Supplementary Information: Experimental Methods

Silicon wafers (Silrac, undoped, mirror finish, (111) orientation) were cut into 0.5 cm × 0.5 cm pieces. The small pieces were etched to remove surface SiO_2 by submersion in an NH_4HF_2 aqueous solution (200 mL, 4 mol/L) for 48 hours under strong stirring conditions. After thoroughly washing with purified water, the small silicon pieces were preserved in purified Tetrahydrofuran (THF). To 100 mL of a solution of 20 vol% Hexyne in purified THF in a 200 mL glass reactor, 10 g of the etched Silicon wafer was added. The reactor and contents were placed in an ice bath for the duration of the sonication experiment. Argon was bubbled through the reaction solution for 20 minutes using a glass pipette. The probe end was placed just below the surface of the liquid (about 1 cm into solution), and the mixture was sonicated in a sonicator (Model UIP1000hd, 20 kHz; Hielscher Ultrasonics, Germany) for 60 minutes under flowing Ar at 65% amplitude with a 1.8 cm diameter titanium probe (model BS2d18F), corresponding to a power intensity of approximately 80 W/cm^2 (see Figure S1). Upon completion of sonication, the reaction solution was centrifuged in two 50-mL centrifuge vials for 10 minutes at 5000 RPM and 12°C. The liquid phase from the centrifugation was decanted into a single, weighed rotary evaporation vessel. The Hexyne/THF solvent mixture was rotary evaporated at reduced pressure. After rotary evaporation, 15 mL of Dichloromethane (DCM) was added to the flask in order to re-suspend the nanoparticles.

The centrifuged and rotary evaporated sample was then washed and dialyzed to remove polar impurities. Approximately 1.5 mL of sample in DCM (after washing) was placed in a dialysis tube (MW 1000 cut off). The dialysis tube was placed in a beaker with 400 mL 95% Ethanol (EtOH) and dialyzed for one day. The 95% EtOH was removed from the beaker and replaced by 400 mL of THF, and further dialyzed for three days. The sample inside the dialysis tube was recovered, and the DCM solvent removed by evaporation. Portions of the purified sample were re-dispersed in purified DCM, THF, or $CDCl_3$ for further characterization.

One portion of the purified sample was subjected to gel permeation chromatographic (GPC) separation, comprising a Varian ProStar325 UV-Vis detector, two Varian ProStar 215 HPLC pumps and a PL-gel 5μm, 300 ×7.5 mm chromatographic column with an 0.2 mL injector loop. The eluting solvent, THF (>99.9%, HPLC grade) was passed through the detector and column at 1.0 mL/min, into which a 0.2 mL silicon nanoparticles solution in THF (2 mg/mL) was injected. The detection wavelength was 360 nm.

A second portion of the purified sample was subjected to size exclusion chromatographic (SEC) separation. Bio-beads S-X1 were swelled overnight in dry THF and packed into a 40 cm × 1.3 cm glass column. DCM was used as an elution solvent. The nanoparticle solution (1 mL in DCM) was added to the column and eluted into 10 fractions collected in 5 mL increments in separate vials. The first fraction was collected when the nanoparticle solution was added into the SEC column. The eluted fractions were irradiated under UV light (360 nm) and photographed.

A third portion of the purified sample was gravity-fed through a packed silica gel column to remove polar impurities; then the entire effluent was analyzed using a gas-chromatograph/mass spectrometer (GC-MS). GC-MS was performed using a Varian 450 Gas Chromatograph with VF5-MS capillary column and a Varian 300 Mass Spectrometer. A 2.0μL diluted Silicon nanoparticles solution in DCM (~0.1 mg/mL) was injected into the system, and the MS signal collected and analyzed with the software library.

Selected solutions and fractions were further characterized using Transmission Electron Microscopy (TEM, Tecnai G2 F30 TWIN; 300 kV / FEG Transmission Electron Microscope) with Energy Dispersive Spectroscopy (SDD EDS), UV/Vis Spectroscopy (Cary 50 spectrophotometer), ^{1}H and ^{29}Si Nuclear Magnetic Resonance Spectrometry (NMR, Bruker Avance 300 MHz high resolution NMR spectrometer), and Photoluminescence Spectroscopy (PL, Varian Cary Eclipse spectrofluorimeter).

Figure S1 Schematic Diagram of Reactive Cavitation Erosion Sonochemical Reactor.

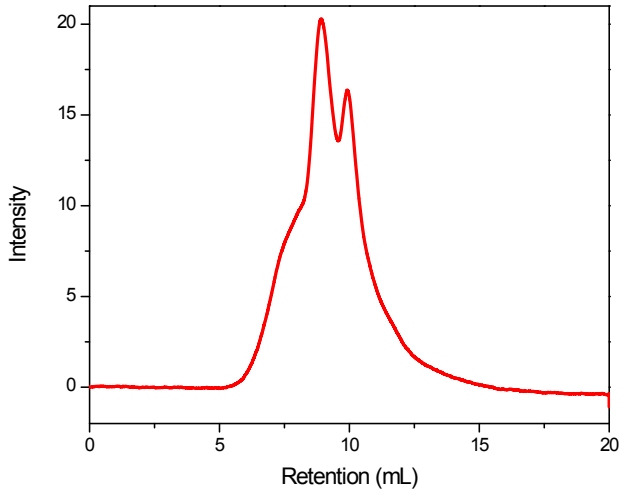


Figure S2 GPC trace of purified functionalized nanoparticles in THF showing three distinct components to the reaction solution.

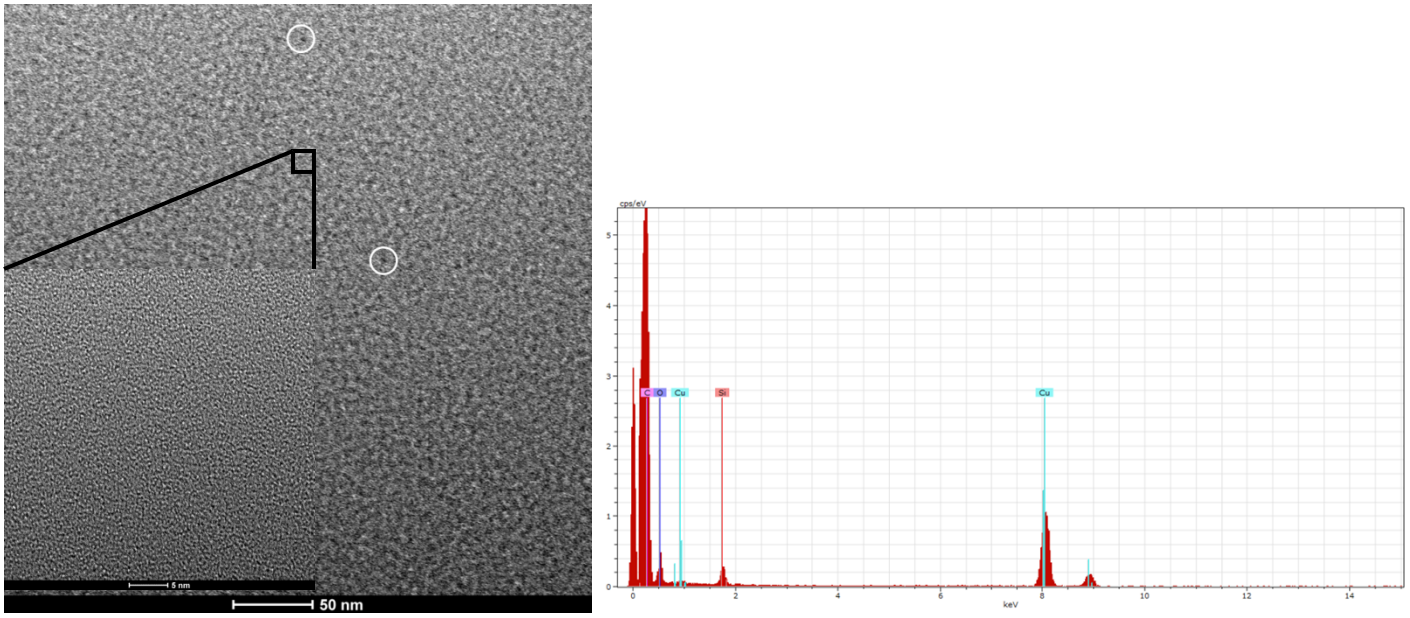
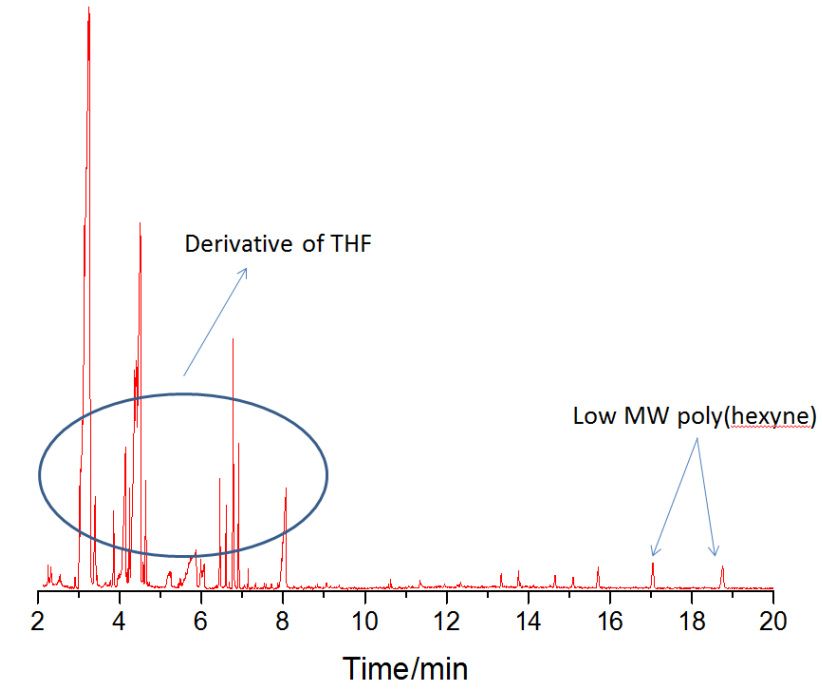


Figure S3 TEM and EDS analysis of un-fractionated sample indicating the presence of Silicon and a proliferation of sub 1-nm nanoparticles (see examples in circles) that cannot be imaged down to the resolution limit of the instrument.



Peak	AMU of molecular species	AMU of major fragment	Peak	AMU of molecular species	AMU of major fragment
1	87.0	42.0	13	71.0	71.0
2	74.0	74.0	14	87.0	71.0
3	92.8	76.0	15	87.0	71.0
4	72.9	57.0	16	98.1	67.0
5	129	71.0	17	103.1	71.0
6	86.0	71.0	18	270.0	270.0
7	121.9	121.9	19	259.0	129.0
8	100.0	42.0	20	285.0	57.1
9	86.0	74.0	21	279.1	149.0
10	125.7	71.0	22	366.3	85.1
11	114.1	86.0	23	380.2	85.1
12	71.0	71.0	24	417.2	71.1

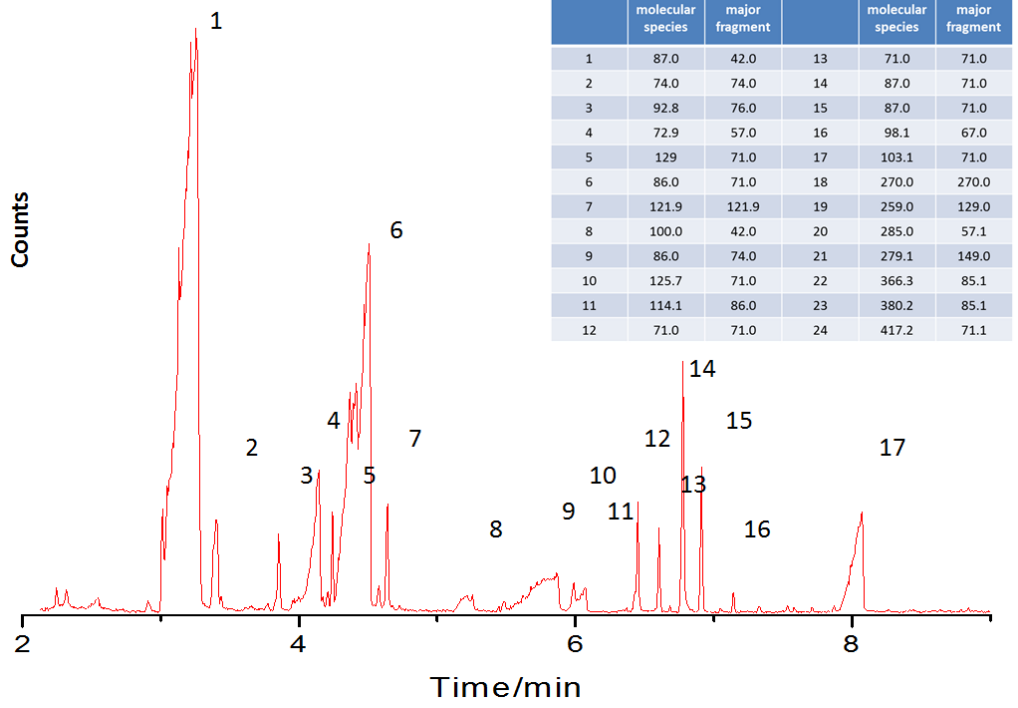


Figure S4 Overall MS trace (top) of GC-MS Sample, with MW analysis of fractions believed to be due to solvent (THF) derivatives (bottom).