Vertically-Aligned Carbon Nanotube Arrays on Fe₃O₄ Nanoparticle-Supported Silicalite-1 Monolayer†

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Monodisperse magnetic Fe₃O₄ nanoparticles with the size *ca.* 4 nm were prepared by thermal decomposition of iron(III) acetylacetonate in organic solvent under a continuous N₂ flow. These nanoparticles were spread on the silicalite-1 microcrystal-monolayer-coated silicon wafers using the simple drop-dry method as the catalysts for the synthesis of vertically-aligned carbon nanotube arrays. By a variety of characterizations, such as X-ray diffraction, scanning electron microscopy and transmission electron microscopy, the impact of catalyst size on the diameter of carbon nanotubes, were observed and discussed and so was the growth mechanism.

Key Words: Vertically-aligned, Carbon nanotubes, Zeolite, Nanoparticle, Catalyst.

INTRODUCTION

Due to their unique nanostructure-dependent physical and chemical properties, carbon nanotubes (CNTs) are the target of intense study. It is well-known that these distinctive characteristics arise from their different atomic structure and size. For instance, CNTs can be either metallic or semiconducting based on their helicity and diameter¹ and the latter can also influence their mechanical properties, thus causing a significant impact on their promising applications in many potential fields, such as nanoelectronic devices², composite materials³, hydrogen storage media⁴ and field emission devices⁵.

In this work, monodisperse Fe₃O₄ nanoparticles with the size approximately 4 nm were synthesized as the catalysts for the synthesis of CNTs by catalytic chemical vapour deposition (CCVD). The difference from others' work is that the silicalite-1 microcrystals were self-assembled onto the silicon wafers in the form of monolayer to be used as a buffer layer to support Fe₃O₄ nanoparticles. Through X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the impact of catalyst size on the diameter of CNTs were observed and discussed and so was the growth mechanism.

EXPERIMENTAL

Preparation of Fe₃O₄ nanoparticles: Monodispersed Fe₃O₄ nanoparticles were prepared by thermal decomposition

of iron(III) acetylacetonate [Fe(acac)₃] in organic solvent using a mixture of surfactant agents. In brief iron(III) acetylacetonate, 1,2-hexadecanediol, oleic acid, oleylamine and phenyl ether were mixed according to a certain molar ratio. Under a nitrogen (N₂) flow, the mixture was continuously stirred and heated to reflux for 0.5 h. The black mixture was cooled to room temperature by removing the heat source. The product was subsequently washed with ethanol, centrifuged and redispersed in hexane. TEM images of typical Fe₃O₄ nanoparticles were shown in Fig. 1.

Fig. 1. (a) High-magnification and (b) Low-magnification TEM images of synthesized Fe₃O₄ nanoparticles

Self-assembly of silicalite-1 monolayer onto the Si wafer: Silicalite-1 microcrystal monolayer was simply formed according to a previous reported procedure⁶. Briefly, Si wafers

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(1 cm × 1 cm) were thoroughly cleaned and subsequently immersed in diluted hydrofluoric solution to eliminate the oxidized surface. Then they were rinsed with distilled water and dried with a stream of high-purity N₂. For self-assembling silicalite-1 microcrystals on the Si wafer, ethanol solution of poly(ethylenimine) (PEI) was first spin-coated on it. Silicalite-1 microcrystals of ca. 5 mg were rubbed on the wafer for 30 s to form a monolayer. Mildly sonicating the coated wafer for several seconds in distilled water is necessary to remove the physically adsorbed crystals on the monolayer of silicalite-1 crystals. After that, silicalite-1-coated Si wafers were dried by N₂ and they are signified as Z/Si. XRD pattern of as-prepared silicalite-1 crystals and SEM images of them are shown in Fig. 2.

Fig. 2. (a) XRD pattern and (b) SEM image of as-prepared silicalite-1 microcrystals; (c) XRD pattern and (d) SEM image of self-assembled silicalite-1 monolayer on the Si wafer (inset shows cross-sectional view)

RESULTS AND DISCUSSION

Synthesis of vertically-aligned carbon nanotube arrays by catalytic chemical vapour deposition: To make the catalyst-supported substrate, a simple method that a drop of hexane dispersion of Fe₃O₄ nanoparticles was dropped onto Z/Si was used. The symbol of the substrate is Fe₃O₄/Z/Si. As soon as it was dried in the air, it was inserted into a horizontal electric tubular furnace. Under a Ar/H₂ atmosphere, the substrates were heated from room temperature to 973 K. After pretreatment for 10 min, C₂H₂ (10 sccm) was fed into the

furnace with the Ar/H₂ (200 sccm) flow at this temperature. C₂H₂ was then cut off and the reactor was cooled to room temperature under Ar/H₂ flow. Fig. 3 shows the SEM images of vertically-aligned carbon nanotube arrays from a cross-sectional view.

Fig. 3. Cross-sectional SEM images of vertically-aligned carbon nanotube arrays synthesized from Fe₃O₄/Z/Si (a) macro-scale view and (b) enlarged view of selected area

Conclusion

This work used a simple drop-dry method to prepare Fe₃O₄ nanoparticle-coated substrates for synthesizing vertically-aligned carbon nanotube arrays. Between Fe₃O₄ nanoparticles and the Si substrates, self-assembled silicalite-1 microcrystal monolayer was applied as the buffer layer to support Fe₃O₄ nanoparticles. Obviously, despite the disturbance of some random carbon nanotubes catalyzed from the nanoparticles directly deposited onto the Si wafer between the gaps of silicalite-1 crystals, an ensemble of vertically-aligned carbon nanotube arrays still were obtained.

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