Colloids and Interface Science Communications 3 (2014) 13–17

Contents lists available at ScienceDirect

Colloids and Interface Science Communications

journal homepage: www.elsevier.com/locate/colcom

Rapid Communication

Modulating SWCNT–silica interactions for enhanced dispersibility and hybrid cryogel formation

Bhuvnesh Bharti [a,b,*], Radovan Kukobat [a], Daiki Minami [a], Katsumi Kaneko [a,**]

[a] Center for Energy and Environmental Science, Shinshu University, Wakasato, Nagano, Japan
[b] Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, USA

ARTICLE INFO

Article history:
Received 16 February 2015
Received in revised form 14 March 2015
Accepted 19 March 2015
Available online 17 April 2015

Keywords:
Single walled carbon nanotubes
Silica nanoparticles
Hybrid materials
Cryogel
Surface interactions
Dispersant

ABSTRACT

Single walled carbon nanotubes (SWCNTs) form a special class of carbon materials with high electric and thermal conductivity. Ordinary SWCNTs exist in the form of bundles, primarily because of intertubular van der Waals attraction. Here we show that silica nanoparticles (NPs) with tunable surface energy can be used as efficient aqueous dispersant for SWCNTs. A subsequent controlled solvent-evaporation leads to the formation of SWCNT–silica hybrid cryogels. We characterize cryogels using gas/vapor adsorption and electric conductivity measurements and show that their porosity and conductivity can be fine-tuned by altering the silica-to-SWCNT relative concentration. We believe that the SWCNT–silica hybrid cryogels can be used as a precursor for fabricating functional electrodes for advanced energy storage devices.

Introduction

Single walled carbon nanotubes (SWCNTs) possess unique electrochemical properties and hence, are of prime interest for making electrodes for supercapacitors [1,2]. However, their low surface hydrophilicity i.e. electrolyte wettability restricts the density of surface bound ions and limits their efficiency as electrodes [3]. Ordinary non-functionalized SWCNTs (diameter 1–2 nm) exist in the form of bundles of lower surface area primarily because of lateral intertubular van der Waals attraction [4]. Surfactants and similar organic amphiphilic molecules have been widely used for dispersing SWCNTs [5]. However, the major drawback of using such molecules is their irreversible binding to the SWCNTs which in turn significantly reduces the specific conductivity of the SWCNTs. Recently, Kaneko et al. [6] have developed a new route to disperse the SWCNTs using nanosilica. The SWCNTs were partially coated with a silica nanolayer, inducing mutual electrostatic repulsions. The method provided a unique way to disperse SWCNTs using inorganic oxide, however the potential capabilities of the silica–SWCNT composite in electrode manufacturing are yet to be explored [7]. In this article, we present a novel class of SWCNT–silica nanoparticle (NP) hybrid cryogels with tunable conductivity, surface area and porosity. Our method emerges from the fact that aqueous colloidal dispersions can be transformed into fully percolated 3D networks by controlled solvent evaporation [8]. We believe that such hybrid cryogels can potentially be used as a support for new catalysts and as supercapacitor electrodes for high energy density storage [9].

Improving SWCNT dispersibility with silica NPs, while retaining their high conductivity holds the key to manufacture future adhesives and efficient electrodes [10,11]. A change in the surface properties of silica NPs is known to alter their interfacial and adsorption behavior [12]. The surface interactions between the silica NPs and SWCNTs will determine the physical characteristics of the cryogel and hence their electrochemical properties. In this article we control the fractional dispersibility of SWCNTs in water by directing the surface binding of silica NPs. For this purpose, two types of silica surface chemistries have been investegated: (a) non-functionalized silanol (Si–OH) and (b) functionalized *N*-propylamine ($Si–C_3H_6–NH_2$). The dissociation of the surface functional group is dependent on the free proton concentration in bulk [13]. Hence, any change in the dispersion pH leads to the protonation/deprotonation of the surface functional groups. Therefore, bulk pH provides an excellent tool to precisely control the surface energy of the silica nanoparticles, thus the SWCNT–silica interaction.

Fig. 1a shows the equilibrium fraction of SWCNTs dispersed by non-functionalized and functionalized 8 nm diameter silica NPs in a wide pH regime (for details see Methods). For non-functionalized silica (Si–OH surface groups), a high fraction of the nanotubes are dispersed at pH 2.6 which decreases with increasing pH. Whereas for functionalized silica NPs ($Si–C_3H_6–NH_2$ surface groups), SWCNT dispersibility

---

* Correspondence to: B. Bharti, Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, USA.
** Correspondence to: K. Kaneko, Center for Energy and Environmental Science, Shinshu University, Wakasato, Nagano, Japan.
E-mail addresses: bbharti@ncsu.edu (B. Bharti), kkaneko@shinshu-u.ac.jp (K. Kaneko).

http://dx.doi.org/10.1016/j.colcom.2015.03.001

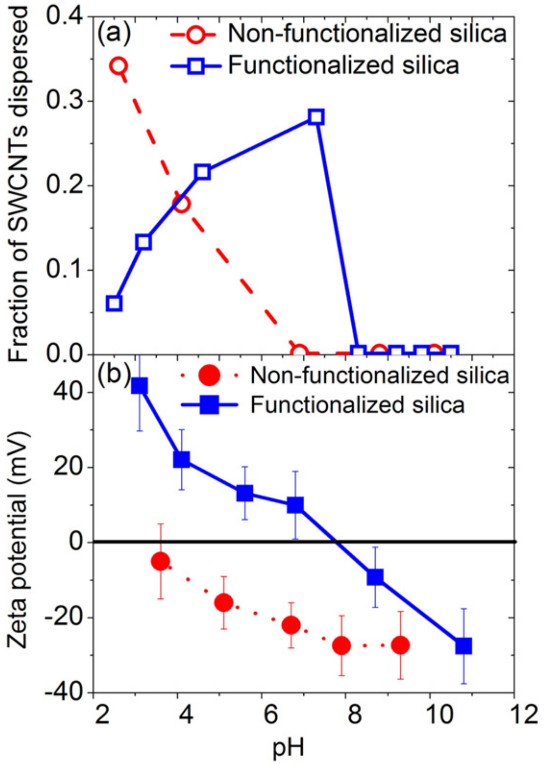

Fig. 1. (a) Fraction of SWCNTs dispersed in aqueous dispersions of non-functionalized (open circles) and *n*-propylamine functionalized (open squares) silica NPs of 8 nm diameter in the pH range of 2–12. (b) Zeta potential–pH titration curve for non-functionalized (filled circle) and functionalized (filled squares) silica NP (8 nm) dispersions in the absence of SWCNTs.

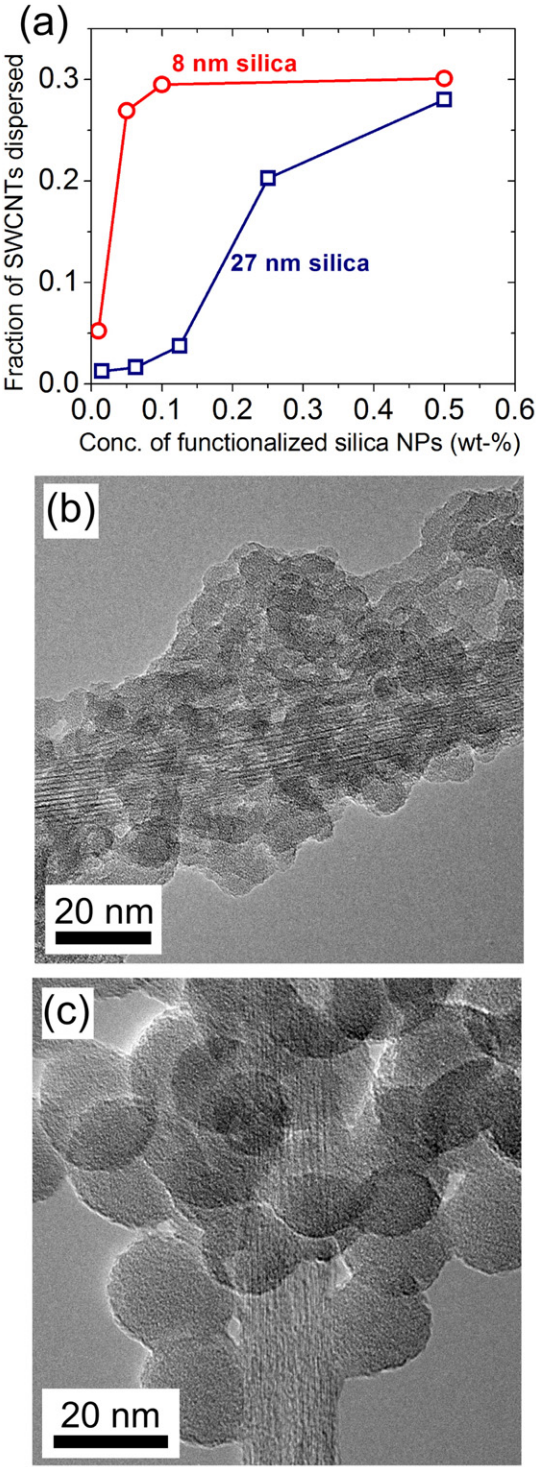

Fig. 2. (a) Effect of silica NP concentration and its curvature (size) on the fraction of SWCNTs dispersed in an aqueous solution. The smaller particles (8 nm, circles) show better SWCNT dispersibility than lower curvature silica beads (27 nm, squares). (b) and (c) respectively are the TEM images of SWCNT nanobundles engulfed by 8 nm and 27 nm functionalized silica NPs.

increases in the pH range of 2–7 and then decreases sharply beyond pH 7 (Fig. 1a and S1). This difference in the equilibrium amount of SWCNTs dispersed for two different silica surface chemistries highlights the role of surface specific interactions between SWCNTs and the silica NPs in the nanotube dispersibility. The pH dependence of SWCNT dispersibility was further investigated by zeta potential–pH titrations for aforementioned silica surface particles. As can be seen from Fig. 1b, the charge on the non-functionalized silica particles remains strongly negative at pH > 4 (ca. isoelectric point (IEP) ~ pH 2). Whereas for *n*-propylamine functionalized silica NPs, the surface charge remains positive until pH < 8 and becomes strongly negative in the pH > 9, with IEP ≈ pH 8. Correlating the SWCNT dispersibility with silica NP surface charge (Fig. 1a and b), we find that higher fraction of nanotubes can be dispersed when the silica surface is weakly charged. Although the exact nature of interactions between SWCNTs and silica is not known but we speculate that less hydrophilic patches between charged groups on silica surface [13,14] would bind preferentially with SWCNTs and lead to their stabilization. This conjuncture is supported by our observation, where a reduction in the number of charged sites on the particles results into better dispersibility of SWCNTs [15]. In addition, it can also be ascertained that a minimum silica surface charge is necessary for achieving a stable SWCNT dispersion (Fig S1). This can be attributed to the fact that for *in-solution* stability, the silica coated SWCNTs must possess mutual electrostatic repulsion which will restrict the re-bundling and phase separation of the nanotubes. Here it should be emphasized that unlike amphiphilic dispersing agents where the SWCNT bundles are dispersed into individual nanotubes, the silica NPs lead to the formation of the particle decorated SWCNT nanobundles. The TEM and AFM images confirm the presence of silica–SWCNT nanobundles (Fig. 2b, c and S2). This difference between the equilibrium state of SWCNTs dispersed by amphiphiles and silica NPs can be attributed to higher diffusive access of molecular amphiphiles over nanosized silica particles. The smaller size and higher diffusivity of the molecular surfactants provide better access to the confined intertubular spaces of SWCNT bundles, which then results into higher nanotube dispersibility.

The role of silica nanoparticle diffusivity and spatial restriction in SWCNT dispersibility can be further confirmed by varying the curvature (particle size) of the dispersing silica nanoparticles. Fig. 2a shows the