

Supporting Information

Template-free Growth of Aligned Bundles of Conducting Polymer Nanowires

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1. FT-IR analysis of poly-*o*-anisidine

The FT-IR spectrum indicates that the aligned poly-*o*-aniline nanowires have the same molecular structure as poly-*o*-anisidine synthesized by other methods (Ref. 10-13). Table S1 contains peaks assignments. The broad peak between 1800 – 3600 cm^{-1} has been attributed to the N—H \cdots O and N—H \cdots N hydrogen bonds (Ref. 13).

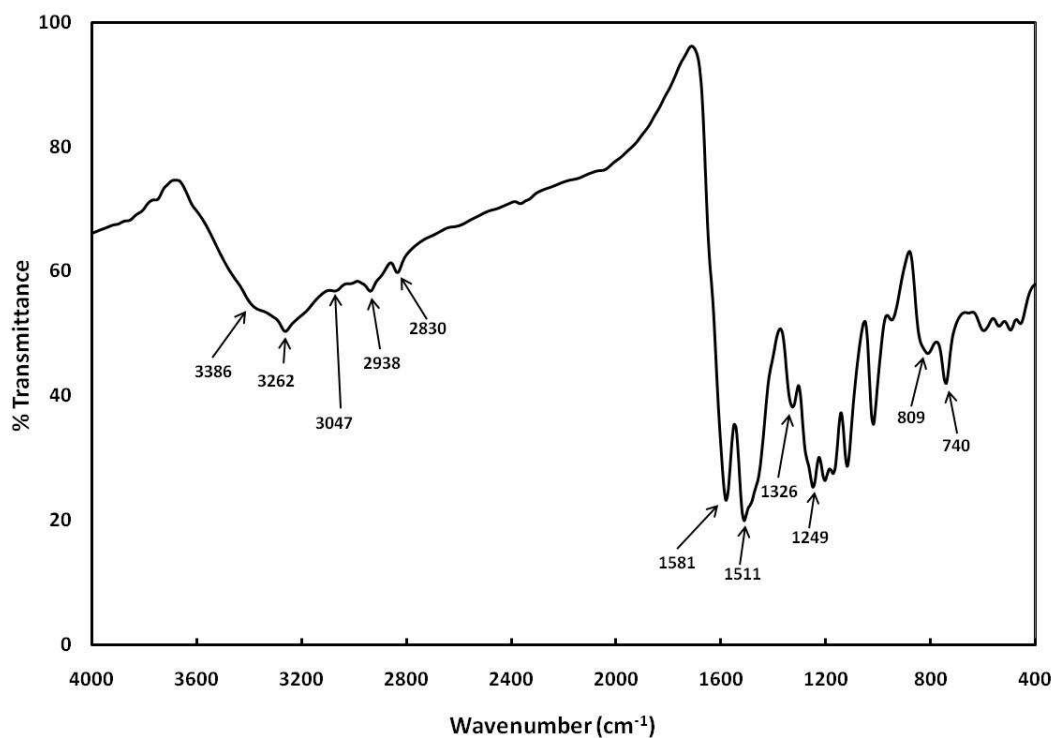


Figure S1. Pellet (KBr) FTIR spectrum of dedoped poly-*o*-anisidine.

Table S1. FTIR peak assignment for poly-*o*-anisidine.

Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)	Assignment
3386	N-H stretch	1511	Benzenoid ring C=C stretch
3262	Hydrogen-bonded O-H stretch	1326	C-N stretch
3047	Benzenoid ring C-H stretch	1249	C-O stretch
2938 & 2830	C-H stretch of the methoxy CH ₃	809	1,4 aromatic substitution C-H out-of-plane bending
1581	Quinoid ring C=C stretch	740	1,2 aromatic substitution C-H out-of-plane bending

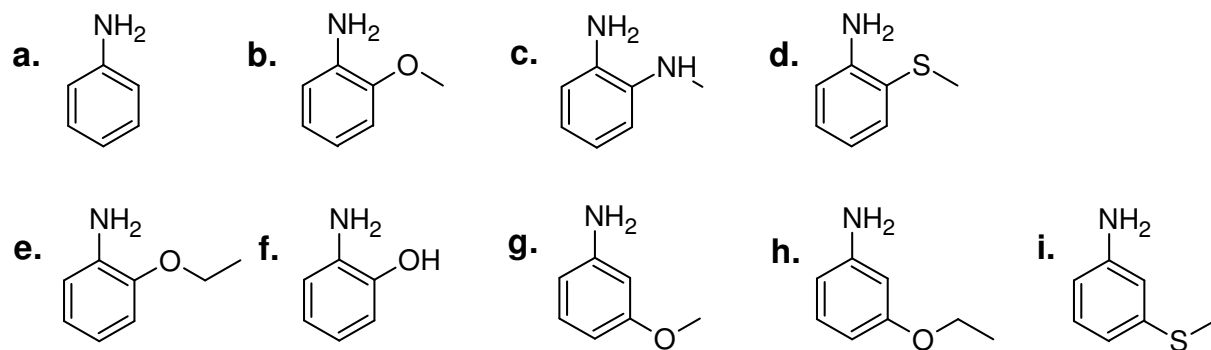
2. Effect of various monomer aromatic substituents on the alignment of conducting polymer supramolecular structures

Instead of the parent monomer(aniline), *o*-anisidine is used as the monomer to facilitate nanowire alignment. The methoxy substituent is believed to promote inter-chain hydrogen bonding and to promote π - π stacking. In order to further elucidate the role of the methoxy group, a number of structurally similar monomers were polymerized under identical conditions. The structures of all the monomers studied are shown in Scheme 1, and their chemical names are as follows: (a) aniline, (b) *o*-anisidine, (c) *N*-methyl-1,2-diamine, (d) 2-methylthioaniline, (e) *o*-phenetidine, (f) *o*-aminophenol, (g) *m*-anisidine, (h) *m*-phenetidine, and (i) 3-methylthioaniline.

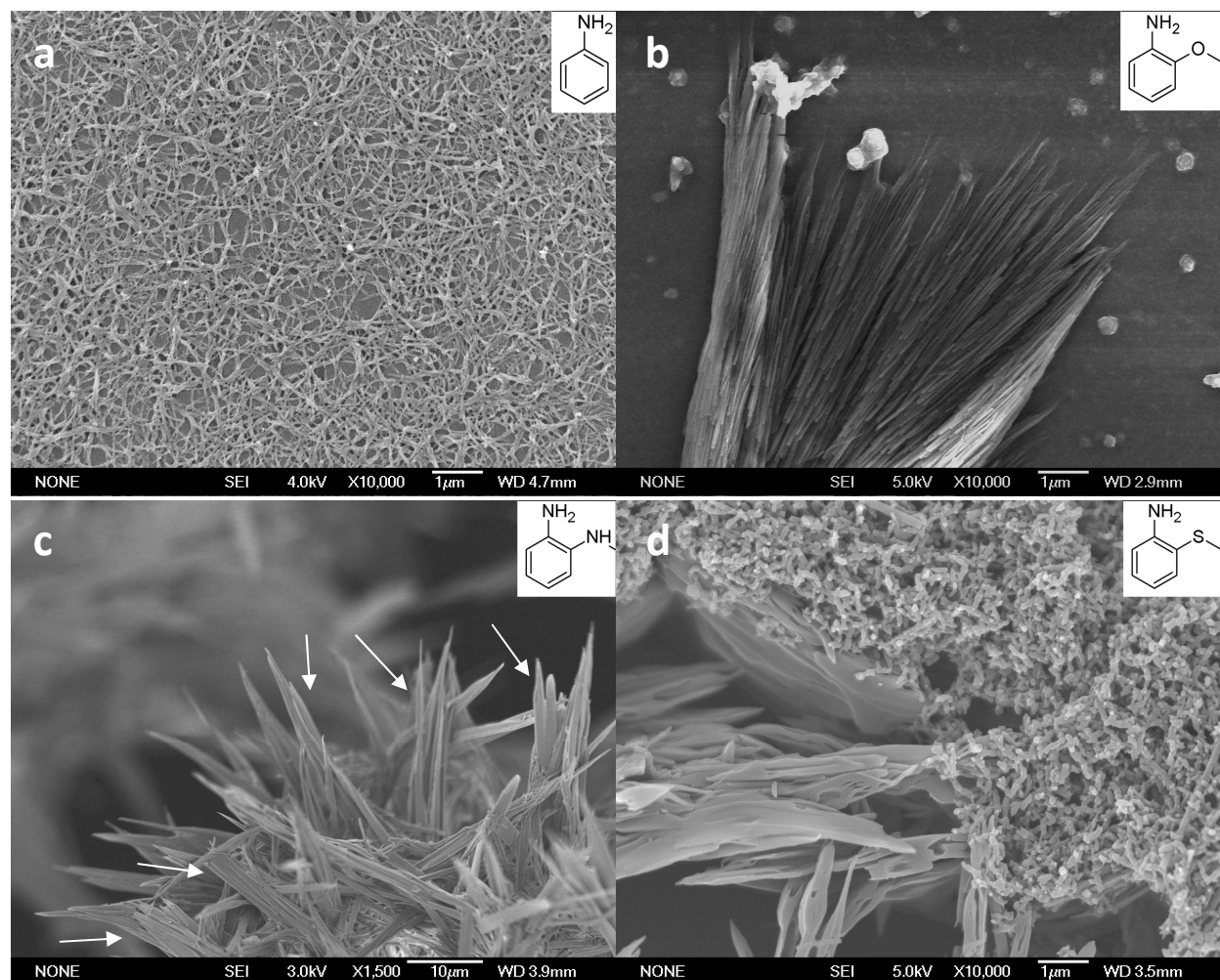
The corresponding SEMs of the resulting polymer of the monomers are shown in Figure S2. The rationale behind choosing each of those monomers and what the corresponding SEM images represent are as follows:

- From (a) to (b): introduce a methoxy substituent on aniline to increase hydrogen bonding interactions. Under identical reaction conditions, the resulting morphology changes from randomly oriented nanofibers for polyaniline (Figure S2a) to a mixture of one layer of nanofibers and one layer of aligned nanowires for polyanisidine (Figure S2b). The top nanofibrous layer for Fig. S2b is not shown here.
- To (c) and (d): substitute the oxygen atom on the methoxy group with other closely related atoms such as nitrogen in *N*-methyl-1,2-diamine and sulfur in 2-methylthioaniline to investigate the effect of hydrogen bonding. As shown in Fig. S2c, poly-(*N*-methyl-1,2-diamine) exhibits some degree of alignment as many of the nanowires are straight and packed in bundles. However, the alignment is not as ordered as that observed for poly-*o*-anisidine. Poly-(2-methylthioaniline) only forms randomly oriented nanofibers, along with some large sheets.
- To (e) and (f): vary the hydrocarbon chain length of the methoxy group to investigate possible steric effects. Poly-*o*-phenetidine (Fig. S2e) also exhibits a bilayered morphology similar to poly-*o*-anisidine. However, the nanowires that comprise the bottom layer only show a small degree of alignment as opposed to poly-*o*-anisidine. Poly-*o*-aminophenol (Fig. S2f) forms large sheets that aggregate into flower-shaped bundles, without any alignment.
- To (g), (h), and (i): the position of substitution also affects alignment. When the methoxy group is moved to the meta position (*m*-anisidine, Fig. S2g), only granular-shaped agglomerates form. Identical results are obtained when the hydrocarbon chain of the methoxy group in *m*-anisidine is increased, or when the oxygen atom is replaced with a

sulfur atom, as shown in Fig. S2h and S2i, respectively. Such results indicate that the position of substitution also plays an important role in promoting alignment.



Scheme S1. A list of structurally similar monomers of *o*-anisidine.



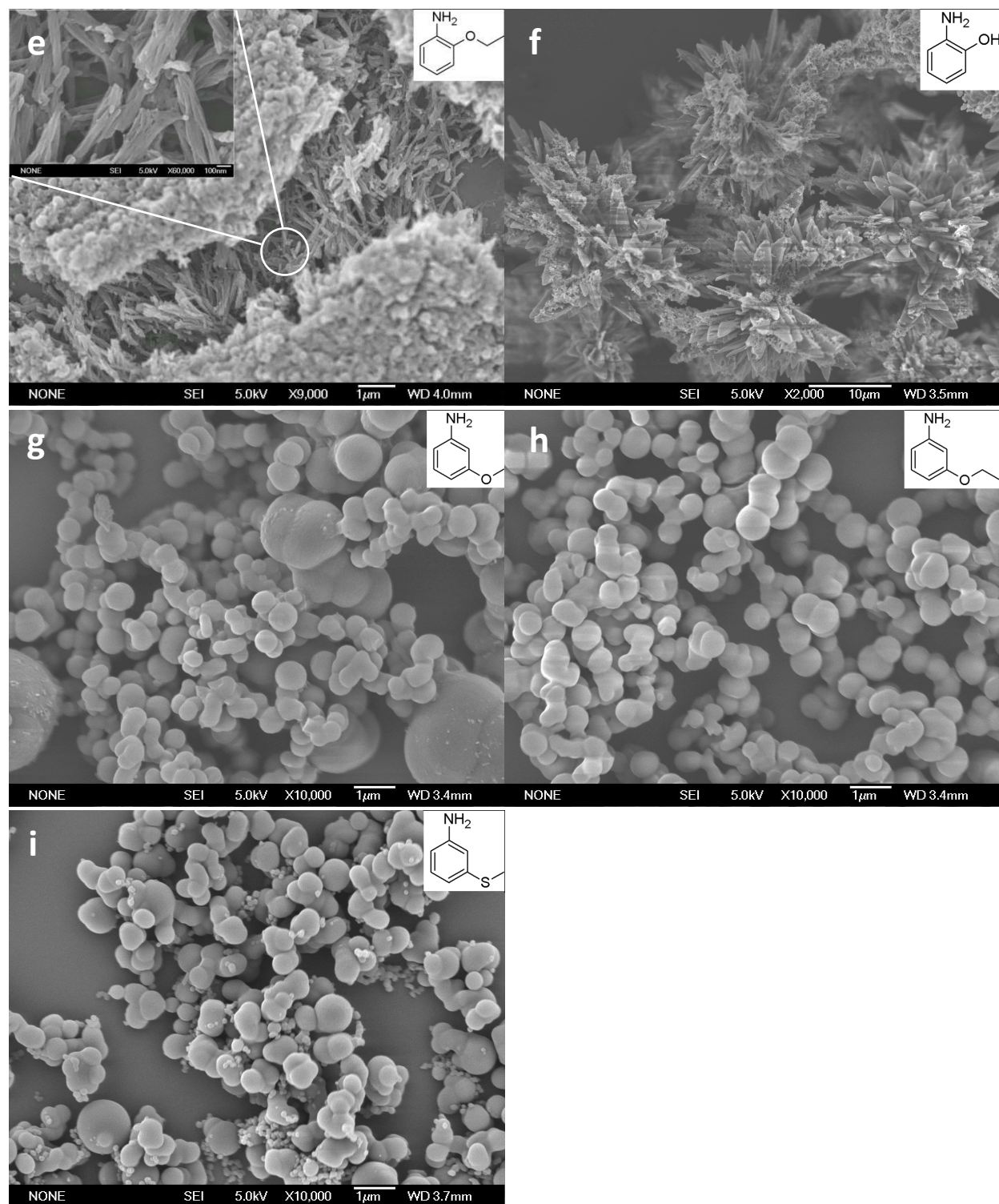


Figure S2. Scanning electron microscope (SEM) images for all the polymers created from the monomers shown in Scheme 1. The insert at the upper right corner of each image corresponds to the monomer that was polymerized.

3. Effect of initiator molecules on nanowire alignment

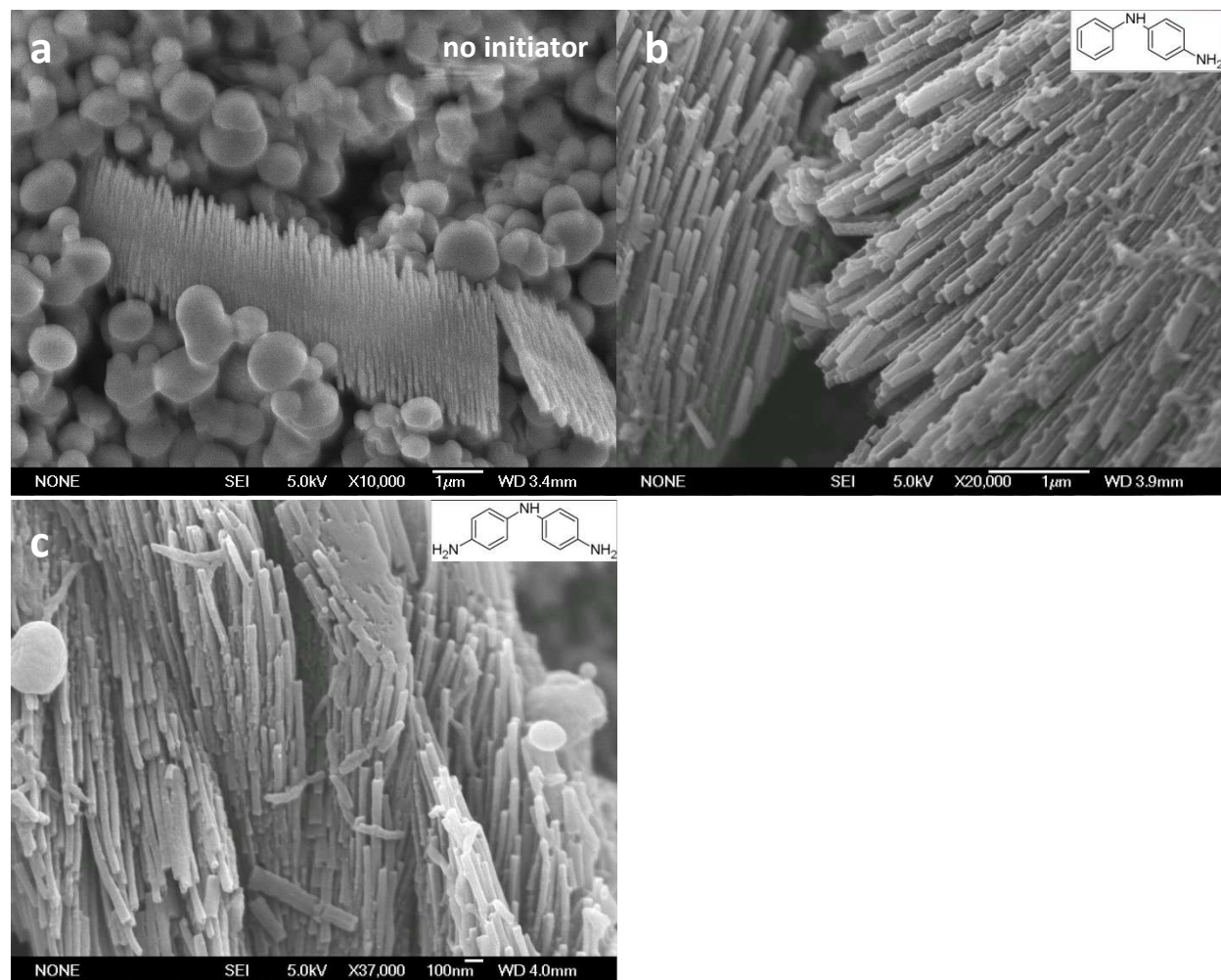


Figure S3. Scanning electron microscope (SEM) images of poly-*o*-anisidine synthesized with (a) no initiators, (b) with aniline *p*-dimer, and (c) with 4,4'-diaminodiphenylamine. The insert at the upper right corner of each image corresponds to the molecular structure of each initiator.

4. Effect of reaction time on the morphology of poly-*o*-anisidine

When the polymerization reaction is quenched at 24 or 48 hours, only entangled and randomly oriented nanofibers form (Figure S4a). However, when the reaction length is

increased to 3 or more days, the aligned nanowire morphology appears (Figure S4b). Such results are supported by a general principle of molecular order—longer reaction time allows better polymer chain stacking and facilitates growth along the long axis of the fiber.

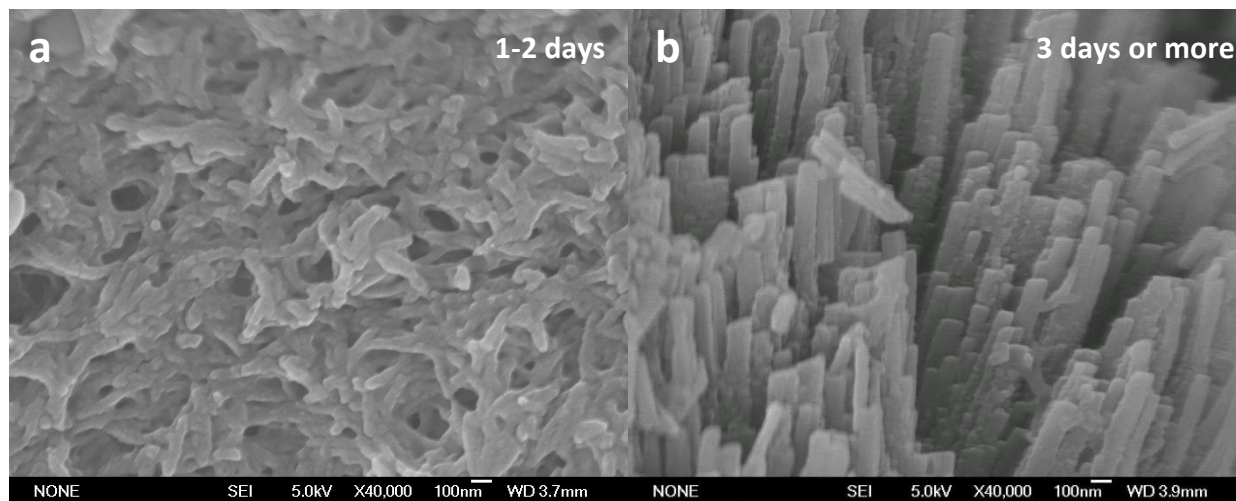


Figure S4. Scanning electron microscope images of poly-*o*-anisidine synthesized with a reaction time of (a) 1 to 2 days, and (b) 3 days or more.

5. Effect of dopant acid

The choice of dopant acid is crucial as HCl is the only dopant acid found so far that promotes alignment. No aligned nanowires or bilayered structures are observed when camphorsulfonic acid (CSA) is used (Figure S5a), and the aligned bottom layer becomes stacked large sheets when the reaction is carried out in an aqueous 1 M HClO₄ solution. This effect could be related to the size of the dopant acid molecules, as larger dopants such as the perchloric ion from perchloric acid or camphorsulfonic ion from CSA could hinder inter-molecular stacking, and thus obstruct the formation of aligned nanowires.

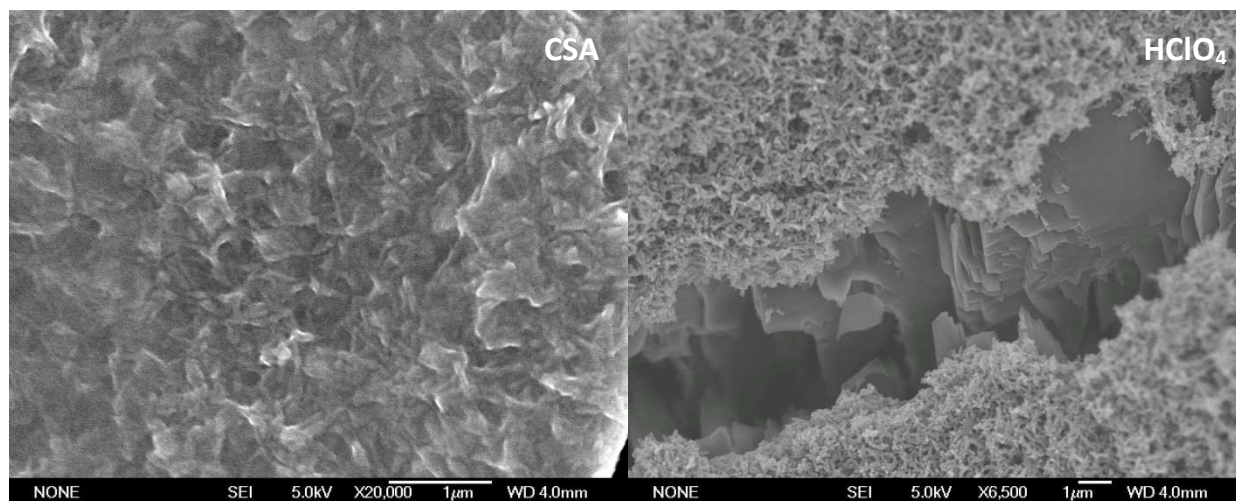


Figure S5. Scanning electron microscope (SEM) images of poly-*o*-anisidine synthesized with (a) CSA, and (b) HClO₄.

6. Effect of oxidants

The choice of oxidant also appears to have an effect on the morphology of poly-*o*-anisidine nanofibers. Ammonium peroxydisulfate (APS) appears to be the best oxidant. Unlike the nanofiber/aligned nanowire bilayered morphology observed when APS is used, when FeCl₃ is used as the oxidant, a mixture of aligned nanowires and micron-sized spheres are obtained (Figure S6a). Since these two morphologies do not form 2 distinct layers, it is difficult to separate the spheres from the nanowires. When the oxidant is changed to FeCl₂, the alignment is replaced with long and randomly oriented nanowires (Figure S6b). If hydrogen peroxide is used as the oxidant, only non-oriented nanofibers can be observed, along with some spheres (Figure S6c).

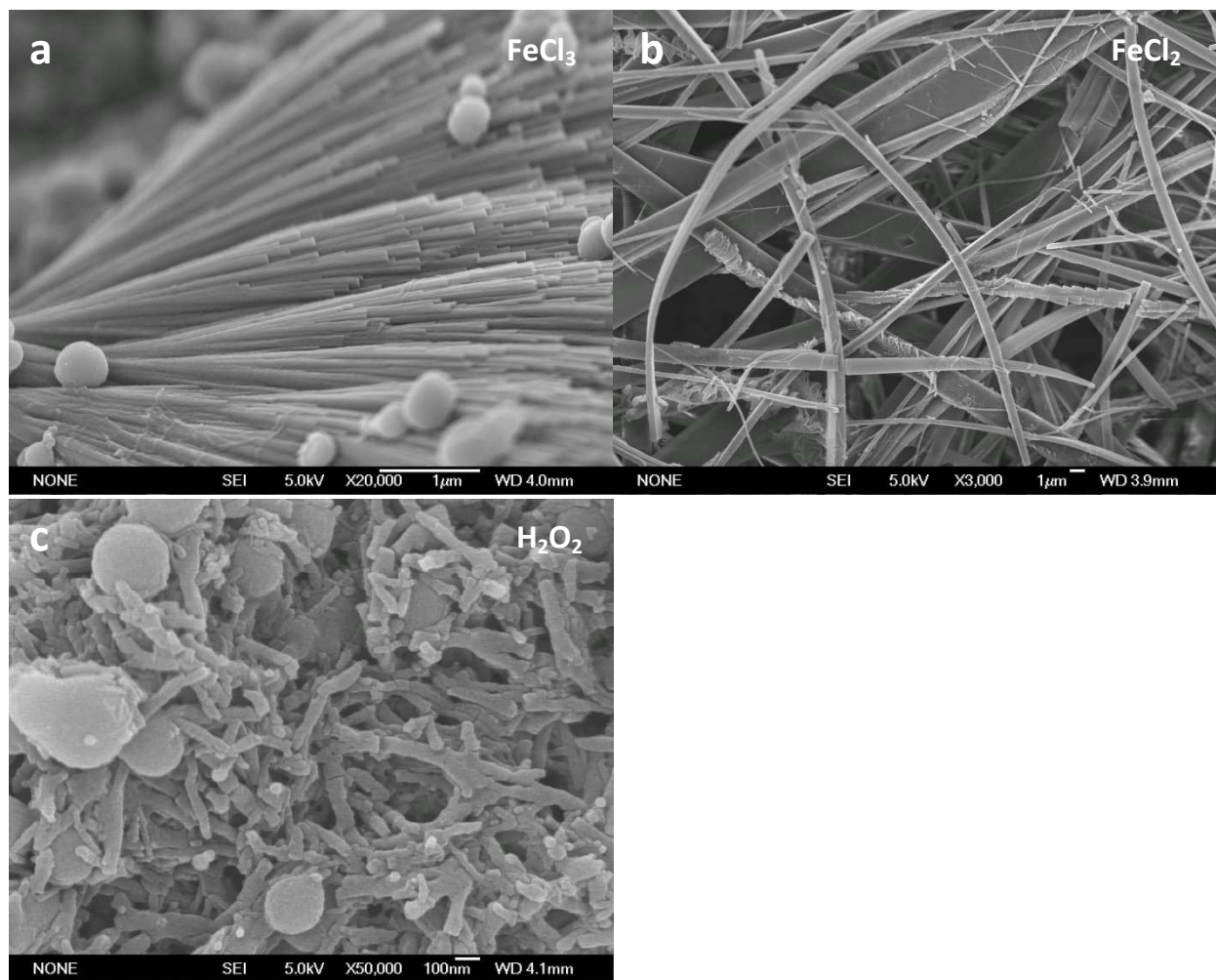


Figure S6. Scanning electron microscope (SEM) images of poly-*o*-anisidine synthesized with (a) ferric chloride, (b) ferrous chloride, and (c) hydrogen peroxide.

7. Effect of monomer-to-oxidant ratio

The formation of aligned nanowires is sensitive to specific reaction parameters. A 4:1 monomer-to-oxidant ratio is optimal for alignment (Figure S7a). As the ratio is decreased to 2:1, the amount of nanowires decreases and the wires appear to coagulate (Figure S7b). A 1:1 monomer-to-oxidant ratio results in large smooth sheets along with nanofibers (Figure S7c), and only agglomerates are observed when the ratio is changed to 1:2 (Figure S7d).

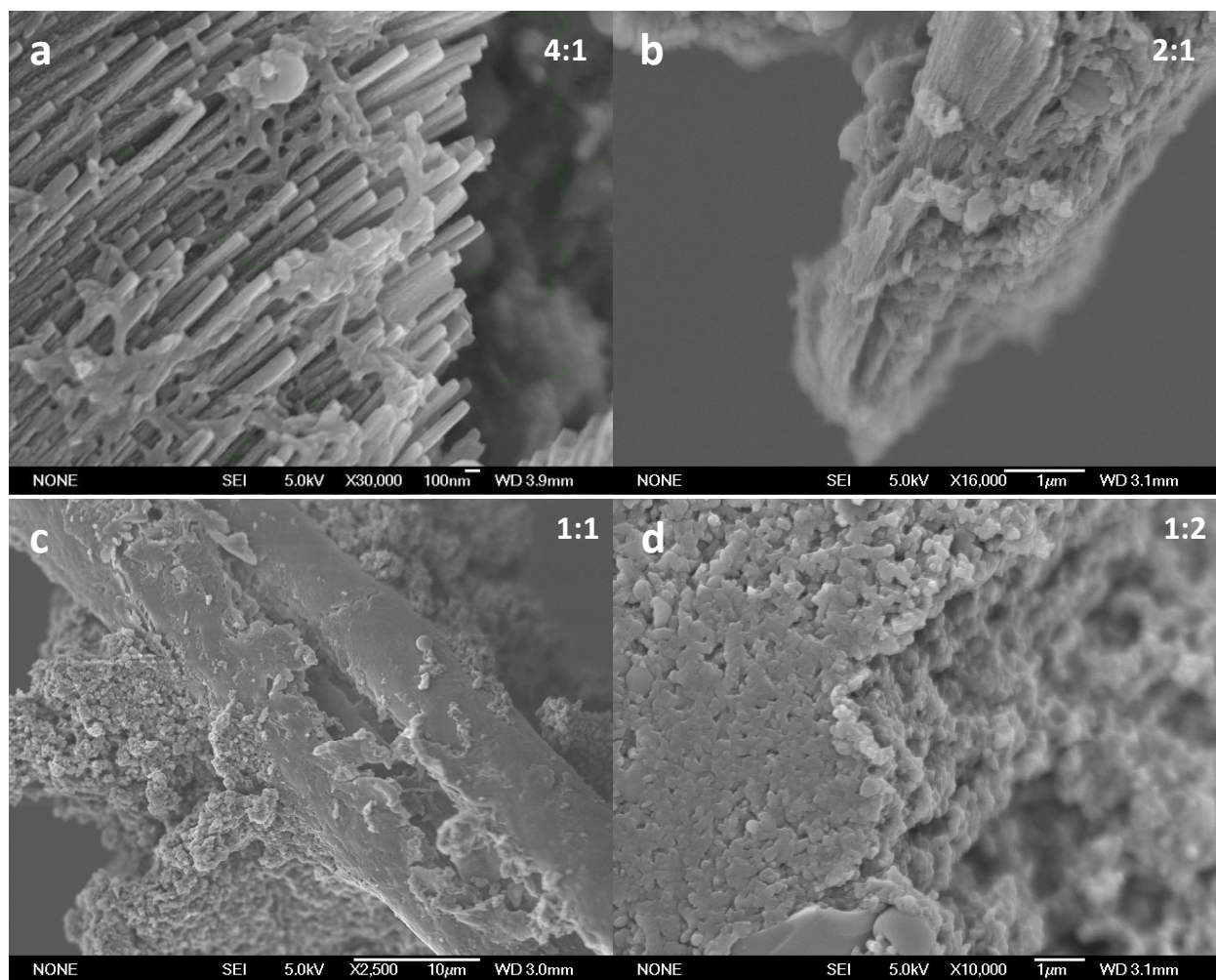


Figure S7. Scanning electron microscope (SEM) images of poly-*o*-anisidine synthesized with a monomer-to-oxidant ratio of (a) 4:1, (b) 2:1, (c) 1:1 and (d) 1:2.

8. Effect of reactant concentration

Similar to the monomer-to-oxidant ratio, the reactant concentration also plays an important role in forming the aligned nanowires. When the monomer-to-oxidant ratio is kept at 4:1, the oriented nanowires only form when the monomer concentration is between 3.2 and 6.4 mmol.

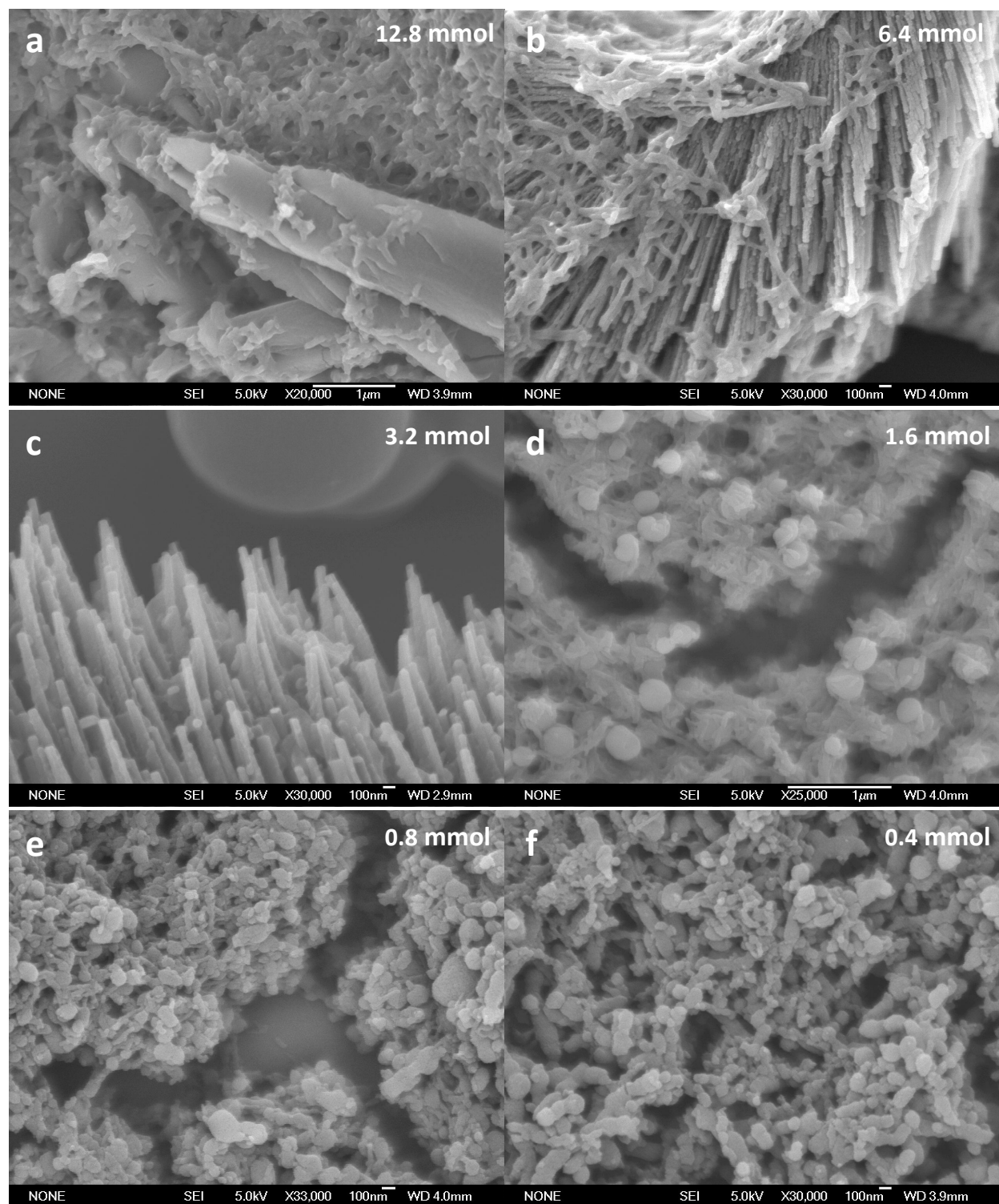


Figure S8. Scanning electron microscope (SEM) images of poly-*o*-anisidine synthesized with *o*-anisidine concentrations of (a) 12.8 mmol, (b) 6.4 mmol, (c) 3.2 mmol, (d) 1.6 mmol, (e) 0.8 mmol, and (f) 0.4 mmol, while the monomer-to-oxidant ratio is kept at 4:1.