Karman vortex street assisted patterning in the growth of silicon nanowires†

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A Karman vortex street was employed to pattern catalysts and grow nanomaterial arrays, which were made of a disk-like superstructure built of silicon nanowires; there also existed nanowires connected with the disks.

One- and two-dimensional nanomaterial arrays, ordered superstructures or complex functional architectures with controllable morphology and size are promising for application in sensors and devices because they reveal excellent collective optical, magnetic and electric properties.[1–5] Hence, patterning to produce such arrays is an area of considerable technical importance and active research, such as: noncovalent interactions,[6] magnetically programmable assembly,[4] biomolecular templates,[7] hydrophobic interactions,[1] hydrothermal methods,[8] block copolymer templates,[9] Langmuir–Blodgett technique,[10] soft templates,[11] spin coating technology,[12] and template-directed seeding growth.[13]

Herein, we introduce an original method employing a Karman vortex street to pattern catalysts and successfully grow silicon nanowire arrays with a disk-like superstructure. The Karman vortex street, an exquisite flow pattern, exists in a variety of flow situations, ranging from flow around the strings of an Aeolian harp on about a 1 millimeter scale to the swirling clouds past Alexander Selkirk Island on a scale of several hundred kilometers.[14] When a stream of fluid flows past a circular cylinder, a flow pattern, known as a Karman vortex street, develops from instability as the Reynolds number is greater than 40.[15] This pattern forms two rows on either side of the wake. All the vortices on one side rotate in the same sense, those on opposite sites in opposite senses. Longitudinally, the vortices on one side are midway between those on the other.[15] As various fluid patterns exist in nature, our efforts might open up new thinking on growing nanomaterial arrays by a new route.

The silicon nanowires integrated into the disk-like superstructure were prepared with a horizontal alumina tube in a tube furnace. The overall fabrication procedure is presented as follows: a small tin particle was placed on a Si wafer, which was located in the central zone of the alumina tube. The furnace was vacuumized to 100 Pa and then the pressure of the tube was kept at 20 000 Pa using Ar gas. When the temperature reached 900 °C, it was re-vacuumized to 100 Pa and sealed, and held for 4 h. Then the furnace was cooled to room temperature.

Fig. 1a shows the schematic diagram of a Karman vortex street. Besides two rows of vortices on either side, there exists a wake between two adjacent ones. The low magnification image in Fig. 1b reveals that the as-prepared products grow as arrays of a Karman vortex street, which has an especially uniform and ordered disk-like morphology. Here, the pre-placed Sn particle is clearly seen on the left end of the array, which served as a circular cylinder to cause the instability of the gas flow, form the Karman vortex street, and pattern the Sn catalyst. It is noteworthy that the disks are connected in turn with several silicon nanowires, which would be very useful in the fabrication of biosensors or nanodevices, such as electron transfer, optical waveguide. Typical silicon nanowire disks under high magnification (shown in Fig. 1c, 1d) show their perfect disk form with a diameter of 6 μm and the silicon nanowires connected with the two disks are clearly seen.

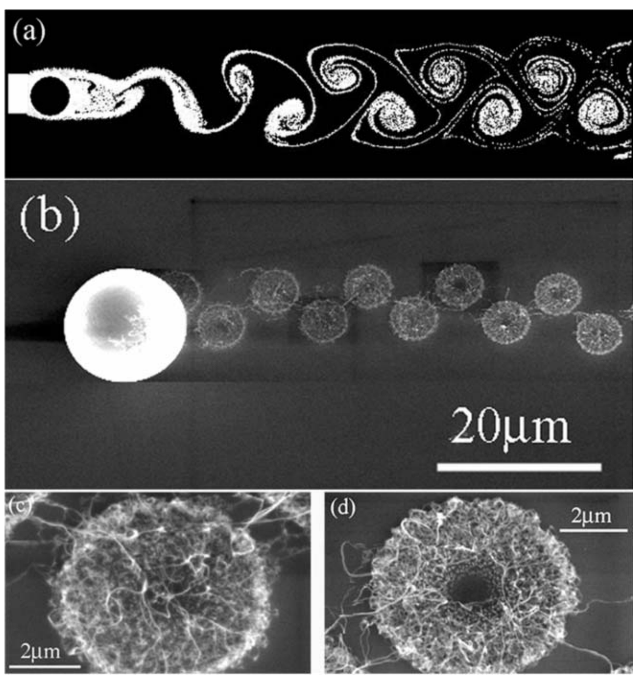

Fig. 1 Images of a Karman vortex street: (a) schematic diagram of a Karman vortex street: there exists a wake between two adjacent vortices; (b) SEM image of a silicon nanowire array with the form of a Karman vortex street in addition to the pre-placed tin particles; (c) and (d) single silicon nanowire disk – the silicon nanowires connected to the disks are clearly seen.

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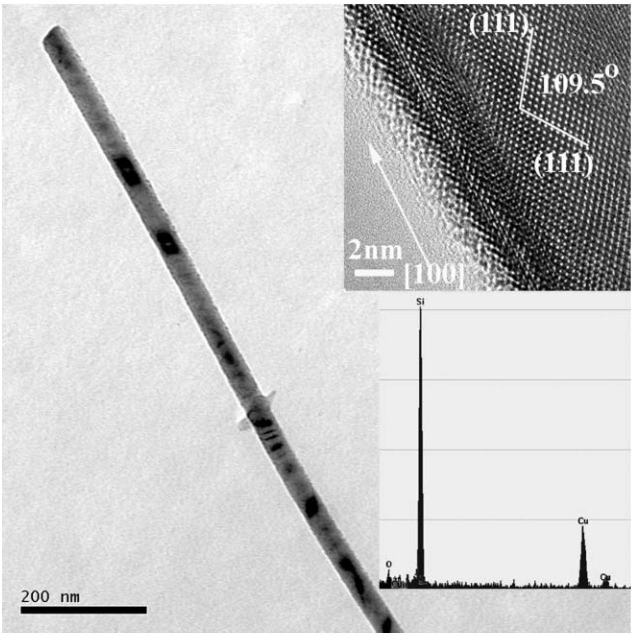

Fig. 2 TEM image of a single silicon nanowire with diameter of *ca.* 40 nm. The EDX spectrum (inset) shows its silicon nature and the HRTEM image (inset) reveals its growth direction of [100].

Fig. 2 displays the TEM image of a single nanowire with a diameter of *ca.* 40 nm after being etched with HF. The nanowire looks quite smooth and straight. EDX (Fig. 2, inset) was used to determine its chemical composition, which reveals that the nanowire is made of silicon. The appearance of copper and oxygen is attributed to the copper grid and oxygen adsorption on the surface of the silicon nanowire. On the basis of EDX, SEM and TEM results, the as-grown products basically present a high-purity material with a two-dimensional ordered superstructure composed of silicon nanowires.

High-resolution electron microscopy was employed to confirm the crystal structure of the silicon nanowire. The HRTEM image (Fig. 2, inset) shows a high degree of crystallinity with a clear crystal lattice, taken along the zone axis of the [0–11] direction, which may be indexed as (111) and (−111) planes. The growth direction of the silicon nanowire was determined as [100].

It deserves to be mentioned that the size of the disks and the distance between the disks may be tuned with operating conditions based on the intrinsic character of a Karman vortex street, which would be useful in the application of a nanomaterial array. The array may be tuned with the following operating conditions: the diameter ratio of disks to Sn particle is 0.42 ± 0.07 and the ratio of the distance between two adjacent disks to the diameter of the Sn particle is 0.53 ± 0.02. The formation of arrays of a Karman vortex street can be explained as follows: when the furnace is heated to 900 °C, the Sn particle is converted into liquid (Sn: m.p. 232 °C, b.p. 2602 °C) and a small part of it into tin vapour. This vapour is then transported by the Ar gas in the re-vacuumizing process. The important parameter of this flow process is the Reynolds number $Re = \rho ud/\mu$, where ρ, μ and u are the density, viscosity and velocity of Ar gas; d is the diameter of the Sn particle. At high Reynolds number, a Karman vortex street develops from instability. When the re-vacuumizing process is stopped, tin vapour descends to the surface of the Si wafer in the pattern of a Karman vortex street, and then forms a liquid Sn–Si alloy acting as a catalyst to grow silicon nanowires.

It is believed that tin plays a crucial role in the growth mechanism of a disk-like superstructure comprised of silicon nanowires. Tin provides a preferential surface site to dissolve silicon from the wafer and grow silicon nanowires. As the process continues, tin is slowly consumed in the growth process, whereas the silicon nanowires elongate in the direction of the radius. After the tin is completely depleted, an individual disk-like structure composed of nanowires is formed. In a similar way, the silicon nanowires connected with the disks grow from the tin catalyst existing in a wake between two vortices as shown in Fig. 1a.

When the Si wafer was treated with ultrasound and the silicon nanowires were moved away, there remained various disk-like dents as Karman vortex street arrays (see Supplementary information, Fig. S1). It is a tangible proof that the silicon nanowires come from the Si wafer.

There is also another unexpected result in this work, namely that a Karman vortex street develops at very low Reynolds number. In our case shown in Fig. 1b, u is about 1 m s^{-1}; d is about 15 μm; and the density ρ and viscosity μ of Ar gas are calculated to be 0.082 kg m^{-3} and 5.78×10^{-5} Pa·s respectively when the pressure and temperature are 20 000 Pa and 900 °C; the Reynolds number is then calculated to be 0.02, which is much lower than the usual value of 40.

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