

## LETTERS

### Diameter-Controlled Synthesis of Discrete and Uniform-Sized Single-Walled Carbon Nanotubes Using Monodisperse Iron Oxide Nanoparticles Embedded in Zirconia Nanoparticle Arrays as Catalysts

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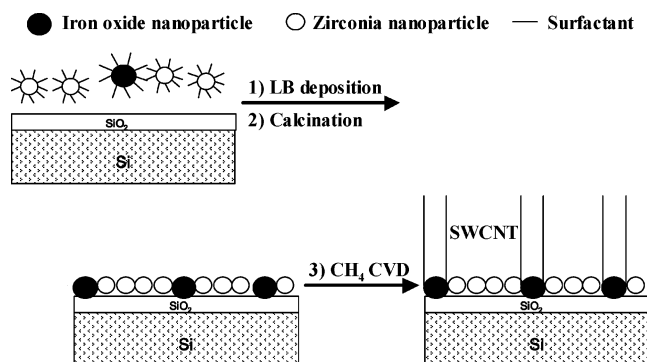
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Discrete single-walled carbon nanotubes (SWCNTs) with uniform diameters of 3.0 and 1.8 nm were synthesized using binary arrays that were composed of monodisperse zirconia nanoparticles with a particle size of 2.0 nm and monodisperse iron oxide nanoparticles with particle sizes of 3.3 and 1.8 nm as catalysts for chemical vapor deposition of methane. The agglomeration of iron oxide nanoparticles during the SWCNT growth was prevented by embedding the active catalyst nanoparticles in an inactive zirconia nanoparticle matrix.

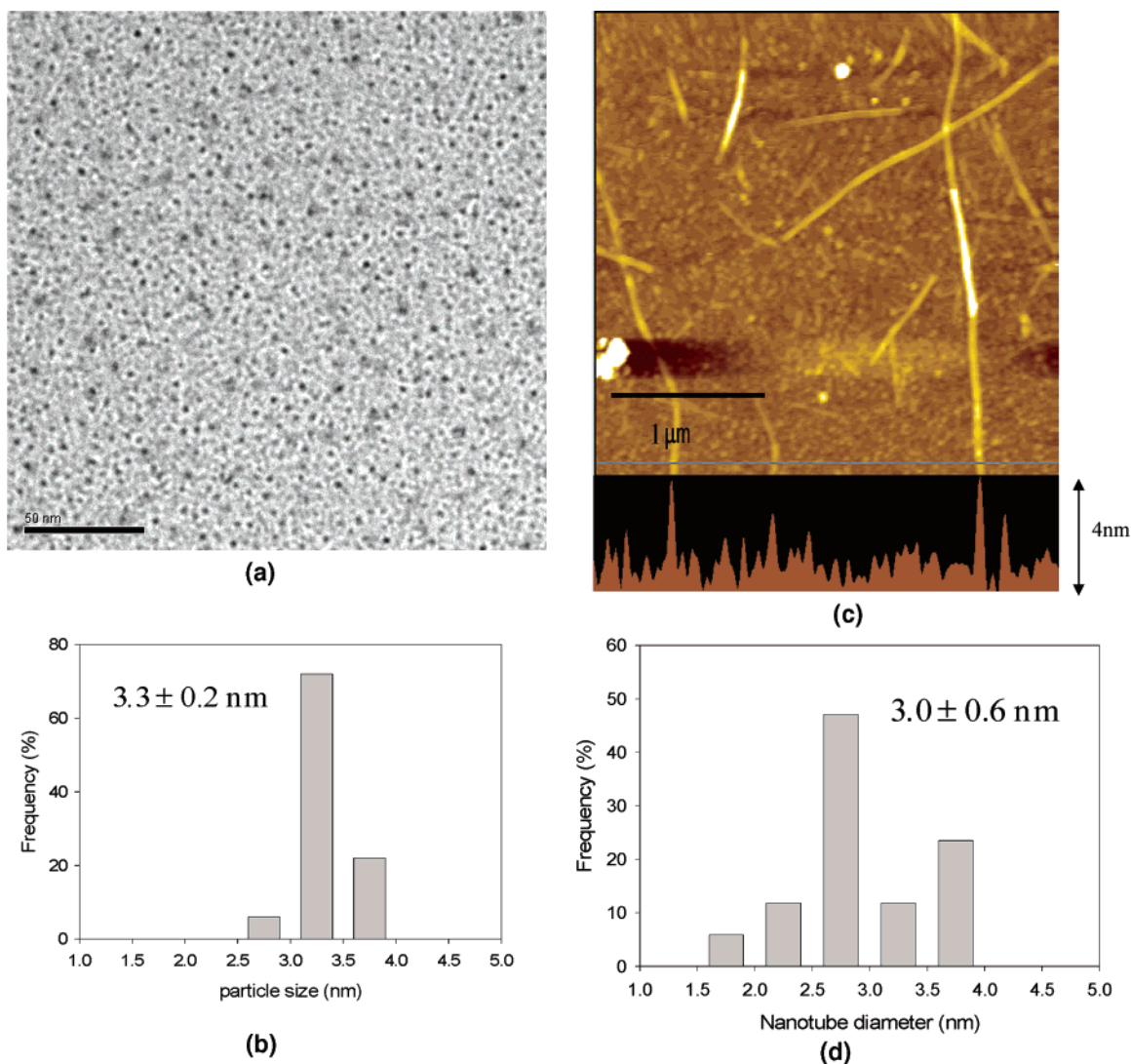
Since the first report by Iijima in 1991,<sup>1</sup> carbon nanotubes have attracted tremendous attention for their many potential applications, including use as electron field emitters for flat panel displays, nanometer-sized electronic devices, electrochemical devices, and nanoscopic sensors, and nanocomposites.<sup>2</sup> Recently, single-walled carbon nanotubes (SWCNTs) have been intensively investigated for their possible applications in nanoscale electronic devices such as single electron transistors and light-emitting diodes (LEDs).<sup>3</sup> For these applications, the synthesis of discrete and uniform SWCNTs is critical, because their electronic properties are dependent on diameter and helicity.<sup>4</sup> Among the various synthetic methods used for SWCNTs, chemical vapor deposition (CVD) that uses transition-metal nanoparticles as catalysts has been successfully applied to synthesize SWCNTs.<sup>5</sup> The diameters of the SWCNTs grown by catalytic CVD process are known to be determined by the diameters of the transition-metal catalyst particles. Several groups reported on the diameter-controlled synthesis of SWCNTs.

#### SCHEME 1: Schematic Representation of the Synthetic Procedure: (1) LB Deposition of Binary Nanoparticle Array, (2) Calcination to Remove Surfactant, (3) CH<sub>4</sub> CVD Process.

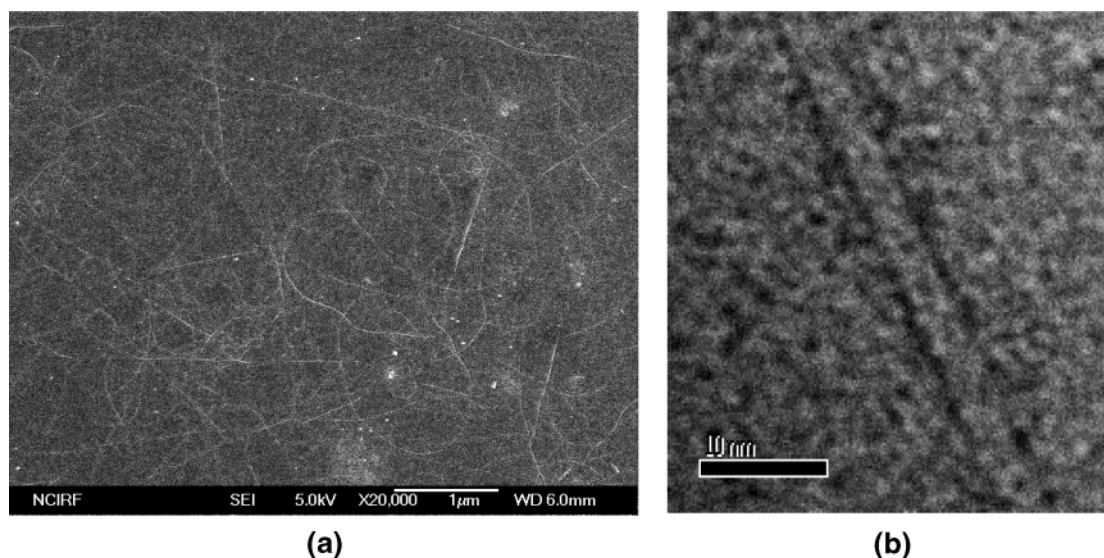


For example, Dai and co-workers reported relatively uniform-sized SWCNTs using iron oxide nanoparticles synthesized using ferritin or dendrimer complexes as catalyst precursors.<sup>6</sup> Liu and

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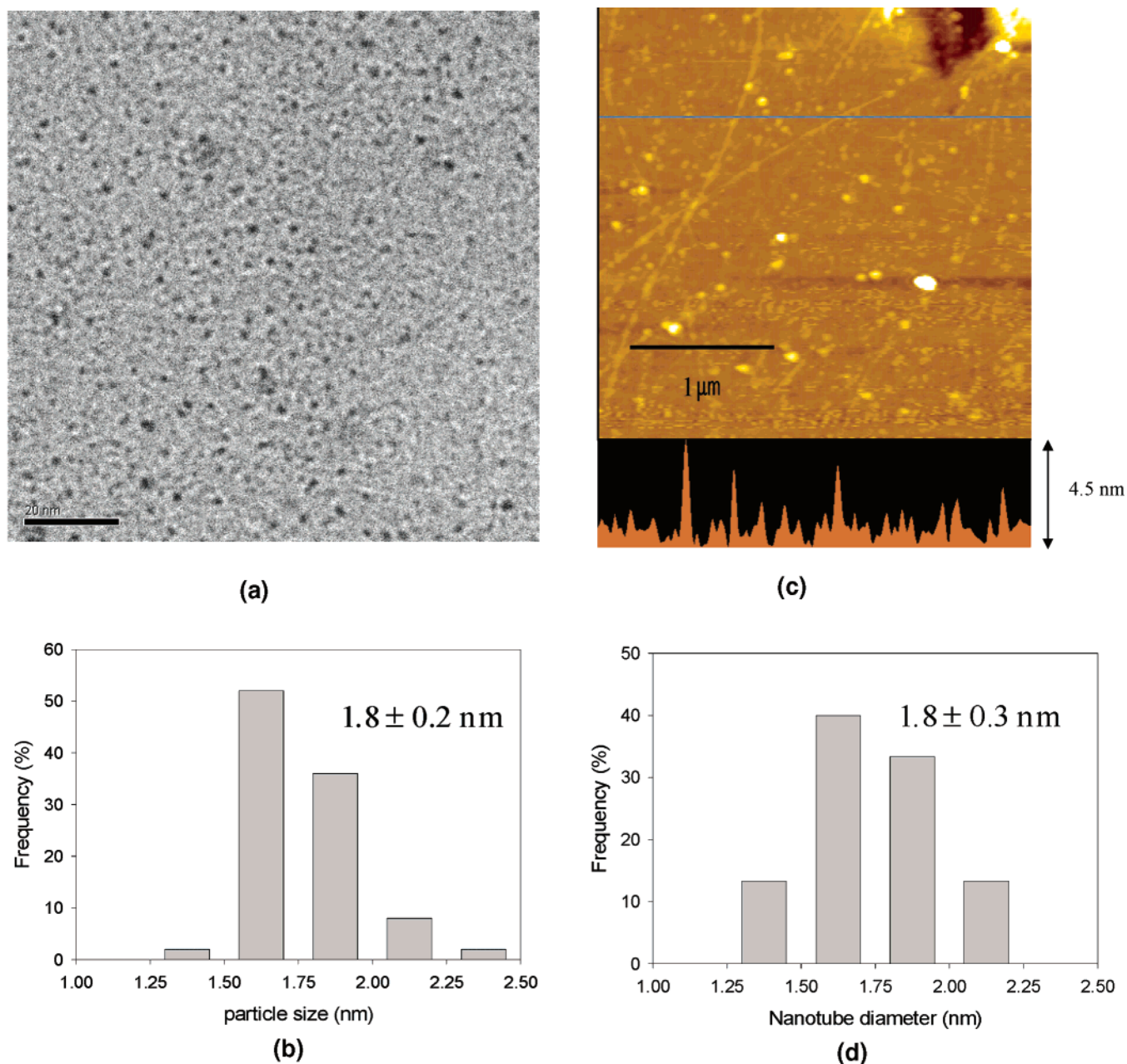


**Figure 1.** (a) Transmission electron microscopy (TEM) image of binary array consisting of 3.3-nm iron oxide and 2.0-nm zirconia nanoparticles deposited on a  $\text{SiO}_2/\text{Mo}$  grid after methane chemical vapor deposition (CVD). (b) Size distribution of iron oxide nanoparticles. (c) Atomic force microscopy (AFM) images of single-walled carbon nanotubes (SWCNTs) grown on binary arrays consisting of 3.3-nm iron oxide and 2.0-nm zirconia nanoparticles deposited on a  $\text{SiO}_2/\text{Si}$  wafer. (d) Diameter distribution of SWCNTs grown using a binary nanoparticle mixture consisting of 3.3-nm iron oxide and 2.0-nm zirconia nanoparticle as catalysts.



**Figure 2.** (a) Field emission scanning electron microscopy (FE-SEM) image of SWCNTs grown on binary array consisting of 3.3-nm iron oxide and 2.0-nm zirconia nanoparticles deposited on a  $\text{SiO}_2/\text{Si}$  wafer. (b) HRTEM image of SWCNT grown on a binary array consisting of 3.3-nm iron oxide and 2.0-nm zirconia nanoparticles.

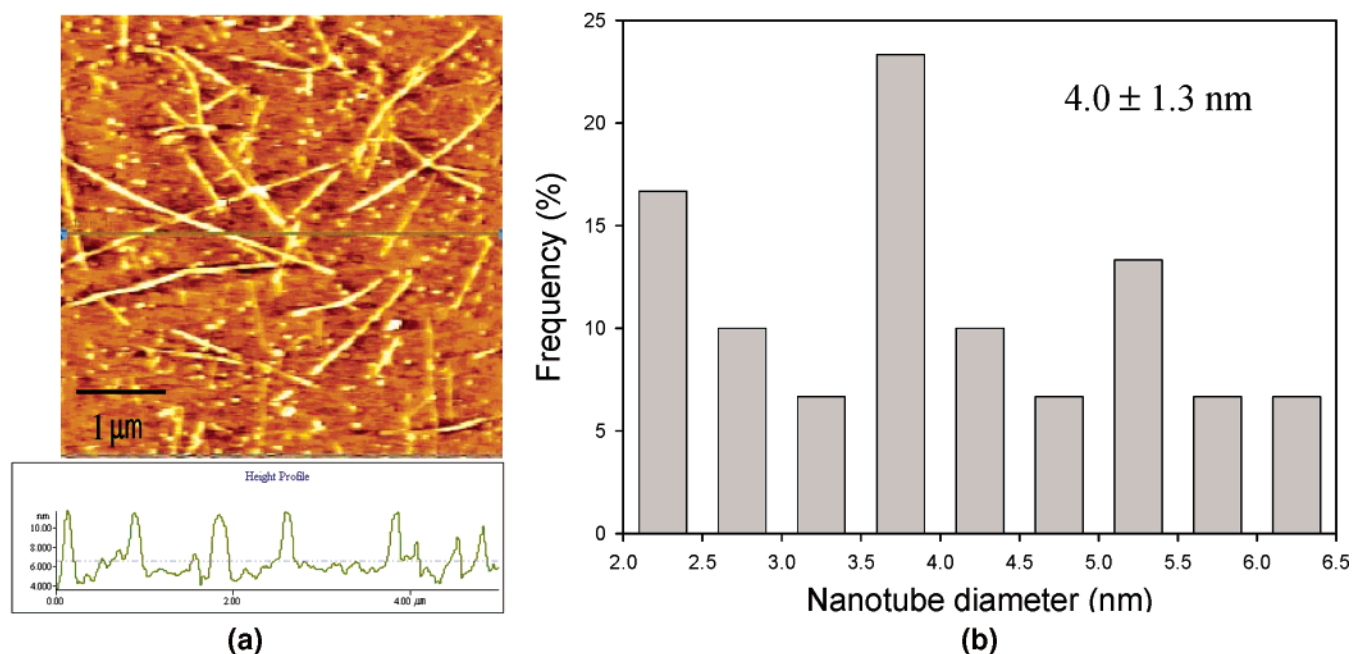




**Figure 3.** (a) TEM image of a binary array consisting of 1.8-nm iron oxide and 2.0-nm zirconia nanoparticles deposited on a  $\text{SiO}_2/\text{Mo}$  grid after methane CVD. (b) Size distribution of iron oxide nanoparticles. (c) AFM images of SWCNTs grown on binary arrays consisting of 1.8-nm iron oxide and 2.0-nm zirconia nanoparticles deposited on a  $\text{SiO}_2/\text{Si}$  wafer. (d) Diameter distribution of SWCNTs grown using a binary nanoparticle mixture consisting of 1.8-nm iron oxide and 2.0-nm zirconia nanoparticle as catalysts.

co-workers used Fe/Mo-containing molecular nanoclusters as the catalyst for the synthesis of uniform SWCNTs.<sup>7</sup> Park, Lieber, and their co-workers demonstrated the diameter-controlled synthesis of carbon nanotubes (CNTs) using iron nanoparticles with variable sizes.<sup>8</sup> Our research group developed new synthetic procedures to produce monodisperse nanoparticles of metals, oxides, and sulfides, including iron oxide nanoparticles, from the thermal decomposition of metal–surfactant complexes.<sup>9</sup> We tried the diameter-controlled synthesis of uniform CNTs using monodisperse iron oxide nanoparticles deposited on an oxidized silicon substrate. However, we obtained CNTs with various diameters, because the agglomeration of nanoparticles occurred during the synthesis. In our current method, we used a binary array that was composed of monodisperse nanoparticles of iron oxide and zirconia as catalysts for the CVD growth of SWCNTs.

The overall synthetic procedure is described in Scheme 1. A monolayer array composed of iron oxide and zirconia nanoparticles on an oxidized silicon wafer was generated using a Langmuir–Blodgett (LB) trough. The key idea of the current report is the prevention of the agglomeration of iron oxide nanoparticles during the SWCNT growth by embedding active catalyst particles in an inactive zirconia nanoparticle matrix. To demonstrate diameter-controlled synthesis, we have used iron oxide nanoparticles 1.8 and 3.3 nm in size as catalysts. In the previous reports, it is well-known that catalyst particles  $<5$  nm in size are necessary to synthesize SWCNTs. Monodisperse nanoparticles of iron oxide and zirconia nanoparticles were synthesized using our previously reported synthetic procedures after some modifications. (Detailed experimental procedure is supplied in the Supporting Information.) Transmission electron



**Figure 4.** (a) AFM images of SWCNTs grown on 1.8-nm iron oxide deposited on a SiO<sub>2</sub>/Si wafer via spin coating. (b) Diameter distribution of SWCNTs grown on 1.8-nm iron oxide deposited on a SiO<sub>2</sub>/Si wafer via spin coating.

microscopy (TEM) images (see Supporting Information) of the as-synthesized iron oxide nanoparticles showed a two-dimensional close-packed pattern, demonstrating the uniformity of the particles. The corresponding particle size distribution, shown in Figure 1b, revealed that the iron oxide nanoparticles are monodisperse with a particle size of  $3.3 \pm 0.2$  nm. Smaller iron oxide nanoparticles (with particle size of  $1.8 \pm 0.2$  nm) were also synthesized (see Supporting Information). Zirconia nanoparticles with a particle size of  $2.0 \pm 0.2$  nm were synthesized (see Supporting Information). Deposition of the mixture composed of nanoparticles of iron oxide and zirconia was conducted using a KSV 3000 Langmuir–Blodgett (LB) trough. A hexane solution that contained a mixture of zirconia and iron oxide nanoparticles with a particle concentration ratio of  $\sim 20:1$  was spread on a water surface using a microsyringe. The compression rate of the film was 2 mm/min, and the resulting compressed film was transferred onto an oxidized silicon wafer and a silica-coated molybdenum TEM grid at the surface pressure of 5 mN/m. Surfactant adsorbed on the nanoparticles was removed by treating the wafer deposited with the mixture of nanoparticles at 550 °C for 30 min under flowing air. The growth of SWCNTs was performed by flowing 1500 sccm of methane and 200 sccm of hydrogen on the catalyst array at 900 °C for 30 min. (The unit “sccm” denotes standard cubic centimeters per minute.) Figure 1a exhibited the TEM image of the mixture of iron oxide and zirconia nanoparticles deposited on a silica-coated molybdenum grid after the CVD process. It was clearly observed that the iron oxide nanoparticles were well-separated and scattered among zirconia nanoparticles, and the size uniformity of iron oxide nanoparticles was preserved, even after the CVD process. The atomic force microscopy (AFM) image and the corresponding diameter distribution of SWCNTs by measuring the heights of nanotubes are shown in Figure 1c and Figure 1d, respectively. The AFM image and field-emission scanning electron microscopy (FE-SEM) images (Figure 2a) showed that SWCNTs are well-separated, and they are uniform in diameter, with a value of  $3.0 \pm 0.6$  nm, demonstrating that discrete iron oxide nanoparticles were successfully applied as

the catalysts for SWCNT growth. The high-resolution transmission electron microscopy (HRTEM) image of a single SWCNT (see Figure 2b) showed that the synthesized SWCNT has clean sidewalls without an amorphous carbon coating. When smaller iron oxide nanoparticles (with a particle size of  $1.8 \pm 0.2$  nm) were used as the catalyst (Figure 3a), SWCNTs with a uniform diameter of  $1.8 \pm 0.3$  nm (see Figure 3c) were synthesized. When we deposited only iron oxide nanoparticles on a SiO<sub>2</sub>/Si wafer via simple spin coating, extensive agglomeration of the nanoparticles occurred, resulting in the synthesis of CNTs with a broad diameter distribution. Figure 4a shows the AFM image of SWCNTs grown on iron oxide nanoparticles 1.8 nm in size that were deposited on the SiO<sub>2</sub>/Si wafer, exhibiting an abundant formation of SWCNTs. However, the diameter distribution of SWCNTs was much broader ( $4.0 \pm 1.3$  nm) and the average diameter was much larger than that of the iron oxide nanoparticles. The results clearly demonstrated that the prevention of the agglomeration of iron oxide nanoparticles by mixing with zirconia nanoparticles was critical for the synthesis of uniform-sized SWCNTs.

In conclusion, discrete SWCNTs with uniform diameters of 3.0 and 1.8 nm were synthesized using binary arrays that were composed of zirconia nanoparticles 2.0 nm in size and iron oxide nanoparticles with particle sizes of 3.3 and 1.8 nm as catalysts for methane CVD.

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**Supporting Information Available:** Details for the synthesis of iron oxide and zirconia nanoparticles; TEM image of iron oxide nanoparticles and FE-SEM image of SWCNTs; SEM image of CNTs synthesized using iron oxide nanoparticles stabilized with oleic acid and zirconia nanoparticles stabilized with trioctylphosphine oxide as catalysts. (PDF.) This material is available free of charge via the Internet at <http://pubs.acs.org>.

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