Preliminary Study on Cogeneration of Carbon Nanotubes and C_2 Hydrocarbon in CH_4/H_2 Corona Discharge

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La-doped carbon nanotubes and valuable C_2 hydrocarbon (C_2H_2 and C_2H_4) are simultaneously generated in CH_4/H_2 corona discharge. The analysis of off gas indicates that the addition of anodic alumina membrane shows no influence on plasma methane conversion reactions.

The interest in carbon nanotube arrays by AAO membrane and the breadth of research activities across the world on their application potential have lasted tens of years. They have shown unique properties in such fields as fuel cells, hydrogen adsorption, heterogeneous catalysis, field emission, and so on.[1–5] Most carbon nanotube arrays have at present produced by the plasma-enhanced chemical vapor deposition (CVD) method.[6] A variety of plasma source and widely varying results have been reported in the literature.[6] Typical hydrocarbon sources used in plasma-based growth of carbon nanotubes include methane, ethylene, and acetylene. Since the plasma can dissociate them creating a lot of reactive radicals, it is desirable to dilute the hydrocarbon with hydrogen. For most of the carbon nanotube reactions, the gaseous effluents are seldom studied and often considered as by-product.

Methane (natural gas) is a potential cheap chemical material, and direct conversion of methane to more valuable hydrocarbons has been an attractive subject of investigation,[7] but the high thermal decomposition temperature of it is a big problem. Corona discharge, as an unconventional technology, has been used for methane conversion.[8–10] Methane molecules can be decomposed into some carbon-containing molecules in corona discharge, such as CH, CH_2, CH_3, and atomic carbon. Therefore, valuable hydrocarbons are synthesized by the combination between them. But carbon deposition is inevitably formed in the corona discharge reactor despite of addition of catalysts.

Considering the fact that the above two reactions are carried out under the same conditions, it is meaningful to combine the production of carbon nanotubes and the plasma methane conversion. But the coverage of AAO membrane on electrode inevitably affects the corona discharge system. Here, we reported the cogeneration of La-doped carbon nanotubes and unsaturated C_2 hydrocarbons produced from methane using corona discharge, and the influence of AAO membrane on the gaseous products also is studied.

Nanoporous anodic alumina (Anodisc 47, 200 nm) was used as a template to synthesize carbon nanotubes. The preparation of La-loaded membrane is similar to that in the literature.[11] A piece of such membrane was immersed into an $La(NO_3)_3$ solution (1 M) for 12 h, and then taken out for drying at 50 °C, followed by calcinations at 550 °C. The corona discharge reactor used here is the same as that used for methane conversion.[12] The quartz tube reactor contained two axially centered electrodes, an upper wire electrode and a plate electrode. The gap between electrodes was fixed at 4 mm. A mixture of methane (2 mL/min) and hydrogen (20 mL/min) was used as the reactants for the carbon nanotubes synthesis. A piece of as-prepared La-loaded membrane was placed on the plate electrode. After the initiation of the corona discharge between the two electrodes with 3600 V, a white-color corona discharge was established. The feed and effluent gases were analyzed by on-line mass spectrometry. The microscopic features of the sample were observed with a TECNAI-F20 transmission electron microscope (TEM, 200 kV) and a Philips XL 30 scanning electron microscope (SEM).

Figure 1 presents a SEM image of La-doped carbon nanotubes produced in corona discharge. As indicated by the dashed narrows, the hollow structure of carbon nanotubes is clearly observed. When one part of these La-doped carbon nanotubes is enlarged, several large particles are obviously found on the outer surface, and their diameter is close to 100 nm. These particles are more obviously observed in its TEM image (Figure 2). The density of them is very low, and the distance between them is longer than 200 nm. The electron diffraction pattern (insert in Figure 2) is composed of weak circles, which indicates that these large particles are amorphous.

EDX spectrum of nanoparticles show some strong La peaks and weak C, O, and Al peaks (Figure 3). Cu peaks are due to the copper grid supporting the sample. The quantification analysis indicates that the atomic contents of La, O, and Al are 18.55, 2.83, and 0.992%, respectively, so the nanoparticles are not La_2O_3. Since La is dominant, they must be metallic La. Consid-

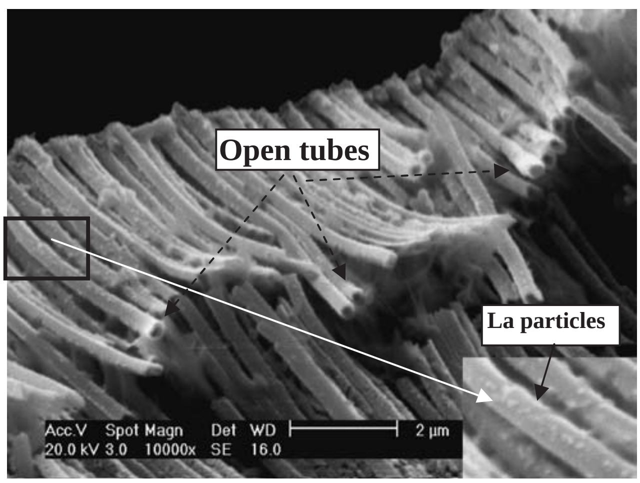

Figure 1. SEM image of La-doped carbon nanotube arrays.

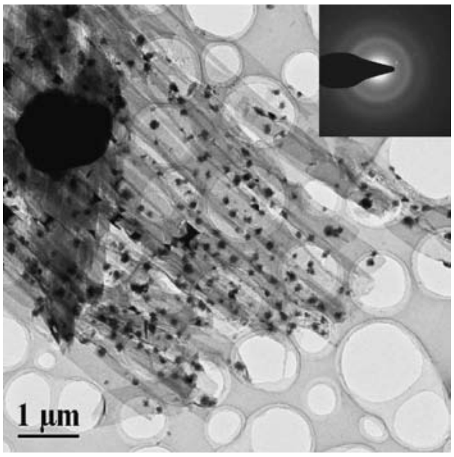

Figure 2. TEM image of La-doped carbon nanotube arrays and HRTEM image of La particles.

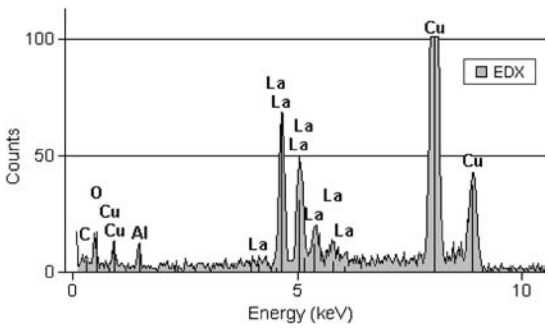

Figure 3. EDX analysis of the large particles on the outer surface of carbon nanotubes.

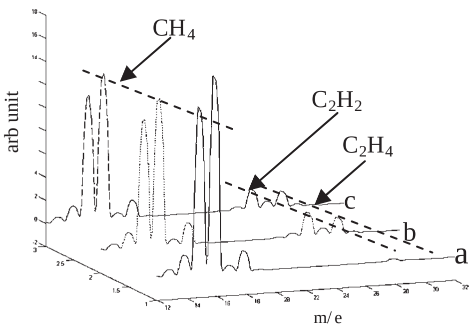

Figure 4. Anlysis of off gas from corona discharge reactor with MS (a) before reaction; (b) without membrane; (c) with membrane.

ering metallic La is easily oxidized in air, a layer is necessary to cover these nanoparticles. O is about 3 times Al in atomic content, so this layer may be $LaAlO_3$ which might be formed in the calcinations.

The off-gas from CH_4/H_2 corona discharge is investigated by mass spectroscopy (Figure 4). The gaseous products of conventional plasma methane conversion reaction are C_2H_2 and C_2H_4 (at $m/e = 26$ and 28) but not C_2H_6 (at $m/e = 30$). If a

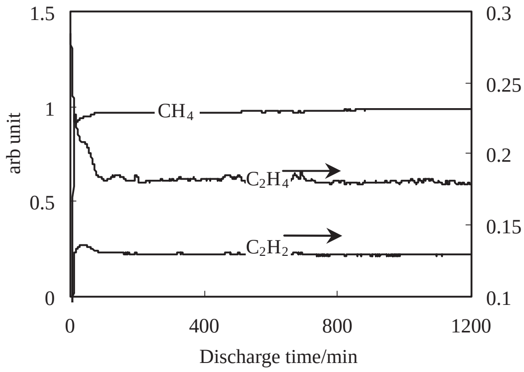

Figure 5. Variety of CH_4, C_2H_2, and C_2H_4 signals with discharge time at the presence of La-loaded membrane.

piece of La-loaded membrane is placed onto the plate electrode, part of the plate electrode has to be covered, which theoretically affect the corona discharge system. Although the increase of electron temperature and density are found, Figure 4 proves the stability of methane coupling reaction. It can be seen that the signal height of methane in the presence of membrane is equal to that without membarne. Furthermore, the same production (C_2H_2 and C_2H_4) and the same signal height of them are also clearly observed. So the addition of membrane does not influence the methane conversion and the selectivity to C_2H_2 and C_2H_4.

Figure 5 presents the variety of CH_4, C_2H_2, and C_2H_4 signals with discharge time in the presence of La-loaded membrane. Obviously, the signals do not vary in 1200 min. Therefore, plasma methane conversion reaction can be carried out for a long time without deactivation. The study results prove the possibility of cogeneration of carbon nanotubes and C_2 hydrocarbons, and further study is under way to optimize the two reactions.

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