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Template function of liquid membranes in the assembly of tube-in-tube carbon nanostructures

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ABSTRACT

Tube-in-tube carbon nanostructures (TTCNTs) have been successfully constructed on liquid membranes via a hydrogen-bonding linkage of small graphene sheets around normal carbon nanotubes (CNTs). The effects of solvent (water, tetrahydrofuran (THF), ethanol, n-hexane and N,N-dimethylformamide (DMF)) and membrane thickness on the assembling process were investigated. Results show that the formed cavity of TTCNTs becomes large with the increase of viscosity of solvent and pressure. The formed liquid membrane on CNTs surface plays a key role in this process, and it can be controlled by adjusting the membrane thickness and solvent nature. Moreover, TTCNTs show excellent catalytic reduction NO ability at low temperatures.

1. Introduction

Creating internal cavities (channels or pores) in nanomaterials can significantly tailor or improve their properties and functions, particularly in the fields of catalysis, separation, micro-reactor, drug delivery, heat insulation, and electronic devices. Understanding the construction of the cavities will influence both the fundamental picture of the properties of matter on nanoscale and the technical realization of the construction. The intrinsic higher density of unstable surface atoms in the cavitary nanomaterials compared with their non-cavity counterparts makes their construction more difficult. The objects with anisotropic structure (e.g. graphitic carbon and metal sulfides) can self-assemble as simple hollow tubular nanostructures [1–4], where the surface atoms are coordinately saturated by structural curvature, but for the objects with isotropic structure, template technology is often necessary for a successful cavity creation [4,5]. As is well known, both the internal surface of nonporous materials (e.g. anode alumina) [6–8] and the outer surface of fibrous nanomaterials [9–11] can serve as hard and confined templates for the assembly of tubular nanostructures of guest objects. Organic or biologic large molecules with special structures can act as soft templates for the construction of tubular and porous nanomaterials [12–15], which were previously often employed to synthesize pore-ordered zeolites [16–18]. The liquid membranes formed in a liquid–liquid system have been also used as templates to build hollow structures [19–22]. However, the required removal of the template objects after a construction is usually difficult without destroying target nanomaterials [18]. More importantly, the construction of complex nanostructures with multiple cavities, which are expected to show more unique properties, has been rarely achieved by the existing technologies [23–26] and is still a big challenge.

Herein, we report that the liquid membranes usually formed at liquid–solid interfaces can act as easily removed templates for the construction of tube-in-tube nanostructures. Notably, cavity dimension can be controlled by the thickness of the liquid membrane, and complex nanostructures with multiple cavities can be rationally designed and constructed, which change the paradigm of the templated assembly of cavitary nanostructures.

2. Experimental

The pristine CNTs employed were commercially supplied by the Applied Science Ltd., USA and pretreated with concentrated nitric acid before use [24,25]. In this process, the carbonaceous impurities which exist in the outer intertubular volume and in the inner voids of the tubes are removed and disintegrated into small fragments at defect sites, and the carboxyl and hydroxyl groups were introduced into the fragment edges and the CNTs surface. To assemble TTCNTs, the as-obtained CNTs (20 mg) were dispersed in n-hexane (20 ml), THF (20 ml), DMF (20 ml), water (20 ml), and ethanol (20 ml), and refluxed for 10 h. The suspension was then filtered, washed with ethanol, and dried at 110 °C in air for 12 h.

To explore the effect of pressure on assembling TTCNTs process, the as-obtained CNTs (10 mg) were introduced into n-hexane

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(10 ml) at a sealed stainless steel vessel (15 ml) under 150 °C for 10 h, and then filtered, washed with ethanol, and dried at 110 °C in air for 12 h.

The catalysts (V_2O_5/TTCNTs and V_2O_5/CNTs) were prepared by pore volume impregnation of TTCNTs and CNTs with an aqueous solution of ammonium metavanadate in oxalic acid, followed by overnight drying at 60 °C and then at 110 °C for 5 h, and by calcinations in Ar for 8 h at 500 °C and preoxidization in air at 250 °C for 5 h. The SCR of NO with NH_3 activity tests of the catalysts (V_2O_5/TTCNTs and V_2O_5/CNTs) were carried out in a fixed-bed glass reactor at 250 °C, with 200 mg catalyst and 100 ml/min of gas flow rate (WHSV, 30,000 h^{-1}). The reaction gases (NO, NH_3, O_2, SO_2 balance Ar) are fed by a control with mass flow controllers and analyzed with a combustion gas analyzer, which is equipped with selective electrochemical sensors.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of the samples were taken using a JEM-2010 High Resolution Transmission electron microscope.

3. Results and discussions

Previous experiments for the assembly of the small graphene sheets around CNTs were based on an esterification linkage between the carboxyl and hydroxyl groups, using H_2SO_4 as an acid catalyst and carried out in THF with a refluxing [24,25]. Under a basic condition given by ammonia, the assembly is unsuccessful, possibly due to an ineffective esterification linkage of the graphene sheets. What surprises us is that a simple refluxing treatment in THF without acid catalysts can also yield TTCNTs (Fig. 1a) with clearly distinguishable inner spaces between the pristine and newly assembled tube moieties. This result implies that the assembly of the graphene sheets can occur in another way since an esterification reaction is usually difficult to take place without catalysts [27]. A logical deduction for the linkage way might be referred to a hydrogen-bonding interaction between the carboxyl and hydroxyl groups since similar hydrogen-bonding linkage strategy has been successfully employed to self-assemble stable organic nanotubes [28,29]. Enlightened by this observation and the intrinsic good hydrophilicities of the carboxyl and hydroxyl groups, we further perform the assembly experiment in deionized water by a refluxing, which readily results in TTCNT structures (Fig. 1b–d). Using TEM, we estimate that 80% of pristine tubes are transformed into TTCNTs. Most of the TTCNTs are constructed by two tubes sheathed together, and a small amount of triple TTCNTs is also observed (inset of Fig. 1d). This hydrogen-bonding organization in aqueous medium gives an efficient and environmentally benign way for the TTCNT assembly. However, both the previous esterification linkage and the present hydrogen-bonding linkage are only related to the way of assembling the graphene sheets but do not seem to provide straightforward information about the interspace creation.

Upon careful contrastive observation of the TTCNTs, it is found that the average interspace of the TTCNTs obtained in THF (5.5 nm) is narrower than that obtained in water (11.4 nm), which leads us to notice the possible effect of solvent nature on the interspace creation. We conjecture that a dense solvent membrane is constituted at the solvent/pristine nanotube interface (step a in Fig. 2). The membrane then acts as a template for the assembly of the graphene sheets (diffused from bulk solvent) into a new tubule (step b) and is finally removed during the subsequent sample-drying process, which leaves behind an interspace between the pristine and new tube moieties (step c). Such a conjecture is

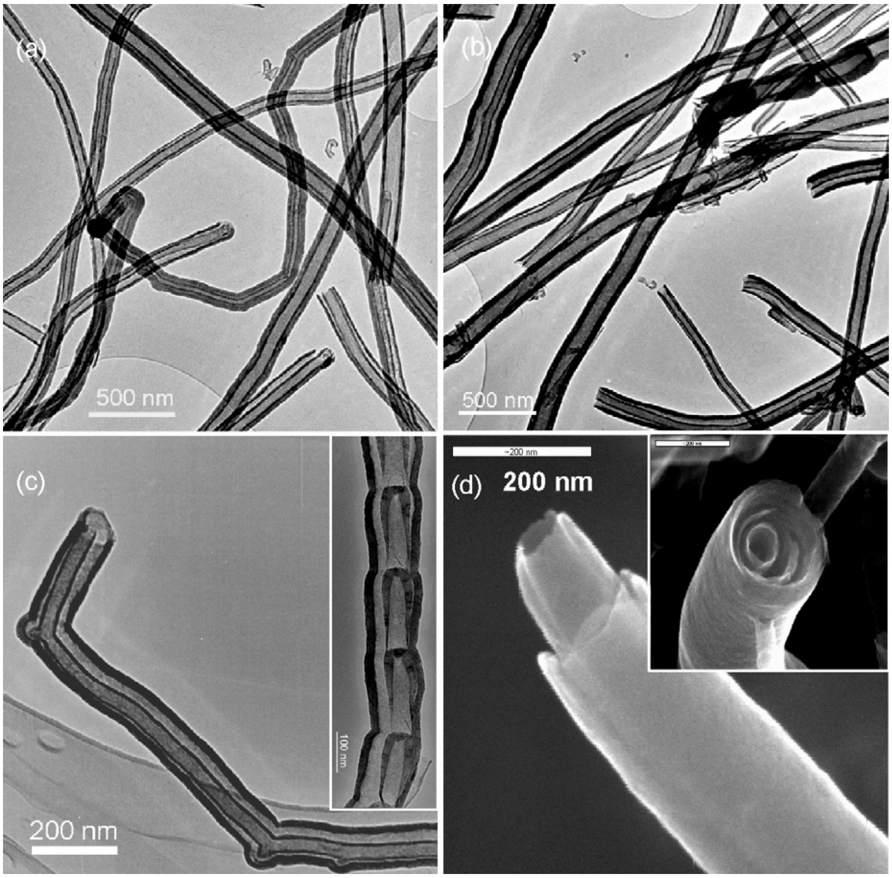

Fig. 1. (a) TEM images of the TTCNTs assembled in THF by a refluxing. (b) TTCNTs assembled in water. (c) An individual TTCNT with comfortably fitted inner and outer tube moieties, inset: a TTCNT with an inner bamboo-like tube and a newly assembled outer tube. (d) Typical SEM image of the TTCNTs, inset: a TTCNT with three encased tubes.