Electronic Supporting Information

Post-Assembly Dimension-Dependent Face-Selective Etching of Fullerene Crystals

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Figure S1. Additional SEM images of FNRs prepared using ULLIP method at liquid-liquid interface of IPA and C\textsubscript{60} solution in \textit{m}-xylene. Inset of the top right image show the representative model structure.

Figure S2. (a) Histogram of length distribution of the FNRs, (b) Histogram of diameter distribution of the FNRs.
Figure S3. Additional STEM images of FNRs prepared at liquid-liquid interface of IPA and C$_{60}$ solution in $m$-xylene.

Figure S4. Additional SEM images of FNS prepared at an interface of IPA and C$_{60}$ solution in $p$-xylene. Inset of the top right image show the representative model structure.
Figure S5. Histogram of size distribution of FNS.

Figure S6. Additional STEM images of FNS prepared at an interface of IPA and C_{60} solution in p-xylene.

Figure S7. Additional SEM images of FC prepared at an interface of IPA and C_{70} solution in mesitylene. Inset of the top right image show the representative model structure.
**Figure S8.** Histogram of size distribution of FC estimated from 100 randomly selected cubes.

**Figure S9.** Additional STEM images of FC.
Figure S10. Additional STEM images of FNR following EDA treatment.

Figure S11. Histograms of length (a) and diameter (b) distribution of FNR-EDA.
Figure S12. Additional SEM images of tubular hollow structures obtained after chemical etching of FNR. Inset of the top right image show the representative model structure.

Figure S13. Additional SEM images of FNS-EDA. Inset of the top right image show the representative model structure.
Figure S14. Histogram of size distribution of FNS-EDA.

Figure S15. Additional STEM images of FNS-EDA.
Figure S16. Additional SEM images of FC-EDA. Inset of the top right image show the representative model structure.

Figure S17. Histogram of size distribution of FC-EDA.
Figure S18. Additional STEM images of FC-EDA.
Figure S19. Typical TEM (a, c, e, g) and HR-TEM (b, d, f, h) images of FNR, FNR-EDA, FNS-EDA and FC-EDA.
Figure S20. The UV-vis absorption spectra of FNR, FNS, and FC before and after EDA treatment. (a) FNR and FNR-EDA. (b) FNS and FNS-EDA. (c) FC and FC-EDA. All the spectra were recorded at 25 °C by dispersing the samples in IPA (0.2 mg/mL).
Figure S21. (a) XPS survey spectra of pC$_{60}$, pC$_{70}$, FNR, FNR-EDA, FNS, FNS-EDA, FC and FC-EDA and (b) C 1s XPS core level spectra with deconvoluted peaks of pC$_{60}$, FNR and FNR-EDA and (c) N 1s XPS core level spectrum with deconvoluted peaks of chemically etched samples; FNR-EDA, FNS-EDA and FC-EDA.

Figure S22. Effect of solvent washing on etching.
**Figure S23.** (a,c) SEM and (b,d) STEM images of FNR incubated for 6 h before and after single washing with solvent mixture (IPA + m-xylene + EDA).

**Figure S24.** Additional STEM images showing hollow tubular structure obtained under optimized conditions.
Figure S25. The amination process of fullerene.
Figure S26. Mass spectra of FNR after chemical etching.
Figure S27. (A) SEM and (B) STEM images of the effect of chemical etching in different mixing ratio of EDA:TEA. (a) EDA:TEA = 0:100, (b) EDA:TEA = 10:90, (c) EDA:TEA = 20:80, (d) EDA:TEA = 50:50, (e) EDA:TEA = 80:20 and (f) EDA:TEA = 100:0.

Figure S28. Contact angles of FNR, macaroni fullerene (MF: for comparison), and FNR-EDA. The FNR and MF have a similar contact angles with superhydrophobic properties. The fullerene tubes (FNR-EDA) obtained after chemical etching of FNR shows hydrophilic properties.
Figure S29. Hydrophilicity of FNR before and after EDA treatment. Prior to etching, FNR cannot be dispersed in water. Following etching, it can be dispersed in water.

Figure S30. The solubility difference of (a) C₆₀ powder or (b) FNR in different solvents. C₆₀ powder (1.4 mg) can be dissolved rapidly in 1 mL pure m-xylene or 1 mL EDA solution after sonication for 10 min. However, in m-xylene/IPA (m-xylene: 1 mL; IPA: 5 mL) and EDA/IPA (EDA: 1 mL; IPA: 5 mL) mixtures dissolution was less rapid. The solubility of C₆₀ powder in m-xylene/IPA and EDA/IPA mixtures are 0.07 and 0.16 mg/mL, respectively. Moreover, the solubilities of post-assembled FNR in the m-xylene/IPA and EDA/IPA mixture are 0.03 and 0.11 mg/mL, respectively.
solubility of FNR is lower than C$_{60}$ powder in the same solvent or solvent mixture. However, while FNR resists dissolution (compared to C$_{60}$ powder), it is still slightly dissolved in EDA/IPA mixture. Green arrow represents the undissolved C$_{60}$ powder and FNR.

**Figure S31.** The possible mechanism of post-assembly FNR etched by EDA. The crystal plane on the wall of FNR is the (001) plane of hcp. The (001) plane of hcp has the highest occupied space of atoms and the smallest vacancy than other planes of hcp, which can effectively resist the infiltration of EDA solution. Hence, the etching order of FNR by EDA was from ends of FNR.

**Figure S32.** Sensing performance of FNR before and after chemical etching (FNR-EDA).