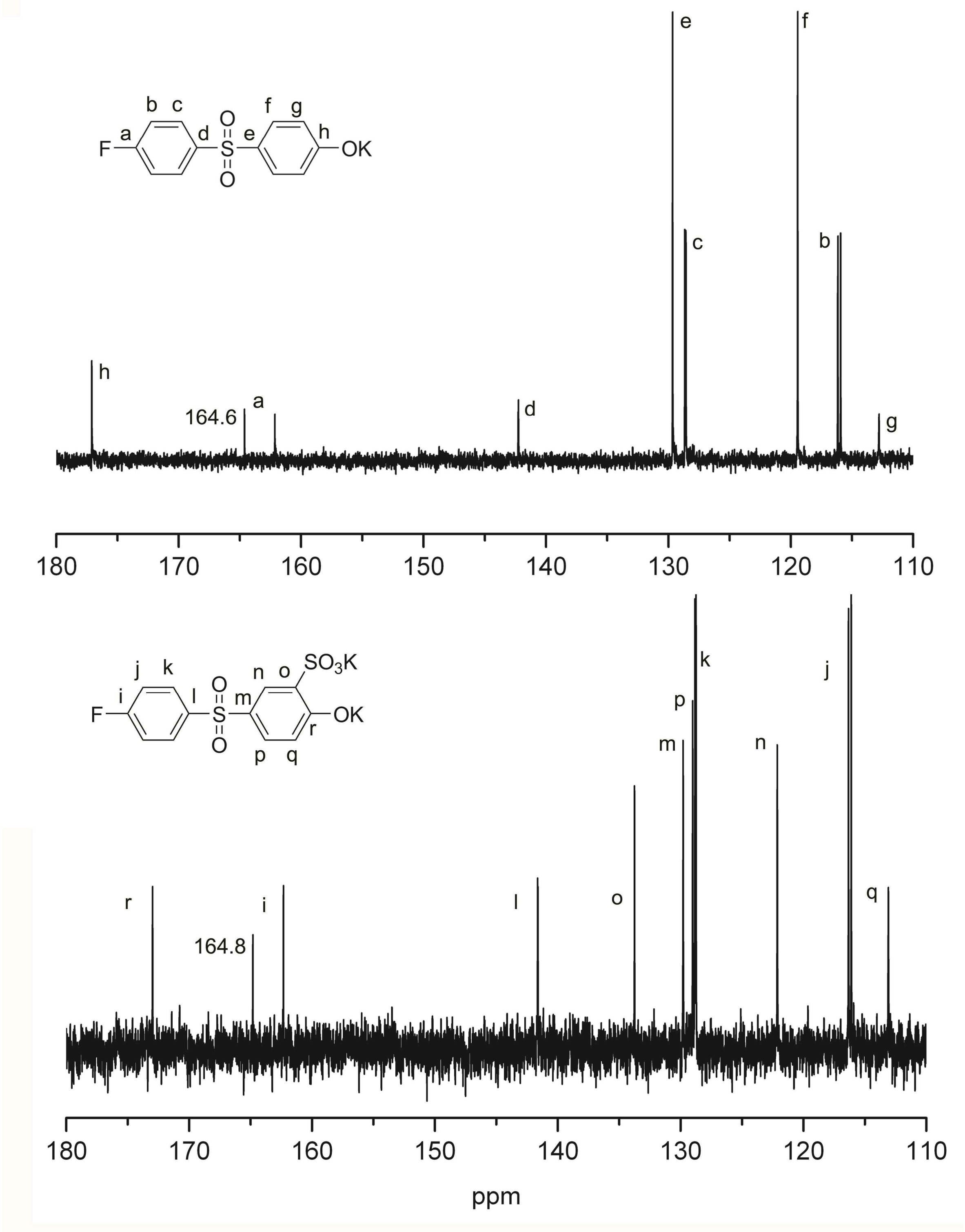


Fig. S1 ^{13}C NMR spectra of hydrophobic monomer **1**, and hydrophilic monomer **2** (100 MHz, DMSO-d_6, 20 °C).

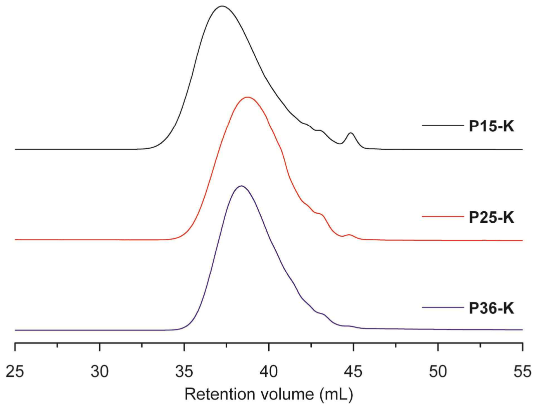
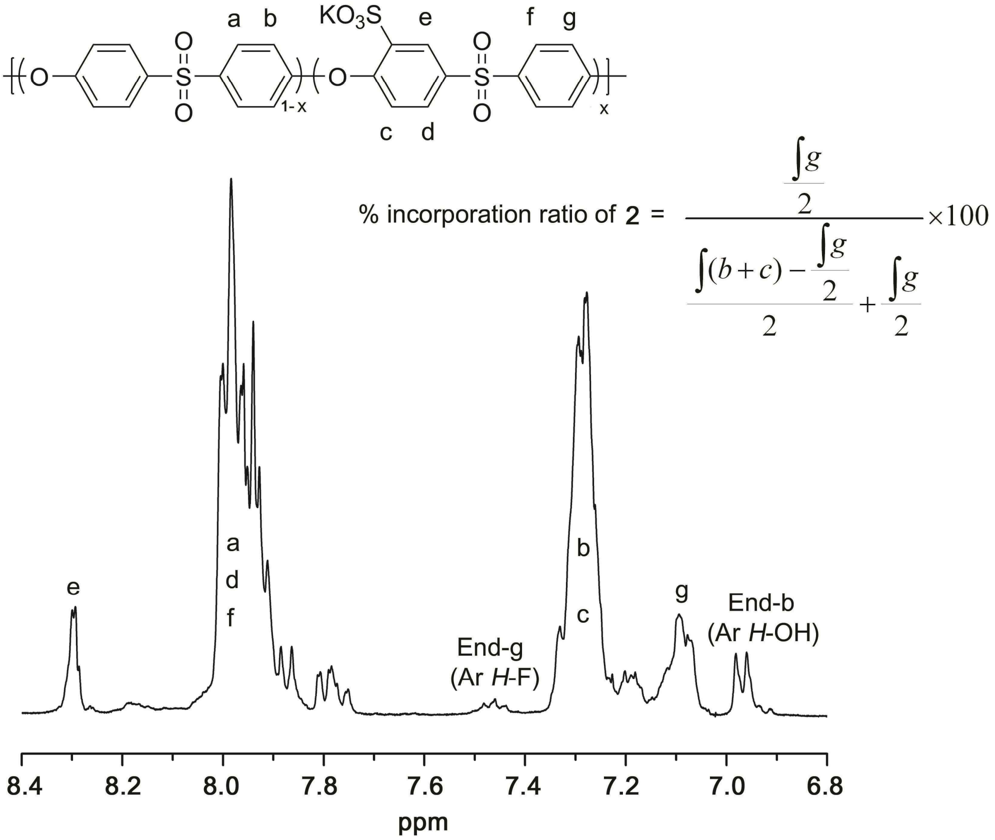


Fig. S2 SEC traces of PSPAESs obtained with UV detector with DMF containing LiBr and phosphoric acid as an eluent.



$$\text{\% incorporation ratio of } \mathbf{2} = \frac{\frac{\int g}{2}}{\frac{\int(b+c)-\frac{\int g}{2}}{2}+\frac{\int g}{2}}\times 100$$

Fig. S3 ^{1}H NMR spectrum of **P25-K** (DMSO-d_6, 400 MHz, 20 °C), and calculation of the % incorporation ratio of **2** based on ^{1}H NMR spectrum.

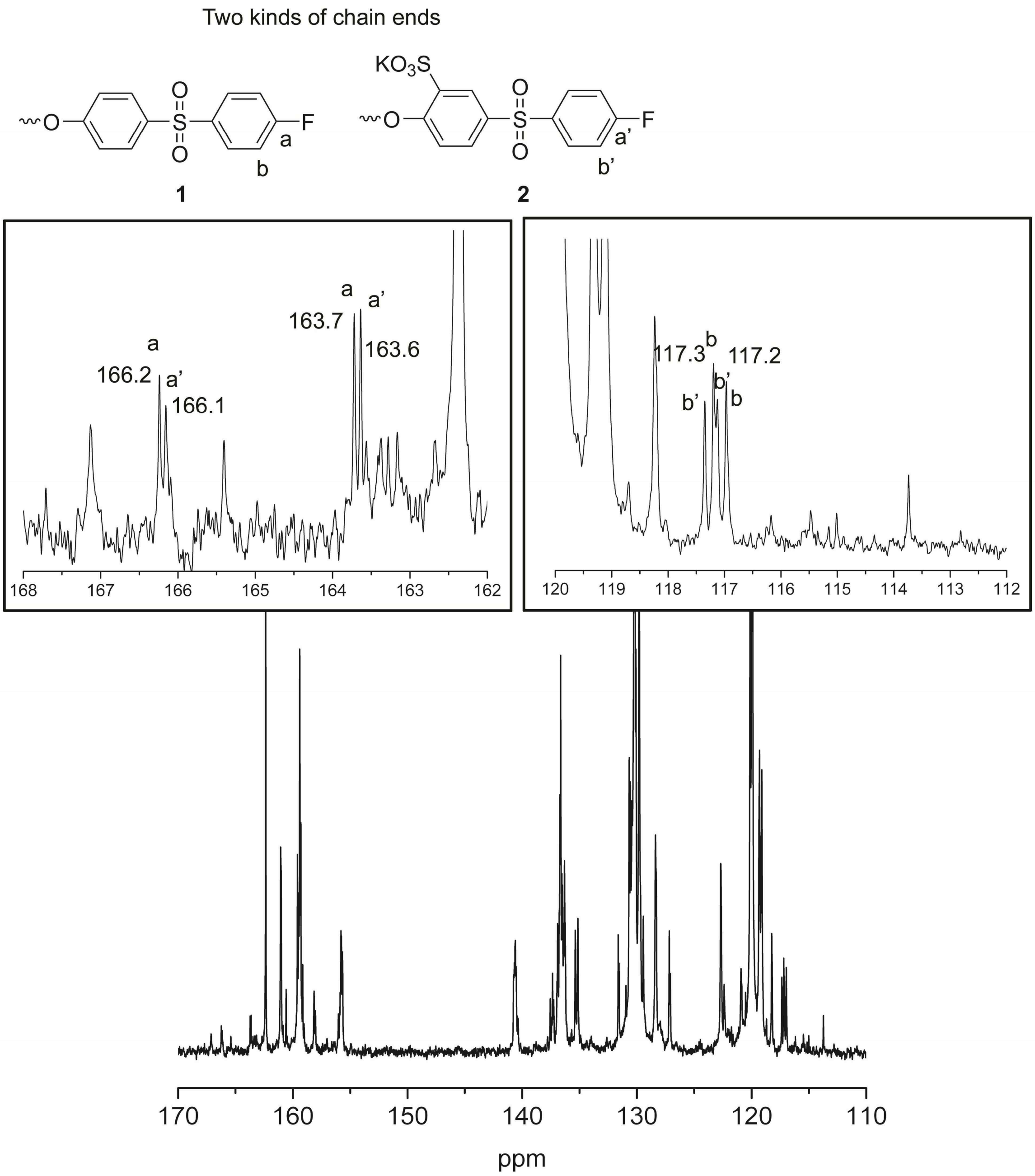


Fig. S4 ^{13}C NMR spectrum of **P25-K** (DMSO-d_6, 100 MHz, 20 °C).

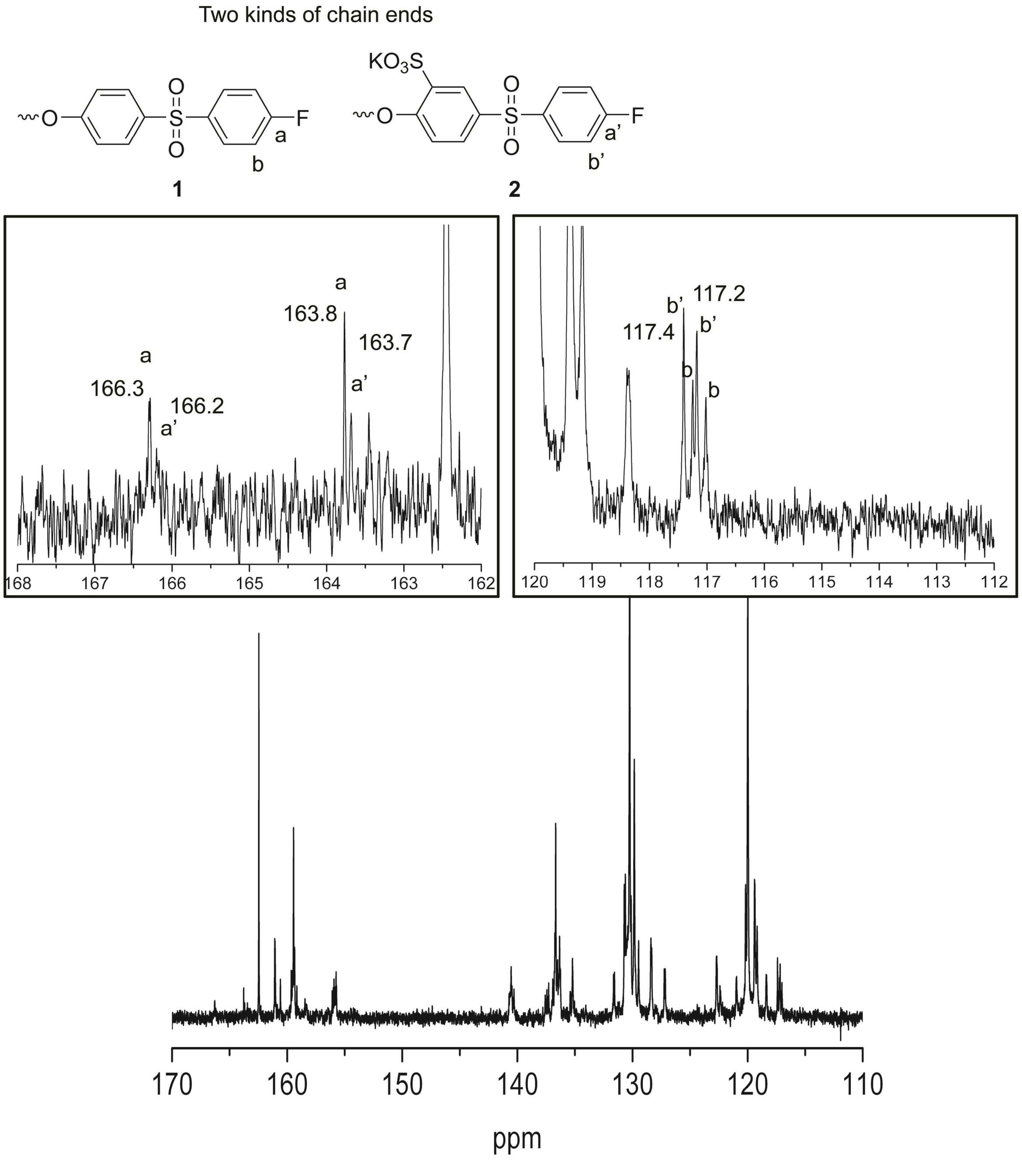


Fig. S5 ^{13}C NMR spectrum of a control experiment where homopolymerization of the monomer **2** was conducted in the presence of a homopolymer of the monomer **1**, synthesized *via* chain-growth condensation polymerization, which has only fluorine end group (DMSO-d_6, 100 MHz, 20 °C). [Experimental details: As a pre-polymeirzation step of the monomer **1**, a dried Schlenk flask was charged with initiator (4-fluoro-3-trifluoromethylbenzamidobenzene), **1** (10 eq to the initiator), 18-crown-6 (1 eq to the monomer), and dried sulfolane (10 wt% to monomer contents). The mixture was degassed three times by “freeze-pump-thaw” cycles. Then, the reaction mixture was heated to 120 °C for 24 hr. After the polymerization was complete, the mixture was poured into an excess of methanol containing acetic acid. The solid was filtered off and dried *in vacuo* to give homopolymer of monomer **1**. As a next-polymerization step of monomer **2**, a dried Schlenk flask charged with homopolymer of **1**, **2**, 18-crown-6 (1 eq to potassium groups of monomers), and dried sulfolane (10 wt% to monomer contents). The mixture was degassed three times by “freeze-pump-thaw” cycles. Then, the reaction mixture was heated for 120 h at 160 °C. After polymerization, the reaction mixture was cooled to room temperature and precipitated into 2 M KCl solution. The precipitated polymer was filtered, and reprecipitated into 2 M KCl solution after dissolving in DMF to remove 18-crown-6. To remove residual KCl salt, polymer solution of DMF after paper-filtration was precipitated into diethyl ether. Then, the solid was filtered off and dried *in vacuo* to give white powder product, which was used in a control experiment.

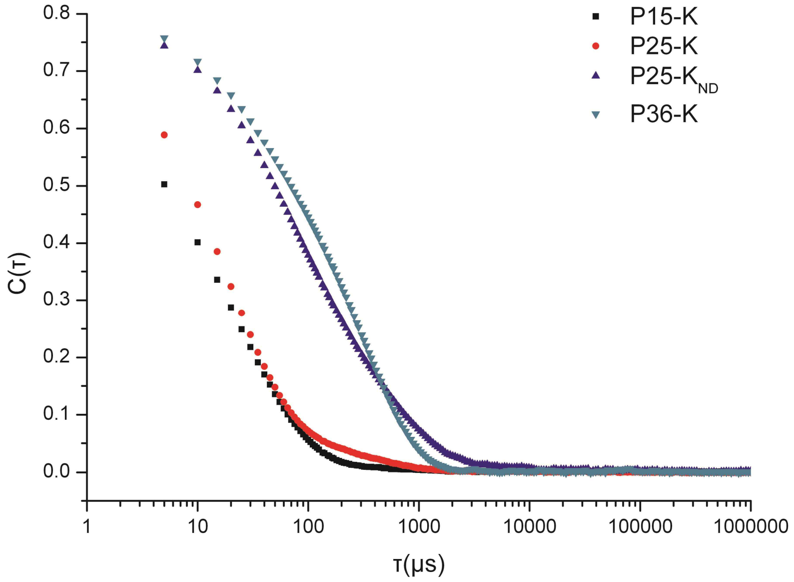


Fig. S6 DLS correlation functions of **P15-K**, **P25-K**, **P25-K$_{ND}$** and **P36-K** (Fig. 3).

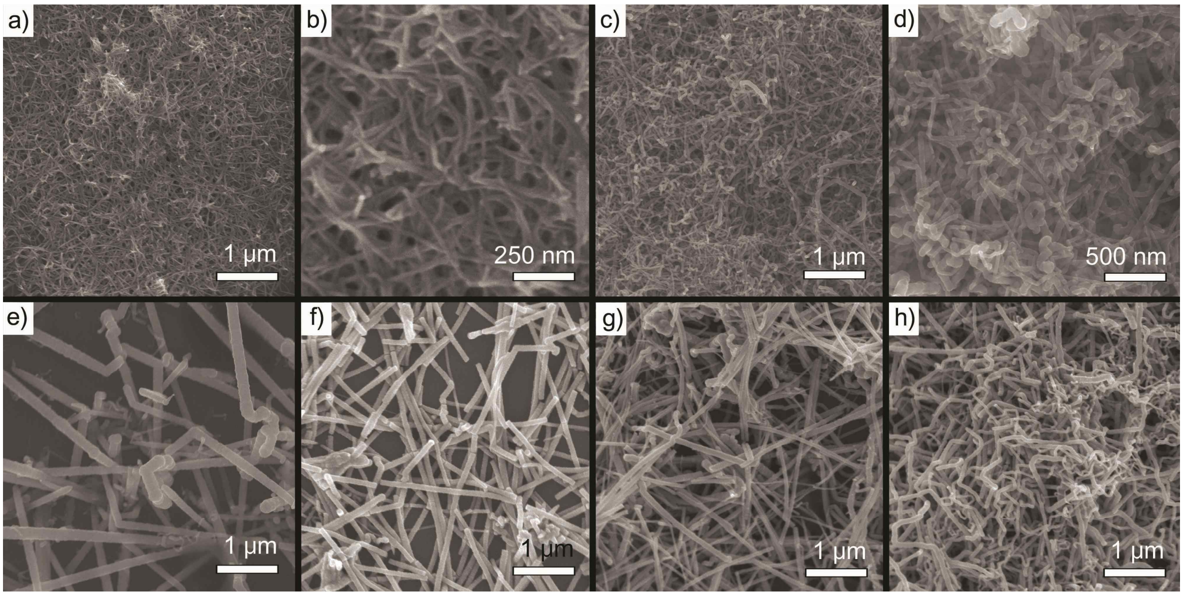


Fig. S7 FE-SEM images of Cu_2S NWs on the Si wafer grown by dipping with Cu foil in aqueous solution of (a-b) **P25-K**, (c) **P25-Cu**, (d) **P25-H**, (e) **P15-K**, (f) **P15-Cu**, (g) **P36-K**, and (h) **P36-Cu** for 3 days.

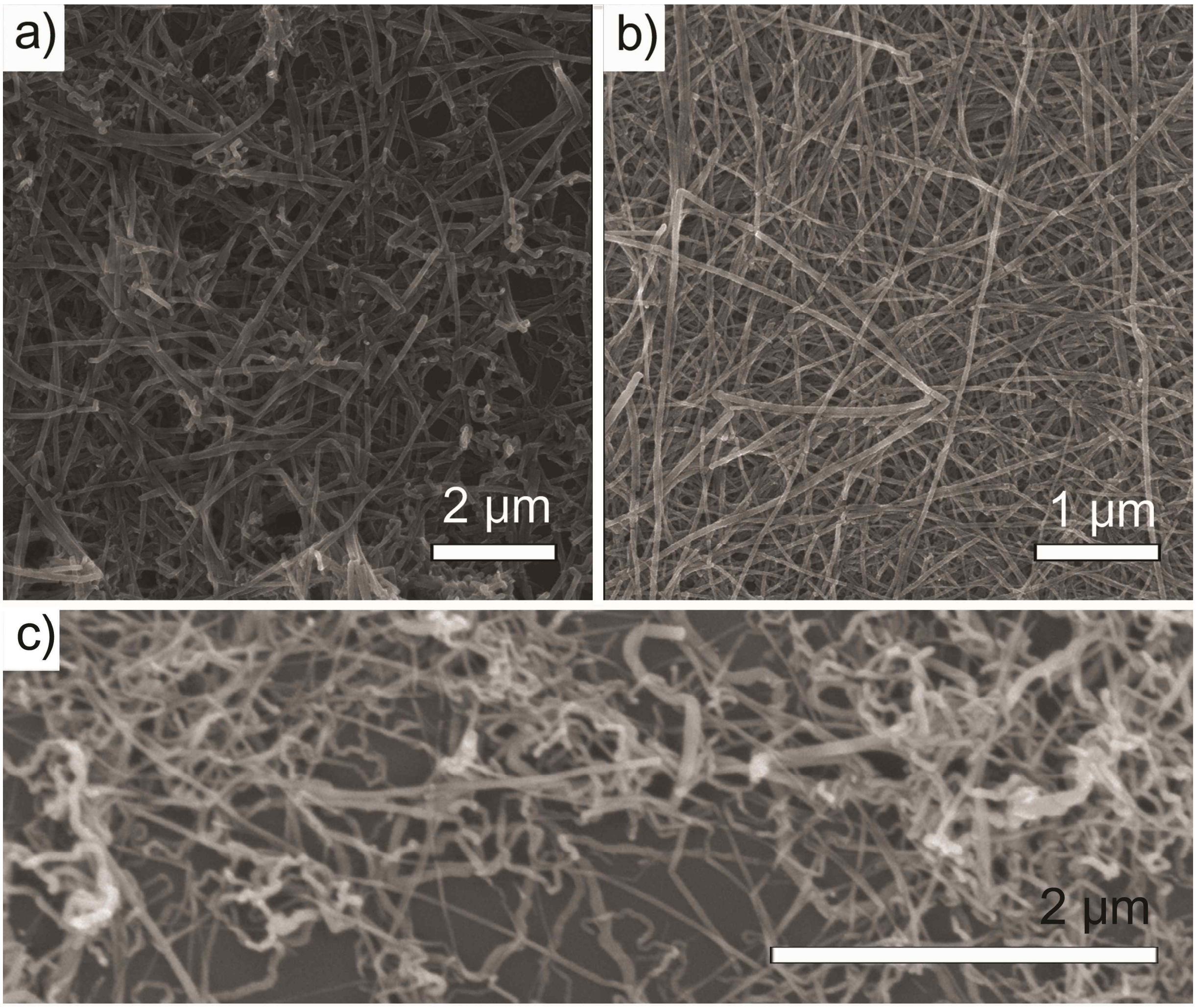


Fig. S8 (a) FE-SEM image of Cu_2S NWs grown on n-type Si wafer by dipping with Cu foil in aqueous solution of **P36-Cu** for 3 days. (b) FE-SEM image of Cu_2S NWs grown on piranha treated Si wafer by dipping with Cu foil in aqueous solution of **P25-K** for 3 days. (c) FE-SEM image of Cu_2S NWs grown on HMDS treated glass by dipping with Cu foil in aqueous solution of **P36-Cu** for 3 days.

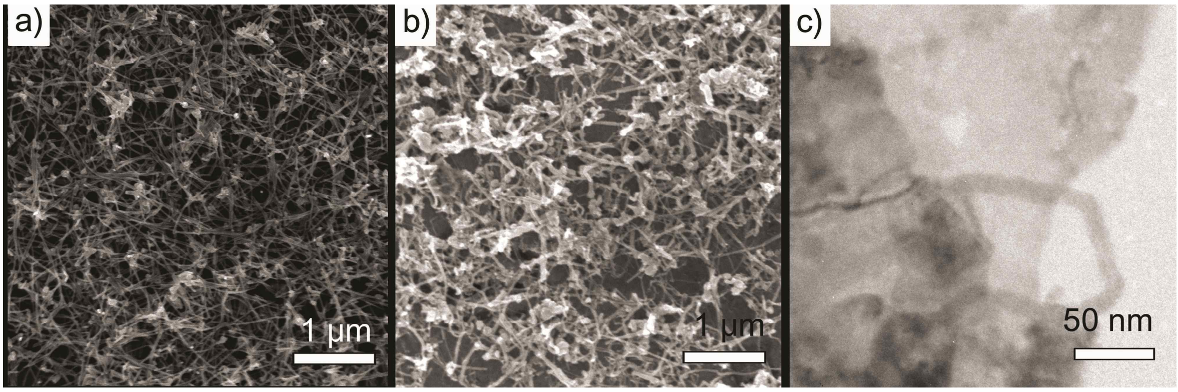


Fig. S9 (a) FE-SEM image of Cu_2S NWs grown on HOPG by dipping with Cu foil in aqueous solution of **P25-K** for 3 days. (b) FE-SEM image of Cu_2S NWs grown on graphene/Cu foil by dipping in aqueous solution of **P25-K** for 3 days, and (c) FE-TEM image of transferred NWs on graphene.

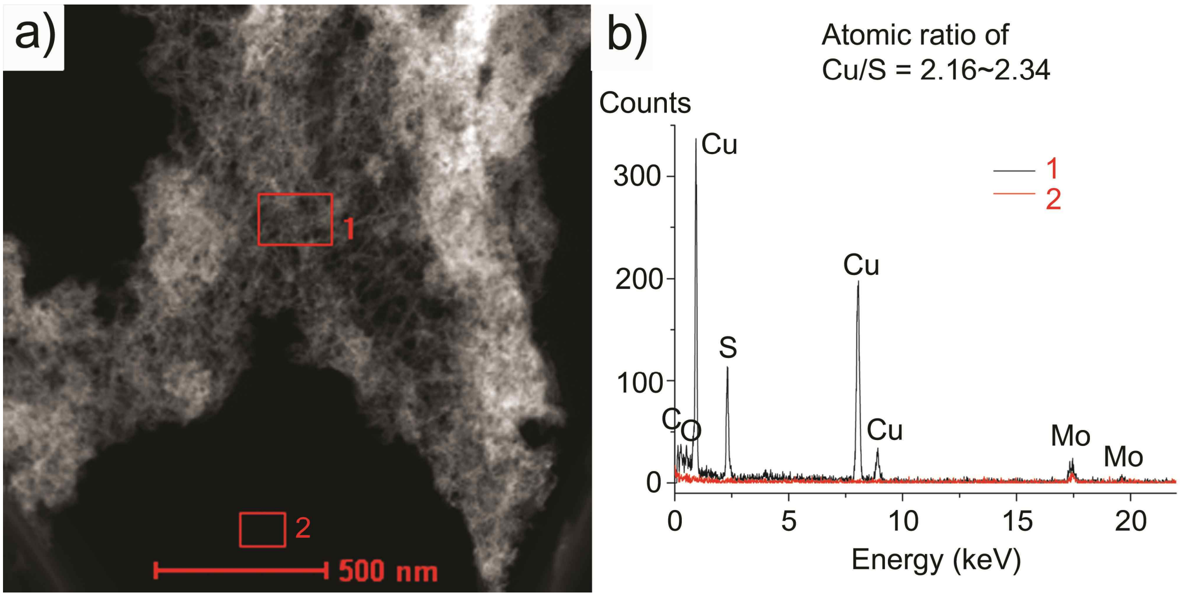


Fig. S10 (a) STEM image of transferred NWs on holey TEM Mo grid, and (b) corresponding EDX analysis (Cu_2S NWs were grown on the Si wafer by dipping with Cu foil in aqueous solution of **P25-Cu** for 3 days).

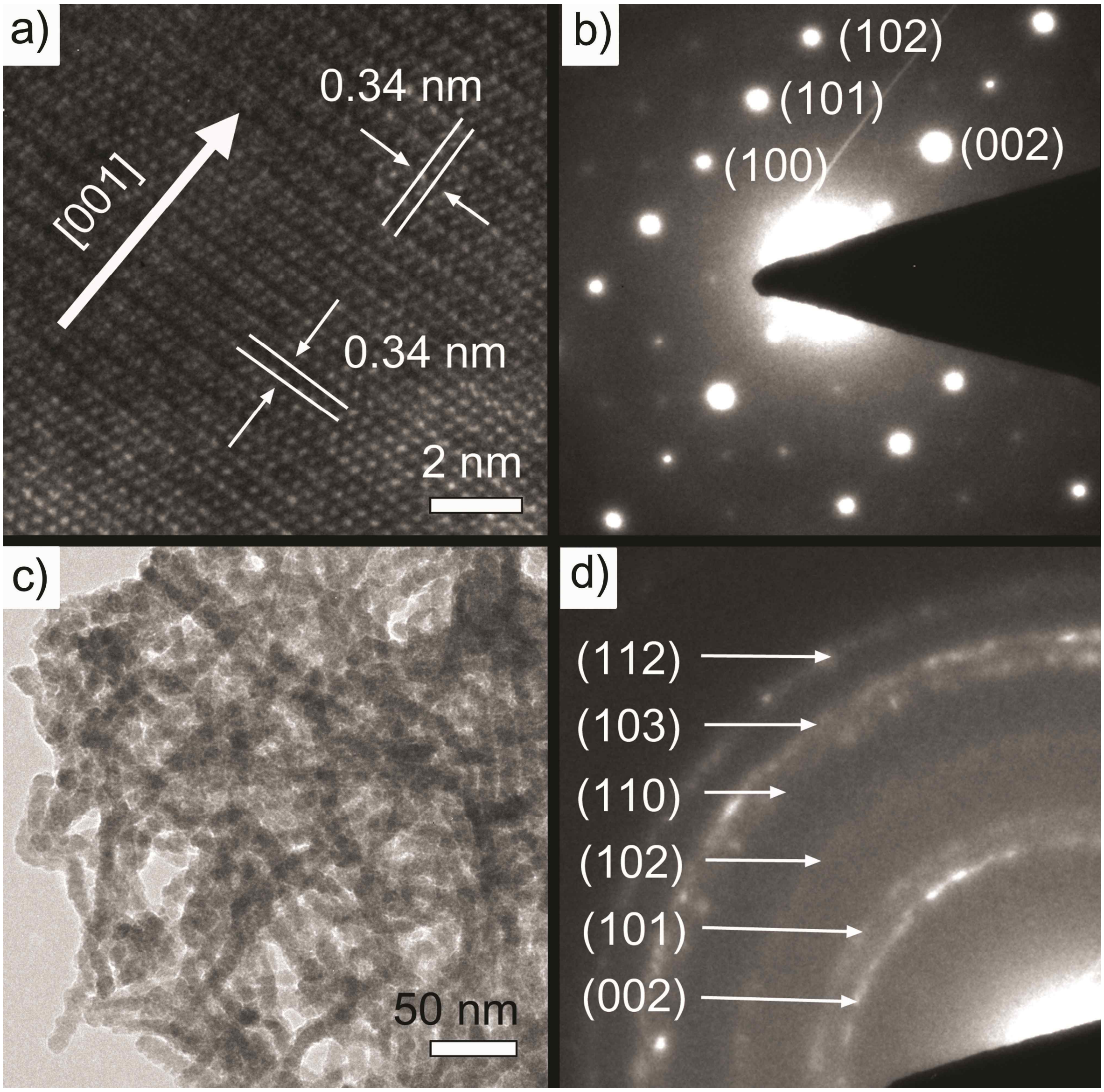


Fig. S11 (a-b) HR-TEM image of Cu_2S NWs grown on the Si wafer by dipping with Cu foil in aqueous solution of **P25-K**, and corresponding SAED pattern from [010] zone axis. (c-d) FE-TEM image of Cu_2S NWs grown on the Si wafer by dipping with Cu foil in aqueous solution of **P25-Cu**, and corresponding SAED pattern (JCPDS card, No. 84-0207).

References.

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