

## Growth of carbon nanotubes on a gold (111) surface using two-dimensional iron oxide nano-particle catalysts derived from iron storage protein

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We report here the preparation of two-dimensional iron oxide nano-particles from the iron storage protein ferritin immobilized on a gold surface. This paper also reports the novel finding of the lattice-oriented like growth of carbon nanotubes on a gold (111) surface using the obtained two-dimensional iron oxide nano-particles on the gold surface as a catalyst.

Since their discovery in 1991, carbon nanotubes have been one of the most actively studied materials because of their many unique properties for not only fundamental studies of atomically ordered materials, but also as promising materials for technological applications.<sup>1,2</sup> Their unique electronic properties make these nanotubes ideal candidate materials for nano-electronic components. For the development of nano-electronic devices, controlled synthesis methods to obtain ordered carbon nanotubes while controlling the location and orientation of the nanotubes are required. Recently, the lattice-oriented growth of carbon nanotubes on Si (111) and Si (100) surfaces has been reported.<sup>3</sup> This oriented growth behavior of the carbon nanotubes demonstrated one possible solution for the synthesis of nanotubes with controlled position and orientation directly on a surface.

The protein engineering of viral cages for constrained nanomaterial synthesis is an attractive research field.<sup>4,5</sup> The formation of solids in biological systems, biomineralization, has provided inspiration for the controlled formation of inorganic materials. Ferritin, an iron-storage protein, is a potential candidate for protein engineering for nanomaterials synthesis.<sup>6,7</sup> The iron uptake and release mechanisms of ferritin are caused by the oxidation and reduction of iron ions (Fe(II)/Fe(III)) in the protein shell.<sup>8–10</sup> The structure of the ferritin core is (FeOOH)<sub>8</sub>(FeOPO<sub>3</sub>H<sub>2</sub>), which is ferrihydrite phosphate. The inner and outer diameters of the protein shell are *ca.* 6 and 12 nm, respectively.<sup>8–10</sup> Recently, the direct electrochemistry of ferritin adsorbed onto tin-doped indium oxide and onto self-assembled mono layers (SAMs)-modified gold electrodes was investigated.<sup>11–13</sup>

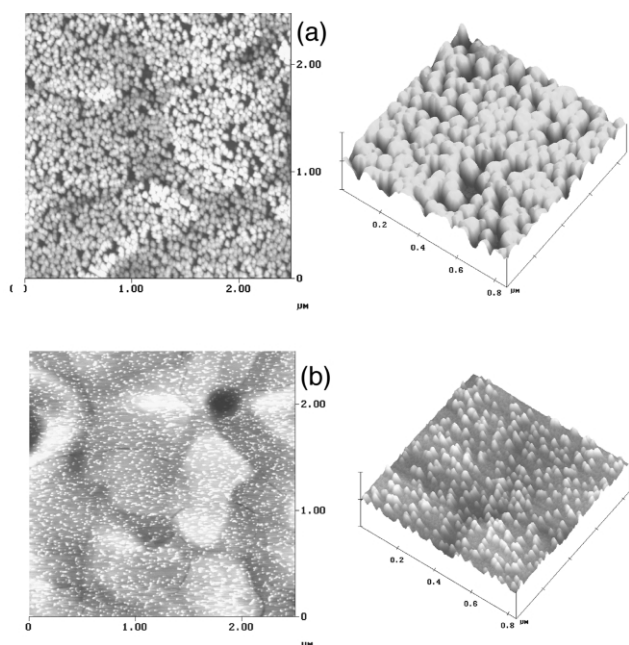
In this study, the fabrication of two-dimensional iron oxide nano-particles based on a ferritin core is reported. Furthermore, we used the iron oxide nano-particles as a catalyst for the synthesis of a carbon nanotube by the chemical vapor deposition (CVD) method. The lattice-oriented like growth of a carbon nanotube on an Au (111) surface was observed. Only the lattice-oriented growth of a carbon nanotubes on a silicon surface has been previously reported. Our obtained result indicates that the lattice-oriented like growth of carbon nanotubes can be demonstrated at not only silicon surfaces, but also on other materials such as gold surfaces. Furthermore, the results support the use of ferritin for constrained nanomaterial synthesis, and demonstrate one possible solution for the synthesis of nanotubes with controlled position and orientation directly on a surface.

Horse spleen ferritin (Sigma) was purified by size exclusion chromatography to remove free iron ions using a Sephadex G-25 column.<sup>10</sup> The SAMs used were 2-aminoethanethiol (AET, 95%, Tokyo Kasei), 6-amino-1-hexanethiol (AHT, 90%, Dojin Chem. Co., Japan), 8-amino-1-octanethiol (AOT, 90%, Dojin Chem. Co.), and 11-amino-1-undecanethiol (AUT, 90%, Dojin Chem. Co.). Water was purified with a Millipore Milli-Q water system. The substrate of gold thin film on mica (Au/mica) was prepared by the vapor deposition of 200 nm of gold (99.999% purity) onto freshly cleaved mica sheets (Nilaco Co., Japan) at a reduced pressure, < 0.1 × 10<sup>-6</sup> Torr. The cyclic voltammograms of the gold thin film surface on mica observed in 0.01 mol dm<sup>-3</sup> HClO<sub>4</sub> solution indicated that the gold surface was enriched with Au(111) facets.<sup>14</sup> The pretreated Au/mica electrode surface was then modified with the SAMs of AET, AHT, AOT and AUT according to methods described in previous papers.<sup>12,13</sup> To immobilize ferritin onto the SAMs, the SAMs-modified gold electrodes were immersed into a phosphate buffer solution (pH 7, μ = 0.1) of 2 μmol dm<sup>-3</sup> ferritin for 60 min. The CVD growth of carbon nanotubes was synthesized in a quartz tube (diameter of 40 mm, volume of 500 ml) equipped with temperature and gas flow controls. The sample was first reduced in H<sub>2</sub> for 30 min at 600 °C, and then a mixture of methane (99.999%) and H<sub>2</sub> gas was introduced into the system with a flow rate of 500 ml min<sup>-1</sup> methane and 500 ml min<sup>-1</sup> H<sub>2</sub> at 600 °C for 10 min. After this reaction, the mixture gas was replaced by H<sub>2</sub> and annealed at 600 °C for 30 min. Tapping mode AFM images were obtained under air atmosphere.

In previous studies, we reported that ferritin was immobilized onto amino terminal alkane thiols-modified gold electrodes by the electrostatic interaction between ferritin and the terminal functional group of SAMs.<sup>12,13</sup> The AFM and QCM results indicated that the ferritin molecule was packed like a full monolayer, which did not depend on the chain length of the amino terminal alkane thiols. To fabricate two-dimensional nano-particles based on a ferritin core, we performed a heat treatment on the ferritin immobilized onto AET-, AHT-, AOT-, or AUT-modified Au/mica substrates. The reflection absorbance IR spectra of the resulting heat treatment of ferritin immobilized onto AHT-modified gold substrates for 60 min at various temperatures under air atmosphere. Before the heat treatment, signals at approximately 1667 and 1545 cm<sup>-1</sup> corresponding to the amide I and II bands, respectively, were observed, which are specific for the peptide bond in the protein. However, the intensities of these signals decreased with increasing heat treatment temperature. Eventually, the signals corresponding to amide I and II disappeared completely after heat treatment at 400 °C for 60 min. This result clearly indicated that the ferritin shells composed of amino acids were eliminated. The elimination of the SAMs on the gold surfaces was also indicated by the FTIR analysis.

Fig. 1(a,b) shows typical AFM images before and after the heat treatment for ferritin immobilized onto an AHT-modified gold electrode at 400 °C for 60 min. Before the heat treatment, ferritin molecules immobilized onto the whole gold electrode surface were observed as shown in Fig. 1(a). The size of each ferritin molecule was evaluated to be approximately 13 (±2) nm in diameter in the xy-plane and the z-plane thickness after accounting for distortions

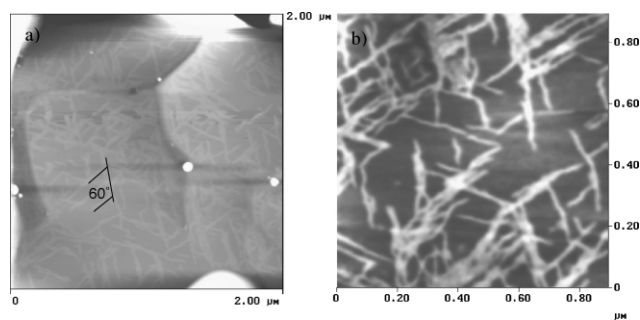
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**Fig. 1** Tapping mode AFM images before (a) and after (b) heat treatment at 400 °C for 60 min for ferritin immobilized onto an AHT-modified Au(111) surface.

due to the shape of the probe tip,<sup>15</sup> which is comparable to the expected ~12 nm diameter determined by X-ray diffraction.<sup>8,9</sup> After the heat treatment, two-dimensional nano-particles derived from the ferritin core covered the whole gold electrode surface as shown in Fig. 1(b). The results of X-ray photoelectron spectroscopy showed that the nano-particles on the gold surface consisted of iron species.<sup>16</sup> This result together with the results of previous papers indicated that the nano-particles observed were iron oxide.<sup>5,7</sup> Taking into account the distortions due to the shape of the probe tip, the size of each iron oxide nano-particle was evaluated to be approximately 6 ( $\pm 2$ ) nm in diameter. These results also indicate that the protein shell of ferritin was eliminated by the heat treatment. The results of the FTIR analysis and AFM images obtained were the same as the AHT-modified gold electrode even if AET-, AOT- and AUT-modified gold electrodes were used. Our simple method combined with the self-assembly of the protein is useful for the fabrication of two-dimensional nano-dot arrays onto a flat surface.

Carbon nanotubes were synthesized by the CVD method using the prepared iron oxide nano-particles as a catalyst.<sup>6,7</sup> First, we tried to synthesize a carbon nanotube on a silicon surface using iron oxide obtained from ferritin as catalyst. Raman spectroscopy measurement with 514.5 nm excitation was carried out after the synthesis process. The Raman shift peaks at approximately 1352 and 1580  $\text{cm}^{-1}$  were observed, which indicated that the nanotubes were synthesized.<sup>2</sup> Next, we synthesized carbon nanotubes using two-dimensional iron oxide nano-particles based on a ferritin core. Fig. 2 shows the AFM images of the carbon nanotubes on an Au (111) surface. Both individual carbon nanotubes and bundled carbon nanotubes due to their adhesive interactions were observed on the gold surface. The AFM images provide two pieces of evidence. First, the diameter of individual carbon nanotube was evaluated to be approximately 6 ( $\pm 2$ ) nm in the xy-plane and the z-plane thickness, which is in good agreement with the diameter of iron oxide obtained ferritin core. This result indicates that the diameter of carbon nanotube can be controlled by the ferritin core



**Fig. 2** Tapping mode AFM images (a: 2  $\mu\text{m} \times 2 \mu\text{m}$ , b: 0.9  $\mu\text{m} \times 0.9 \mu\text{m}$ ) of the lattice-oriented like growth of carbon nanotube on a gold surface.

size. Secondly, the carbon nanotube growth on the Au(111) surface takes place in three directions separated by approximately 60°. We believe that this observation reflects the influence of the Au(111) surface lattice on the growth of carbon nanotubes under our CVD conditions.

In conclusion, we demonstrated the preparation of two-dimensional iron oxide nano-particles on a gold substrate from the iron-storage protein ferritin. Furthermore, the lattice-oriented like growth of carbon nanotubes on an Au (111) surface was synthesized using the iron oxide nano-particles derived from ferritin by the chemical vapor deposition (CVD) method. These results support the possibility of using ferritin for constrained nanomaterial synthesis and one possible solution for the synthesis of nanotubes with controlled position and orientation directly on a surface.

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