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Production of well dispersible single walled carbon nanotubes via a "floating catalyst"-method

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HIGHLIGHTS

- Process chain for the production and dispersion of single-wall carbon nanotubes (SWCNT).
- Relationship between the process parameters in gas phase production, the dispersibility of SWCNTs in aqueous solutions of sodium cholate and their properties.
- SWCNTs are about 1 nm in diameter and about 2/3 of the SWCNTs behave semiconducting.

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ABSTRACT

In this paper, we present a unique process chain for the production of single-walled carbon nanotubes (SWCNT) and document the relationship between the process parameters in gas phase production, the dispersibility of SWCNTs in aqueous solutions of sodium cholate and their properties. SWCNTs were prepared by a "floating catalyst" method using a solution of ferrocene in ethanol as precursor. Production rates in the range from 5 to 20 mg/h were achieved by using an optimized riser reactor design, which enables reduction of undesired wall-sticking of the catalyst particles and SWCNTs. Products featuring iron catalyst contents less than 30 wt% were obtained for low precursor concentrations in combination with short residence time in the reactor. Transmission electron microscopy (TEM) and statistical Raman analyses of the products reveal that the SWCNTs exhibit a diameter distribution ranging from 0.5 to 2.0 nm. Processing conditions, including precursor concentration, residence time, etc. were found to have only a slight impact on the mean geometric SWCNT diameter. Sonication based post-processing of the as-prepared SWCNTs in aqueous solutions of sodium cholate leads to an effective individualization of SWCNTs as proven by atomic force microscopy (AFM), 3D fluorescence spectroscopy, and by multi-wavelength analytical ultracentrifugation (AUC). Overall, the dispersibility of the non-purified SWCNTs in a 2 wt% aqueous solution of sodium cholate increases as the ferrocene partial pressure is decreased and, in turn, the catalyst concentration is reduced in the gas phase. Statistical Raman spectroscopy performed with the SWCNTs reveals that more than 75% of the produced carbon species are SWCNTs and that about 2/3 are semiconducting.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are widely used in fuel cells (Yamaguchi et al., 2013; Kanninen et al., 2014), lithium ion batteries (Nomura et al., 2014; Dekker et al., 1998), and thin film transistors (Yamaguchi et al., 2013; Dekker et al., 1998; Reynaud et al., 2014) owing to their unique properties such as excellent electrical and thermal conductivity, and high tensile strength. Many of the extraordinary properties of SWCNTs depend, however, on the carbon network and the related chirality (Wang et al., 2015). Depending on their chirality, SWCNTs behave metallic (m-SWCNT) or semiconducting (s-SWCNT) with a band gap up to 2.0 eV (Wildöer et al., 1998). For the application of SWCNTs in nano- and opto-electronics high purity s-SWCNTs are necessary (Avouris et al., 2007).

Abbreviations: SWCNT, single-walled carbon nanotube; TGA, thermogravimetric analysis; AUC, analytical ultracentrifugation

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Success in large scale applications requires good dispersible SWCNTs with desired properties like controlled diameter and chirality (Kumar and Ando, 2010). The most promising synthetic method for the production of SWCNTs with controlled properties is the catalytic chemical vapor deposition (CCVD) (Kumar and Ando, 2010) due to high yields and good quality of the produced SWCNTs (Kumar and Ando, 2010). Production of SWCNTs by CCVD involves the decomposition of a carbon source on nanometer sized catalyst particles followed by SWCNT growth. Catalyst particles are produced ex situ or in situ. The well-known CoMoCAT®-method is a prominent example for SWCNT production using an ex situ produced catalyst (Zhang et al., 2005). This method uses silica supported catalyst particles in a fluidized bed reactor to produce SWCNTs of tunable chirality (Lolli et al., 2006; Jansen and Wallis, 2014).

In this respect, gas phase synthesis with in situ produced catalyst particles like the “floating catalyst” method are most promising because the reactor can run continuously and the size of the catalyst particles can be tuned via process parameters (Kumar and Ando, 2010; Motta et al., 2007; Kumar, 2011). Several publications focus on the experimental conditions for SWCNT production via the “floating catalyst” method (Nikolaev et al., 1999; Nikolaev, 2004; Zhu et al., 2002; Li et al., 2004; Gspann et al., 2014; Hou et al., 2014). Most riser reactor concepts, which are described in the literature, feature however, a considerable disadvantage, that is, in situ produced catalyst particles stick to the reactor wall so that SWCNT growth from these particles may lead to clogging of the reactor (Singh et al., 2003; Vivekchand et al., 2004; Aguilar-Elguézabal et al., 2006). Concepts to avoid the blocking of the reactor involve the direct spinning of SWCNT fibers in the gas phase (Zhu et al., 2002; Li et al., 2004; Gspann et al., 2014). Spinning macroscopic assemblies of SWCNTs find, for example, use in power cables and micromechanical actuators (Li et al., 2004). Since the method of direct spinning SWCNT fibers is not designed for their dispersion, very dense SWCNT agglomerates are obtained.

Other floating catalyst methods, which avoid direct spinning, are only able to produce SWCNTs in low yields (Moisala, 2006), do not report the yield (Hou et al., 2014; Nasibulin et al., 2005; Tian et al., 2011a, 2010b; Oikonomou et al., 2012) or the residual iron at all (Oikonomou et al., 2012), but are able to tune diameters (Hou et al., 2014; Nasibulin et al., 2005; Tian et al., 2011a, 2010b) and/or specific chirality (Hou et al., 2014; Yu et al., 2011).

Another example for SWCNT production via the “floating catalyst” method is the well-known HiPco process established by Smalley (Nikolaev et al., 1999). In their first publication the tuning of the SWCNT diameters was reported (Nikolaev et al., 1999), but at this time the yield was quite low (0.6–1 mg/h) (Nikolaev et al., 1999). In a follow-up publication Carver et al. (2005) showed a correlation between the initial precursor concentration and SWCNT diameter, catalyst diameter, residual iron but no information was given on the chirality or the dispensability of these tubes. Large-scale productions of SWCNTs (10 g/d) were reported but the resulting products were not fully characterized in terms of SWCNT diameter, chirality, quality, dispersibility, etc. (Nikolaev, 2004; Bronikowski et al., 2001). Therefore no comprehensive picture of this method has been presented so far.

As SWCNTs bond to each other through van der Waals forces (Girifalco and Hodak, 2002) to form bundles and agglomerates, dispersing of individualized SWCNTs has become a major challenge. The residual catalyst metal content also influences the dispersibility of the SWCNTs (Chowdhury et al., 2012) nanotube materials can be dissolved in superacids (Ramesh et al., 2004; Ericson, 2004), organic solvents (Bergin et al., 2008a, 2010) solutions of polymers (Nish et al., 2007; Chen et al., 2007) and DNA (Zheng et al., 2003; Tu et al., 2009; Koh et al., 2011). Using solutions of poly(2,7-carbazole) (Rice and Adronov, 2014) or poly(3-alkylthiophenes) (Wang et al., 2014) preferably semiconducting SWCNTs with diameters < 1.1 nm are dispersed. The most common approach to produce stable dispersions with large fractions of individualized SWCNTs involves the use of surfactants because for correct product characterization all SWCNT species present in the sample have to be dispersed (Shin et al., 2008; Goak et al., 2011; Blanch et al., 2010; Backes et al., 2010b; Sun et al., 2008; Haggenmueller et al., 2008a). A high degree of individualization is typically achieved by ultrasonic processing followed by consecutive centrifugation which removes remaining agglomerates. The surfactant is not only important for debundling during sonication, but also prevents individual SWCNTs from re-aggregation. In comparison with conventional surfactants as sodium dodecyl sulfate (SDS) bile salt surfactants such as sodium cholate have proven to disperse SWCNTs much more effective (Arnold et al., 2006; Hertel et al., 2005). The dispersing efficiency of bile salts for SWCNTs can further be enhanced by introducing aromatic substituents into the molecule (Gubitosi et al., 2014).

In contrast to prior works using the "floating catalyst" method our approach avoids direct spinning (Gspann et al., 2014; Li et al., 2004; Paukner and Koziol, 2014) and the use of sulfur-containing additives (Reynaud et al., 2014; Li et al., 2004; Hou et al., 2014). Instead, we use an optimized riser reactor, which prevents contact of the produced SWCNTs with the reactor walls by a well controlled sheath gas flow. This way, SWCNT production rates up to 20 mg/h are obtained for our lab-scale riser reactor with a cross-section of 50 mm. From prior experience we are sure that an increase in diameter by a factor 4 and by numbering up the precursor inlet nozzles from 1 to 5 the production rate will increase by 5. Therefore having 5 nozzles in parallel a production rate of 2.4 g/d is realistic.

Any significant increase of the precursor concentration unfortunately leads to a more rapid growth of the catalyst particles due to collisions. Therefore, the effect on the initial precursor concentration is one crucial parameter. For the dispersibility of the SWCNTs also the number concentration of the SWCNTs is crucial. An increasing number concentration of the SWCNTs in the gas phase leads to a higher agglomeration/bundling probability and therefore the dispersion/individualization of the SWCNTs need more effort. Another possibility is the increase of the transport velocity to a certain extent in the reactor and thus the reduction of the residence time which will reduce the tendency of agglomeration accordingly. This will bring another order of magnitude in productivity.

With the “floating catalyst”-method no ex situ catalyst preparation is necessary. Compared to other methods using a “floating catalyst”-approach no sulfur additives or direct spinning are required since we limit catalyst particle diffusion to the wall by means of a well-controlled sheath gas flow. We report a full process chain showing the relationship between the production process parameters in the gas phase using an advanced riser reactor design, the production rate, the dispersibility of SWCNTs in liquids and the comprehensive characterization of their properties. In particular, the obtained products were fully characterized in terms of quality, yield, diameter, and chirality distributions by a unique combination of advanced imaging and spectroscopic methods as well as sedimentation velocity analysis.

2. “Floating catalyst” growth model

The “floating catalyst” method is characterized by in situ catalyst particle production with subsequent SWCNT growth. In Fig. 1 this mechanism is illustrated. Overall, the SWCNT synthesis can be divided into the three sections (a) precursor generation, (b) generation of the catalyst particles and (c) CNT growth.

In the precursor generation step, droplets of the dissolved precursor (ferrocene dissolved in ethanol) are carried into the reactor via a helium gas stream. As the droplets and the gas stream heat up along the temperature ramp of the furnace depicted in Fig. 1 left, the droplets evaporate at around 78 °C and solid ferrocene particles are formed. Heating-up of the gas and the precursor is mainly realized by