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Purification of titanate nanotubes using a mesh-stacked dielectrophoretic separator equipped with carbon nanotube electrodes

Noriaki Sano*, Satoru Matsuoka, Hajime Tamon

Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

HIGHLIGHTS

- Carbon nanotubes were grown on mesh-stacked electrodes for dielectrophoresis.
- Titanate nanotubes were purified by dielectrophoresis with developed electordes.
- Large bandgap energy titanate nanotubes were concentrated.

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ABSTRACT

A mesh-stacked dielectrophoretic (MS-DEP) separator whose electrodes were covered with multi-walled carbon nanotubes (MWCNTs) was built to purify titanate nanotubes (TNTs) synthesized by hydrothermal conversion from *anatase* TiO_2 powders. MWCNTs were synthesized directly on the surface of stainless mesh electrodes. It was experimentally observed that this MS-DEP separator could be useful to purify TNTs. It was found that relatively low frequency for AC voltage applied on the MS-DEP separator was preferable when it was required to collect TNTs possessing a large energy bandgap. In addition, a model calculation was carried out to qualitatively discuss the effect of MWCNT to enhance the electric field strength at MWCNTs, which could generate the strong DEP force on small particles.

1. Introduction

Dielectrophoresis has been known as a separation method to separate particles dispersed in liquid depending on their dielectric properties (Pohl, 1978; Jones, 1995; Hughes 2002; Gagnon et al., 2010; Sano et al., 2011, 2012a, 2013a). In some cases, this separation is superior to other conventional particle separation methods, such as filtering, sedimentation, centrifuge, etc. (Nagumo et al., 2012; Nakamura et al., 2012; Cao et al., 2013; Kanemaru et al., 2013; Lee et al., 2013; Shimada et al., 2013; Yoshioka et al., 2013) For example, the dielectrophoretic (DEP) separation may be useful even when there is no significant difference in particles' sizes and densities so that it is difficult to use the conventional separation methods. However, as the DEP force is in principle proportional to the cube of the particle diameters (Pohl, 1978; Jones, 1995; Hughes 2002), the manipulation of nanoparticles by this force should be extremely difficult when the particle size is extremely small. Nevertheless, one may expect that nanoparticles can be selectively captured when appropriately small-size electrodes are employed.

There is a considerable number of reports to fabricate small-size electrodes to enhance the electric field. For example, patterned electrodes were fabricated by photolithography techniques on substrates to capture carbon nanotubes (CNTs) for fabricating a chemical sensor and semiconductor devices (Cicoria and Sun, 2008; Li et al., 2011). Also, a technique using micro-electro-mechanical-systems (MEMS) was used to fabricate fine electrodes for dielectrophoresis (Zou et al., 2006). Although the efforts have been made to realize DEP particle separators using small electrodes like these examples, it should be recognized that also CNTs can be promising candidates as electrode materials for further development of DEP separators which can generate high electric field strength. Such property should be useful to realize the particle separation for the cases when the conventional separation methods are not useful. Similar idea can be found in the application of CNTs to the development of low-voltage field emission devices using the extremely high electric field strength generated by CNTs (Zhao et al., 2013; Sano et al., 2007).

In the present study, titanate nanotubes (TNTs) synthesized by hydrothermal reaction is chosen as target nanoparticles. TNTs are

* Corresponding author. Tel.: +81 75 383 2684.
E-mail address: sano@cheme.kyoto-u.ac.jp (N. Sano).

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promising materials for variety of applications, such as photocatalyst (Grandcolas et al., 2011; Hosseini and Momeni, 2012; Li et al., 2012), catalyst support (Chang et al., 2011), adsorption media (Harsha et al., 2011; Kasap et al., 2012), and so forth. Here, the mesh-stacked stainless steel electrodes entirely covered with aligned CNTs were used to build a DEP separator to realize the selective capture of the TNTs.

2. Experimental

2.1. Synthesis of titanate nanotubes

TNTs were synthesized from commercial *anatase* TiO_2 powders (Wako Chemical) by a hydrothermal reaction (Kasuga et al., 1998; Viriya-Empikul et al., 2009). A stainless steel autoclave with a Teflon inner vessel (50 mL) was used to synthesize TNTs. This autoclave, in which 1.5 g of TiO_2 powders were dispersed in 10 mol L^{-1} NaOH aqueous solution, was placed in an electric oven to keep the temperature at 150 °C for 3 days. The powdery products collected from this autoclave was neutralized by HCl, and washed by distilled water on a filter paper.

2.2. Synthesis of MWCNTs on stainless steel mesh used for DEP electrodes

Multi-walled carbon nanotubes (MWCNTs) were directly synthesized on the stainless steel meshes by a chemical vapor deposition technique which did not require catalyst coating step (Baddour et al., 2009; Gaikwad et al., 2012; Sano et al., 2012b, 2012c, 2013b; Hashempour et al., 2013; He et al., 2012; Hordy et al., 2013). This technique is superior to other MWCNT growth techniques in an aspect that MWCNTs can be synthesized on solid surfaces of complicated shapes. In the present study, the surface of the stainless steel was activated for MWCNTs growth by an oxidation in air at 800 °C for 30 min followed by a reduction in H_2 atmosphere in a tubular furnace at 700 °C for 30 min. By this way, catalytic Fe nanoparticles would be generated and MWCNTs were synthesized thereon when a synthetic gas containing ethylene (C_2H_4) mixed with H_2 (molar ratio C_2H_4:H_2=1:1) were fed with keeping temperature at 700 °C for 1 h. The structure of MWCNTs synthesized was analyzed by a scanning electron microscope (SEM) (Technex Lab Co., Tiny-SEM1710) and a transmission electron microscope (TEM) (JEOL, JEM1010).

2.3. DEP particle separation

A DEP particle separator system using a mesh-stacked dielectrophoretic (MS-DEP) separator unit was prepared as depicted in Fig. 1. It can be considered that the 3-dimensional structure of this MS-DEP separator unit is suitable for large scale operations (Sano et al., 2012d). Two kinds of stainless steel meshes, (1) stainless meshes on which MWCNTs were synthesized and (2) bare stainless steel mesh without MWCNT preparation, were used to construct the DEP separator for comparison. (In Fig. 1, only MS-DEP with MWCNTs is described.) In the DEP separator unit, 11 stainless steel meshes (type SUS314, inter wire aperture.0.5 mm, wire diameter.0.29 mm) were stacked with a distance of 0.5 mm using acrylic-plate spacers.

An automatic particle separation system was built here by connecting a programmable relay (Omron Co., 10C1DR-D-V2) to motor sliders to shift the positions of the separator unit and the liquid vessels, etc. In this system, the MS-DEP separator unit can automatically move in five steps repeatedly as follows; (1) The separator unit was shifted down to submerge in the liquid (0.5 wt % ethanol aqueous solution, 200 mL) contained in a sonication bath (Velvo-Cleaner Co., VS-25) with the dispersing target particles. Prior to this motion, this liquid was sonicated for 30 s and this sonication was stopped just before the separator unit was submerged. (2) AC 200 V of peak-to-peak voltage with 40 kHz was applied on the alternately placed mesh electrodes in the DEP separator for 10 s during the DEP separator unit was submerged. (3) The DEP separator unit was lifted up from the liquid and was transferred to a recovery liquid (0.5 wt% ethanol aqueous solution, 75 mL) in which target particles were not dispersed. During the transport of the MS-DEP separator unit from the target liquid to the recovery liquid, the AC voltage was sustained to keep the captured particles. (4) When MS-DEP separator unit was dipped into the recovery liquid, the captured particles were released there by turning off the AC voltage. (5) After releasing the particles, the DEP separator was transferred back to the target liquid. These steps were repeated by 10 times before the collected particles were analyzed.

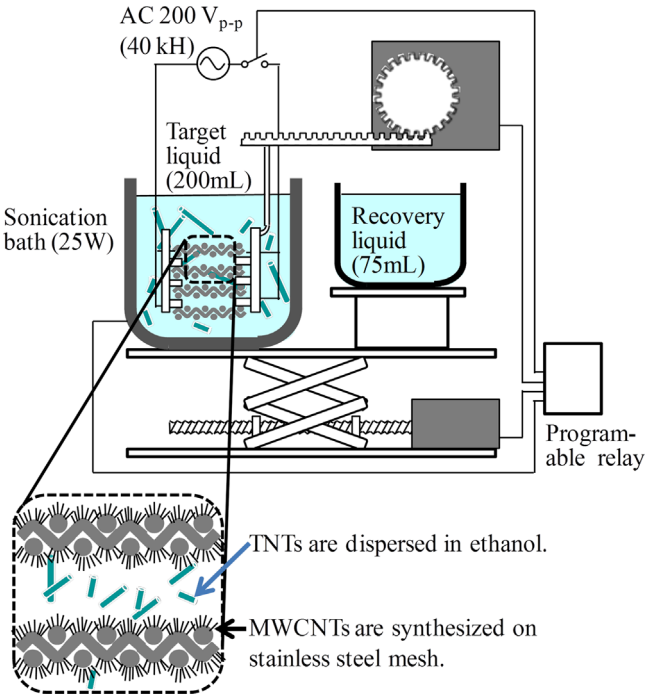

Fig. 1. Set up for particle separation experiment using MS-DEP separator with mesh electrodes on which MWCNTs were synthesized.

The particles collected by the MS-DEP separator were analyzed by the TEM, a dynamic light scattering analyzer (DLS) (Otsuka Electronics Co., Ltd., ELS-8010 M), and an ultraviolet-visible light (UV–vis) absorption spectrometer (Shimadzu Co., UV-260).

3. Results and discussion

The microscopic images of MWCNTs synthesized on the stainless steel meshes are shown in Fig. 2. From the SEM images shown in Fig. 2a, b, it was impressed that MWCNTs have aligned structures like a blush, and the length of the MWCNTs seemed to be approximately 20 μm. One can confirm in the TEM image of Fig. 2c that the products are tubular, and the diameter of the MWCNTs ranged in 8–40 nm.

Fig. 3 shows a TEM image of the particles collected by the MS-DEP separator equipped with the stainless steel mesh electrodes covered with MWCNTs. When MS-DEP separator with the MWCNT electrodes was used, most particles captured by this separator were TNTs as seen in this figure. By the TEM observation, it was