Supplementary Materials

Synthesis of Millimeter-Long Vertically Aligned Carbon Nanotube Arrays on Aluminum Oxide Buffer Layers Prepared by Layer-by-Layer Assembly of Boehmite Nanoplates

by

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1. Experimental Procedures

1.1. Synthesis of Boehmite Nanoplates

Five grams of aluminium isopropoxide ($Al(OC_3H_7)_3$ 98+%, Sigma-Aldrich) was dispersed in 50 mL deionized (DI) water and hydrolyzed at 80 °C for1 h under vigorous stirring. The mixture was then transferred into a 125-mL Teflon-lined hydrothermal reactor. The reactor was sealed and placed in an oven for 12 h at 200 °C and then allowed to cool down to ambient temperature. The suspension was used without further treatment.

1.2. Synthesis of Magnetite Nanoparticles

Two millimoles of $Fe(acac)_3$ (99%, Alfa Aesar) was dissolved in 25-mL triethylene glycol (TREG) (99%, Sigma-Aldrich) with the aid of sonication. Under the protection of argon, the mixture was slowly heated to reflux (~280 °C) and kept at reflux for 30 min under vigorous stirring. After cooling down to ambient temperature, a black homogeneous colloidal suspension containing magnetite nanoparticles was obtained. The as-synthesized magnetite nanoparticles were negatively charged due to the adsorption of triethylene glycol molecules. The colloidal suspension was diluted 10 times using ethanol.

1.3. Fabrication of γ-Al_2O_3 Buffer Layer

A piece of silicon chip was cleaned using Piranha solution, washed with DI water, and dried in air. Boehmite nanoplates was assembled on the substrate using a layer-by-layer assembly process as illustrated in Scheme 1 in the main text. First, the silicon chip was immersed in a 1 g L^{-1} polyethyleneimine (PEI, MW ~25,000, Sigma-Aldrich) solution for 30 min. Second, the substrate was immersed in 1 g L^{-1} polyacrylic acid (PAA, MW ~1,800, Sigma-Aldrich) solution for 30 min. Third, the silicon chip was immersed in the boehmite suspension (see section 1.1) for 1 h. The chip was thoroughly rinsed with DI water after each step. Finally, the chip was heated to 750 ^oC at 3 ^oC min^{-1} and held for 30 min to remove organic molecules and to transform boehmite to γ-Al_2O_3.

1.4. Deposition of Magnetite Catalysts

The γ-Al_2O_3 coated silicon chip was immersed in the PEI solution for 30 min. After rinsing with water and drying in air, the chip was immersed in the magnetite nanoparticle suspension for 30 min. At the end of deposition, loosely adsorbed nanoparticles were removed by rinsing with DI water. The silicon chip was blown dry using nitrogen.

1.5. Growth of Vertically Aligned Carbon Nanotube Arrays

The silicon chip was placed in a quartz boat at the center of a 2-inch quartz tubing. The quartz tubing was then placed in a tube furnace. The furnace was ramped to 750 ^oC in air. On reaching 750 ^oC, the quartz tubing was sealed and purged using 500 sccm argon for 5 min. Subsequently, 100 sccm hydrogen was introduced to activate the catalyst. Growth of carbon nanotubes was initiated by introducing 100 sccm ethylene. A trace amount of water vapor was also introduced

to the reactor by bubbling a small amount of argon through a water tank. After 15 min of growth, the furnace was cooled to ambient temperature under argon protection.

1.6. Material Characterization

Transmission electron microscopy observation was conducted using FEI Titan 80-300 operated at 300 kV. Scanning electron microscopy was conducted using FEI Magellan 400. Atomic force microscopy was performed using a Park System XE-70 instrument. X-ray diffraction (XRD) patterns were conducted using a Bruker Advance 8 X-ray diffractometer at 40.0 kV and 120 mA with Cu-Kα radiation.

2. Characteristics of Magnetite Nanoparticles

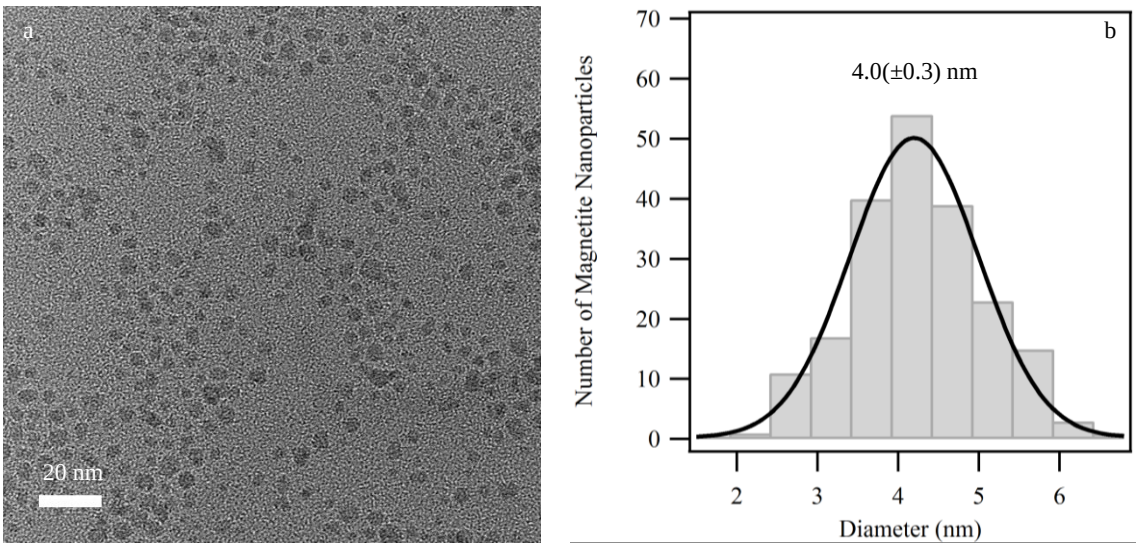

Figure S1. Transmission electron micrograph and size distribution of magnetite nanoparticles.

2. Estimation of Porosity in Annealed Nanoplates

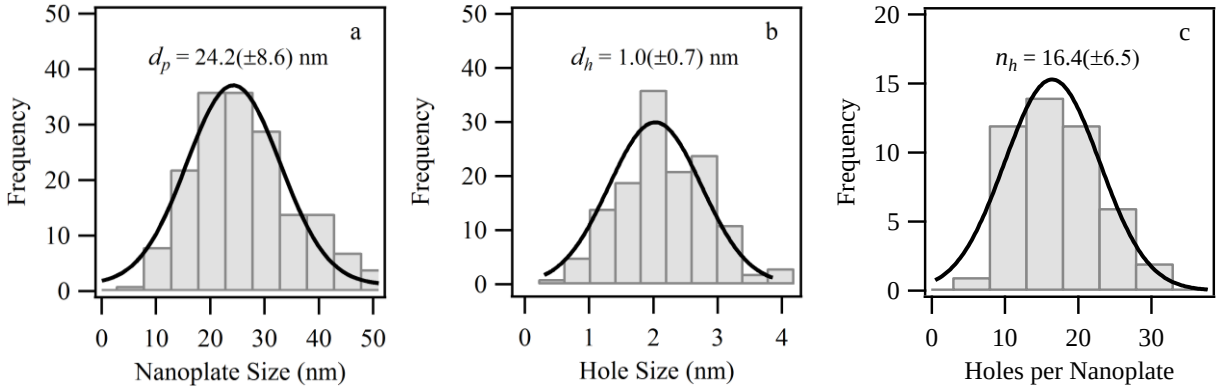

Figure S2. Statistical analyses of (a) the nominal diameter of annealed nanoplates, (b) the nominal diameter of holes in annealed nanoplates, and (c) the number of holes per nanoplate. Porosity is defined as $\theta = n_h d_h^2/d_p^2$. Because of the large uncertainty associated with the estimate of d_p, d_h, and n_h, θ is estimated to be 2.8(±6.1)%. This estimate may be interpreted as (1) nearly all nanoplates have holes because 2.8% – 6.1% < 0 and (2) with a 95% confidence, the porosity is less than 2.8% + 1.66×6.1% = 12.9%.

3. Vertically Aligned Carbon Nanotube Arrays Grown on Silicon Chip Prepared Using E-Beam

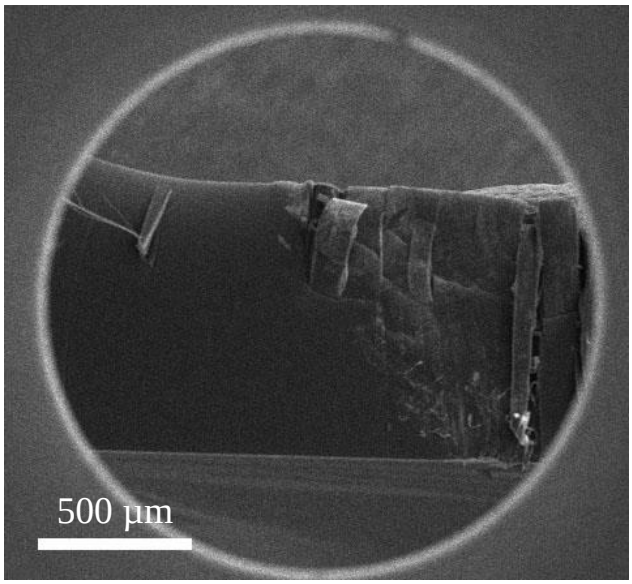

Figure S3. Long vertically aligned carbon nanotube arrays prepared on a silicon chip with buffer and catalyst layers deposited using e-beam. The buffer layer was 20-nm thick Al_2O_3 and the catalyst was 1.5-nm thin Fe. They were deposited onto the chip sequentially at 1×10^{-6} Torr in an electron beam evaporator (Denton Explorer). The thicknesses of buffer and catalyst layers were controlled by deposition times. The deposition rates used to calculate the thicknesses were calibrated using a quartz crystal monitor, which were measured at 0.5 nm s^{-1} for Al_2O_3 and 0.0333 nm s^{-1} for Fe. VA-CNT arrays were grown using the same CVD parameters as for Al_2O_3/magnetite-decorated silicon chips prepared using the wet chemistry-based method that we report in this *Letter*. Details are described in Section 1.5 on Page S2.