Grafting Branches and Diameter Adjustment to Nanotubes

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Control of channel diameter and branching of a hierarchical tubular nanostructure are two essential operations for fabricating nanotubes into nanodevices such as nanochannels or nanocontainers for applications. Here, we present a thermo-evaporation approach to synthesize branching SiO nanotubes using ZnS and SiO as alternative sources. In this process, ZnS nanowires were first synthesized by Au-catalyzed vapor−liquid−solid growth as templates on which to form amorphous SiO nanotubes via evaporation of the ZnS wire core. A temperature gradient redistributed the Au nanoparticles, which catalyzed the growth of new ZnS wire branches onto the original SiO tube. Successive SiO coating and ZnS core removal would graft new branches to the original tube. The diameter of SiO nanotubes could be postprocessed by electron beam irradiation. The present template growth approach may be applicable to the formation of a nanofluidic channel network for applications in bioanalytical and chemical separations.

Introduction

Use of nanotubes to manipulate nanovessels for nanofluidics,[1–3] detection of ions and biomolecules,[4–7] and chemical reactions in the nanocavity[8] have recently attracted much attention. The basal operations for handling and implementing nanotubes as building blocks for nanoscale systems are as follows: (1) adding branches to nanotubes to create side branches and (2) adjusting the diameter of nanochannels to alternate internal tube space. In recent years, methods have been developed to synthesize nanotubes of different morphologies. For example, single- or multiwalled carbon nanotubes have been prepared using metal nanoparticles as catalysts,[9–15] inorganic nanotubes grown by rolling up thin films,[16,17] and nanotubes fabricated by coating templates with selected materials followed by template removal.[18–21] The diameter of nanostructures may be controlled by the size of catalyst particles,[13] and an aligned nanotubes array may be produced.[14,15] However, it remains difficult or impossible to add bypasses to nanotubes or to form hierarchical or branching nanostructures.

Despite its complexity, the templating approach remains a facile pathway to control the shape of nanostructures.[22] However, the morphology of the subsequent nanotubes would be mostly predetermined by the morphology of the template and difficult to alter. To change the dimension of the resultant tube, postprocessing of the nanotube using electron beam has been shown to be effective. We report in this paper a versatile strategy to fabricate branches onto tubular nanostructures and the use of an electron beam process to change tube diameter.

Experiment Details

Preparation of branching SiO nanotubes was carried out in a high-temperature alumina (Al_2O_3) tube furnace with a glass tube attached to each of the two ends of the furnace tube (Figure 1a). Inside each glass tube a sample holder (an Al_2O_3 boat with a magnet holder attached to the Al_2O_3 stick) was placed, and the holder could

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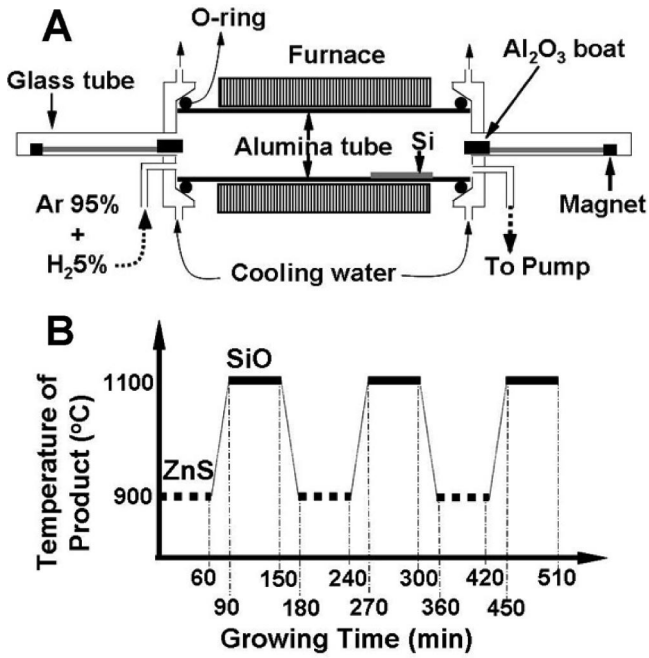

Figure 1. (A) High-temperature tube furnace with two movable sample holders for synthesis and branching of SiO nanotubes. (B) Temperature profile of the furnace tube during growth.

be moved using a movable magnet during experiment without breaking vacuum. The temperature at various spots of the high-temperature tube could be measured using a movable thermometer. SiO (Aldrich, 325 mesh, 99.9%) and ZnS (Acros, 99.99%, <10 μm) powders were loaded separately in the two sample holders. A silicon wafer coated with 100 nm Au film was placed in the low-temperature area to serve as the substrate. The furnace was evacuated to 9×10^{-3} mbar by a mechanical rotary pump. Premixed gas consisting of Ar (95%) and H_2 (5%) was then fed into one end of the Al_2O_3tube. The furnace was ramped at 50 °C/min and kept at 1150 °C and 300 mbar for 30 min.

Subsequently, ZnS and SiO sources were pushed to the high-temperature zone of 1150 and 1350 °C, respectively, and kept there for 60 min. The whole experimental process is illustrated in Figure 1b. After three cycles of growth, a dark product was obtained on the silicon wafer. The product was examined with scanning electron microscopy (SEM; Philips XL 30 FEG). Some of the sample was dispersed in ethanol and a drop of the dispersion was placed on a carbon-coated copper TEM sample grid for examination by transmission electron microscopy (TEM; Philips, CM20, operated at 200 kV) and high-resolution TEM (TEM; Philips, FEG-TEM CM200, operated at 200 kV).

Results and Discussions

SEM and TEM Characterization of SiO Nanotubes. SEM images in Figure 2a,b show that the product consists of ribbon- and wire-like nanostructures with black and white sections on the same body. Typical wire-like nanostructures have a diameter of about 100 nm and a length of tens to hundreds of micrometers. The nanostructure was further studied with TEM, and the low-resolution TEM images are shown in Figures 3a−d. These images reveal that the black section of the product is a hollow tube (Figure 3a−d). The hierarchical or branching structure of the nanotube can be clearly observed in Figure 3c,d. The branches are connected to the main body or trunk without any internal blockages,

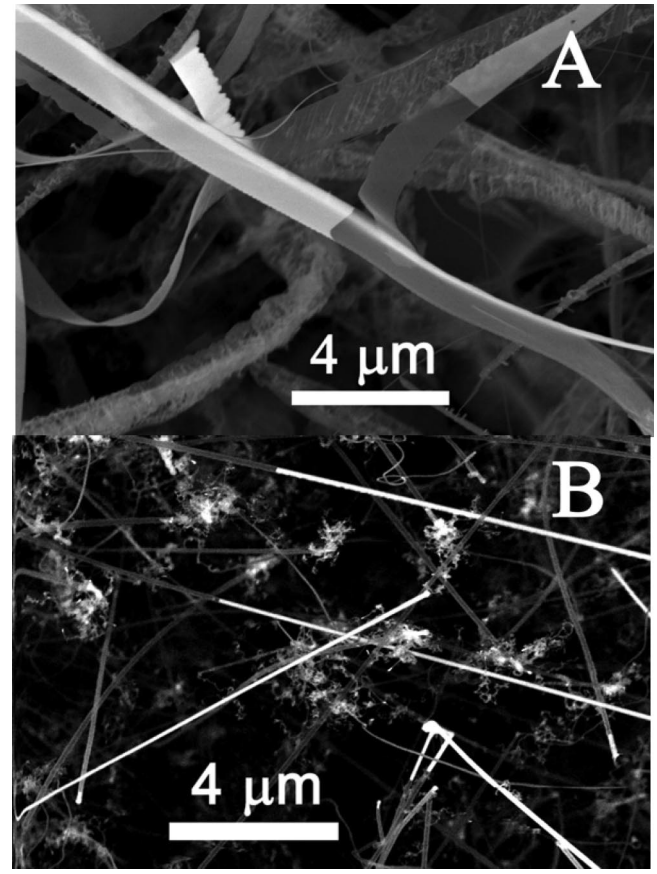

Figure 2. SEM images of the as-prepared sample showing ribbon- and wire-like nanostructures.

and the branches and trunk are both smooth and almost of the same diameter. Branches can grow in different directions from the same trunk (Figure 3c) or connect to each other, forming a network (Figure 3d).

Figure 4a is the TEM image of the white section of the product, showing the core−shell structure and a spherical tip at the end of the nanostructure. An energy dispersive X-ray (EDX) spectrometer attached to the TEM confirmed the elemental and stoichiometric composition of SiO for the shell, ZnS for the core, and Au for the spherical particle (results are not shown). The composition is similar to that found in the ZnS/SiO_x nanocable structure.[23] High-resolution TEM (HRTEM) characterization further confirmed that the ZnS core is single crystalline and grows along the [001] direction (Figure 4b). The HRTEM image reveals that the SiO shell is amorphous with a thickness of about 20 nm, and it shows the distinctive boundary between the core and shell.

Production and Branching of SiO Nanotubes. The formation of the hierarchical nanotube structure is supposed to follow a coating-and-template removal process, as reported previously.[23] The single-crystal ZnS nanowires were first formed by Au-catalyzed vapor−liquid−solid (VLS) process at 900 °C. Afterward, the source was switched to SiO, and SiO vapor would then coat the preformed ZnS nanowires, forming a porous polycrystalline SiO layer. As the growth

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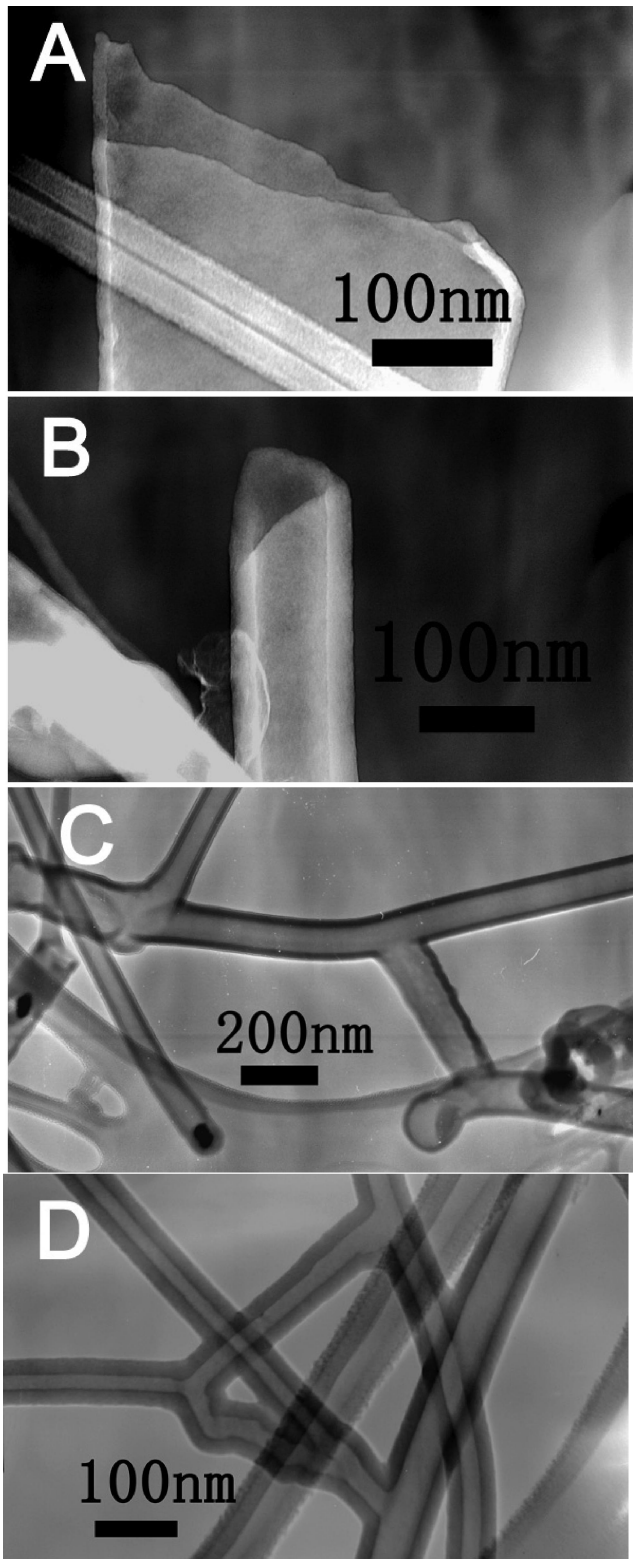

Figure 3. TEM images of nanotubes showing the branches.

temperature for the SiO shell was 1100 °C, the ZnS nanocrystal core would decompose into gaseous Zn and S, which would evaporate through the open end or the porous wall of the tube, transforming the SiO shell to a tube.

While the traditional template approach can form a nanocable or nanotube, it is not possible to graft branches onto the tube body to form a hierarchical structure. In this

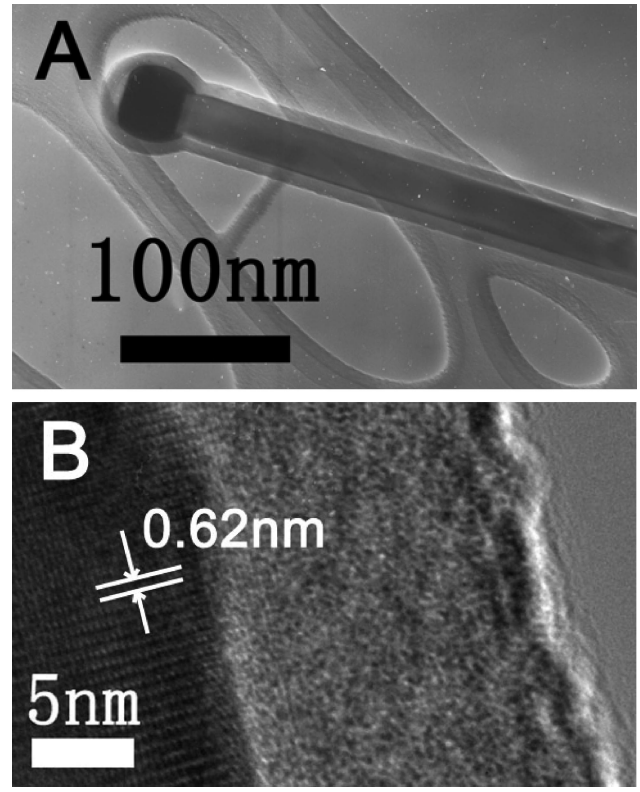

Figure 4. (A) Low-resolution TEM image and (B) high-resolution TEM image of the white section of the sample.

work, we find that branches can be introduced to the nanostructure via reactivation of Au particles to direct the growth of new ZnS nanowires. Figure 5a−d shows the TEM images of Au particles inside the nanotubes. These images clearly reveal the moving process of the Au particles from the spherical tip to the middle of the nanotube. Movement of the molten metal inside a nanotube driven by a temperature gradient has been observed[24,25] previously and was attributed to expansion and contraction of liquid inside a channel. The moving process is influenced by the viscosity of liquid metal; when the viscosity is large, the liquid metal may break into segments due to volume contraction as shown in Figure 5c.[26] Figure 5d shows a nanotube with an Au nanoparticle at the tip of a branch. The presence of Au nanoparticles inside the tube indicates that branch growth originated from the internal Au segments since ZnS nanowires, once formed, would be covered by SiO immediately and would have no opportunity to obtain Au particles from the outside.

Based on the TEM results and the discussion above, we propose the synthesis and branching process of the SiO hierarchical nanostructure as shown schematically in Figure 6.

(1) Formation of ZnS nanowires: In the growth zone (900 °C), ZnS nanowires are grown with Au catalyst following the metal-catalyst VLS process (Figure 6a).

(2) Formation of the SiO shell and removal of the ZnS template core: When ZnS source is replaced by SiO

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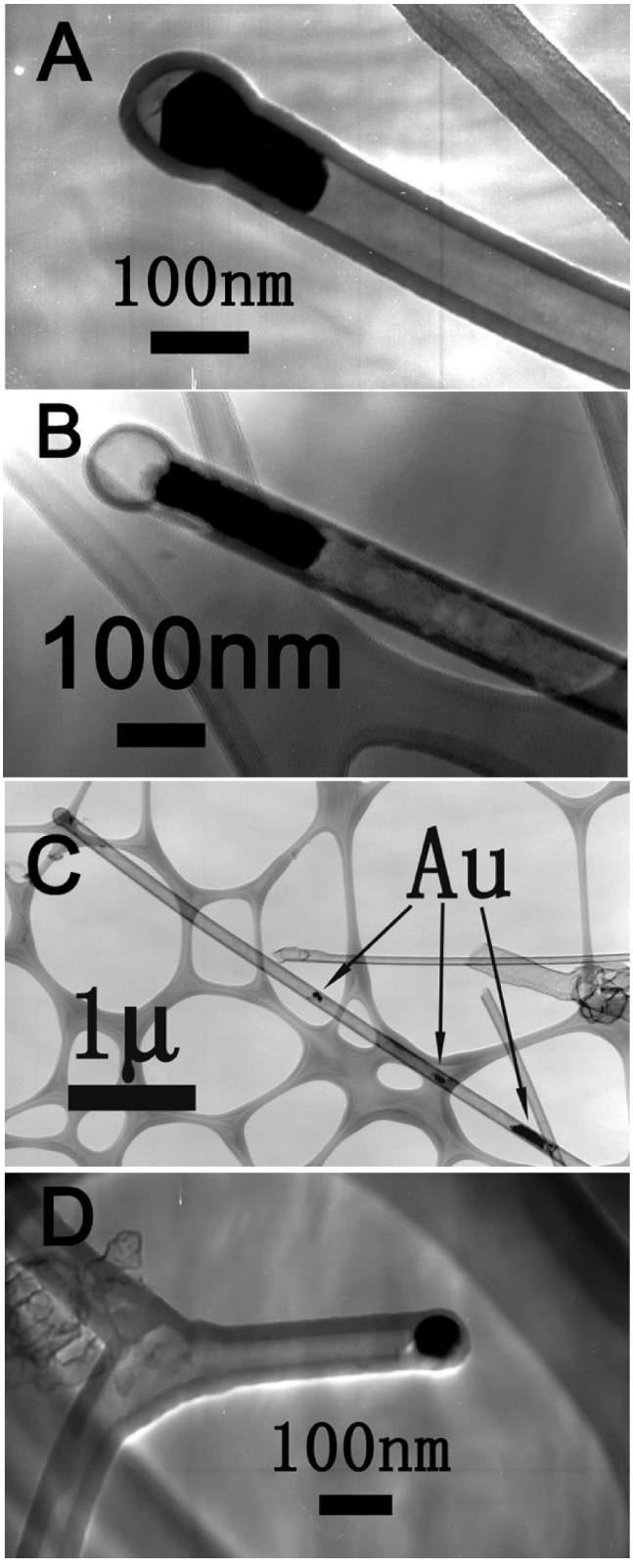

Figure 5. TEM images of nanotubes containing Au particles.

source and the tube temperature is increased to 1100 °C, ZnS nanowires are coated with a porous SiO shell. At 1100 °C ZnS template would decompose into gaseous Zn and S, which would evaporate from the open end or through the porous SiO shell. Tubes would form only if decomposition of ZnS and vaporization of Zn and S take place after the SiO shell is formed on the ZnS template (Figure 6b).

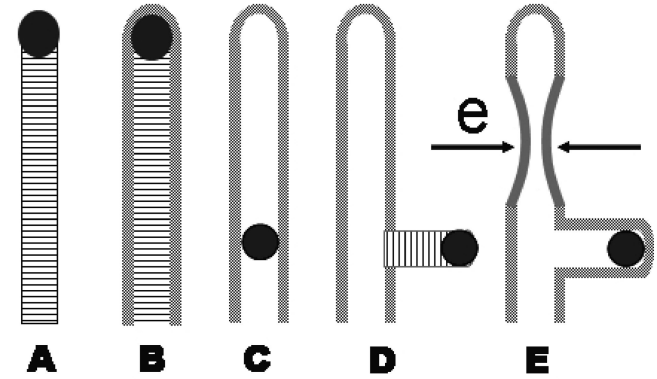

Figure 6. (A) Growth of ZnS nanowires via Au catalyst. (B) Formation of the SiO shell. (C) Removal of the ZnS template core through heating and transport of liquid Au in nanotubes. (D) Reactivation of Au catalyst and regrowth of ZnS template. (E) Formation of the nanotube network and diameter adjustment.

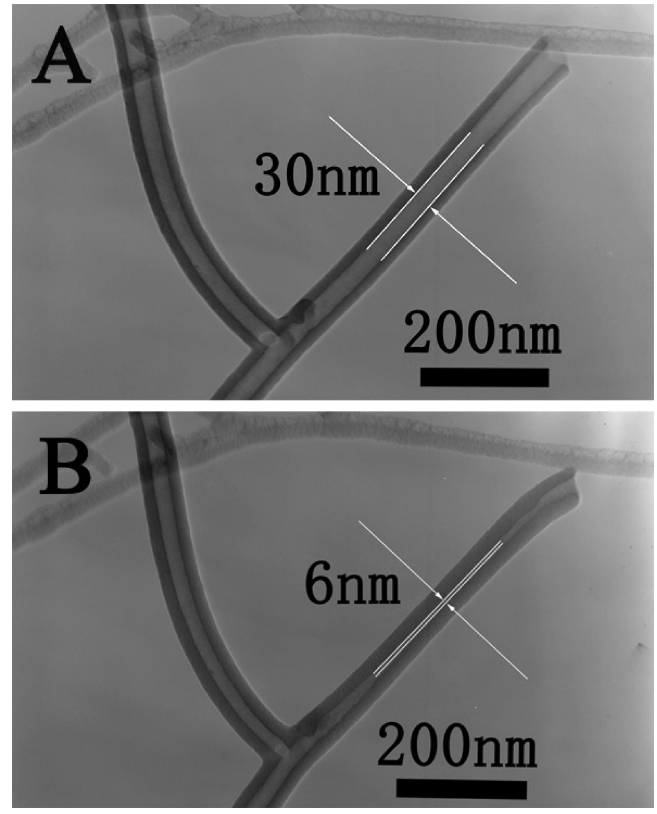

Figure 7. Diameter change of a T-nanobranched pipe before (A) and after (B) exposure to an electron beam.

(3) Transport of liquid Au in nanotubes: While vapors can pass through the porous wall of the nanotube, liquid Au cannot. Au is thus trapped inside the hollow cavity and moves toward the open end of the nanotube when the temperature increases. As temperature decreases, Au would break up into small segments, as shown in Figure 5c (Figure 6c).

(4) Reactivation of Au catalyst and regrowth of ZnS template: When the source is switched back to ZnS and the tube temperature is decreased to 900 °C, the concentration of Zn and S vapors in the tube would again increase. When the concentration difference between the nanotube cavity and environment is large

enough, Zn and S would penetrate into the nanotube. Then, ZnS would dissolve in the liquid Au and form a new ZnS nanowire via the VLS process (Figure 6d).

(5) Formation of the nanotube network: Cycling of the above processes several times with ZnS and SiO as alternate sources, nanotubes branches can form in different directions (Figure 6d) into a network.

Diameter Change of Nanonetwork. Since the nanotube is composed of porous SiO, it can be expected that the tube diameter could be adjusted by altering the density of the pores. Figure 7a,b shows the diameter change of a nanosize T-branch tube. After the sample is exposed to a 200 kV electron beam for 30 min, the inner diameter of the tube is reduced from 30 to 6 nm without any noticeable damage. The detailed mechanism for the change in diameter is unclear, but induced oxidation of the SiO shell by e-beam exposure may be a plausible cause.

Conclusions

Branching of SiO nanotubes has been achieved through secondary growth of a ZnS nanowire core inside the SiO shell. In this process, ZnS nanowires were first prepared from an Au-catalyzed VLS process to serve as the removable template for the SiO shell. The ZnS wire core would decompose and evaporate during SiO deposition at a higher temperature, forming the SiO tube. The remaining liquid Au particles could redistribute via expansion and contraction inside the tube and serve as the catalyst for the secondary growth of ZnS nanowires, which would graft branches onto the original SiO nanotube. The internal diameter of nanotubes could be modified by electron beam irradiation. The present template growth approach may be applicable to the formation of a nanofluidic channel network for bioanalytical sciences and chemical separation technologies.

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Supporting Information Available: Elemental analysis at different sections of the product are presented (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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