



## Rapid Communication

## In-situ Adsorption of Polymer Particles on Multi-wall Carbon Nanotubes Using Colloidal Techniques



Tetsuya Yamamoto\*, Naoya Toyoda

Department of Materials Design Innovation Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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## ABSTRACT

A novel technique for the adsorption of polymer particles on carbon nanotubes was developed. First, the surfaces of multi-wall carbon nanotubes (MWCNTs) were coated with poly(*N*-vinyl acetamide) (PNVA) to confer them hydrophilicity together with good dispersion stability in water owing to a steric effect between the hydration layers. Second, the hydrophilic MWCNTs were covered with polymethyl methacrylate (PMMA) particles bearing positive charges—synthesized using V-50—through electrostatic interactions. These polymers were obtained by soap-free emulsion polymerization. The in-situ adsorption of PMMA particles on surface MWCNTs were attributed to the hydration layers of the modified MWCNTs, and electrostatic interactions between PMMA particles and the modified MWCNTs. It can be expected that the PMMA particles adsorbed on the carbon nanotubes hold the potential to serve as glue between carbon nanotube and PMMA in the composite.

Carbon nanotubes (CNTs) [1] have been widely studied in many fields. Numerous studies reported different methods to disperse CNTs in water using surfactants [2–6], polymers [7–9], and metallic complexes [10,11]. These suspensions were employed for electronic devices because of the excellent conductivity of CNTs [12]. In the present study, we developed a fundamental technique for the dispersion of CNTs in water using polymer colloids, which can be prepared by various polymerization methods. In particular, polymerization in water in the absence of surfactants—known as soap-free emulsion polymerization—was performed in this study to prevent the surfaces of the CNTs from being contaminated by the surfactants during the process using polymer colloids. Furthermore, the synthesized particles with sizes smaller than 300 nm were suitable for the surface modification of CNTs. A water-soluble initiator is generally used in soap-free emulsion polymerization and the charges of the particles are required to maintain dispersion stability in water originating from functional group decomposition of the initiator [13,14]. Ionic functional groups were present on the particle surface to confer good dispersion stability in water. These charges aid to stabilize the CNTs in water when the polymeric particles are adsorbed on their surfaces. Few studies have reported effective techniques for the adsorption of polymer colloids on CNTs dispersed in water probably because the addition of polymer colloids for the adsorption using electrostatic interactions led to instability of the CNTs in the aqueous phase. Hence, we developed an alternative method for the in-situ adsorption of polymer particles on CNTs keeping their dispersion stability good in water and evaluated the stability of the CNT colloids.

The water used in the soap-free emulsion polymerization was purified using a purification system (WG250, Yamato Scientific), and nitrogen gas was then bubbled into the water to remove any dissolved oxygen. Methyl methacrylate (MMA, Tokyo Chemical Industry) was used as received and served as monomer for the soap-free emulsion polymerization. Potassium persulfate (KPS, Sigma Aldrich Co. LLC) or 2,2'-azobis(2-methylpropionamide)dihydrochloride (V-50, Sigma Aldrich Co. LLC) was used as radical initiator without further purification. KPS or V-50 enabled the particles synthesized by polymerization to be charged negatively or positively, respectively [13–15]. *N*-Vinyl acetamide (NVA) (Showa Denko K.K.) was used in the polymerization promoted by V-50 to produce amphiphilic polymers according to Table 1. Their chemical structures are shown in Fig. 1. The temperature of the reactor and the impeller rotation speed were controlled by a magnetic stirrer equipped with a heater (RCH-20L, EYELA). The reaction time was set to 6 h.

Multi-wall carbon nanotubes (MWCNTs, VGCF-H, Showa Denko K.K.) with fiber length of from 1 μm to 10 μm and average diameter of 150 nm were surface-modified using the polymers. The synthesized PNVA solution was diluted ten times with water and used to make the surfaces of the MWCNTs hydrophilic by adsorption. Thus, 10 mg of MWCNTs was added to 20 mL of the PNVA solution to be coated and dispersed using an ultrasonic bath at 38 kHz (US-5KS, SND) for 1 h. The hydrophilic MWCNTs were obtained by removing the excess of PNVA polymer from the solution using a filtration membrane with 800 nm pores (ATTP01300, Millipore). Then, 10 mg of the hydrophilic

\* Corresponding author.

E-mail address: [yamamoto.tetsuya@material.nagoya-u.ac.jp](mailto:yamamoto.tetsuya@material.nagoya-u.ac.jp) (T. Yamamoto).

**Table 1**  
Experimental conditions for the polymerization of NVA.

Water [g]	20
NVA monomer [mmol/L]	320
V-50 initiator [mmol/L]	2.03
Temperature [°C]	70
Impeller rotation speed [rpm]	130

MWCNTs collected on the filter were dispersed again in 20 mL of water to prepare the hydrophilic MWCNT colloids.

The polymerization reaction was performed in a 30 mL round-bottom reactor. The conditions employed for the polymerization are listed in Table 2. The reaction time was set to 6 h. In order to prepare the polymer colloids, the polymerization experiments were carried out as follows. The given amounts of pure water and initiator were poured into the reactor, and the monomer was then added. The reactor was sealed with a cap, and heated to 70 °C using an electric heater. The reaction mixture was agitated at 130 rpm with an impeller using a magnetic stirrer. Then, the desired PMMA colloid was obtained by diluting the reaction mixture five times with water.

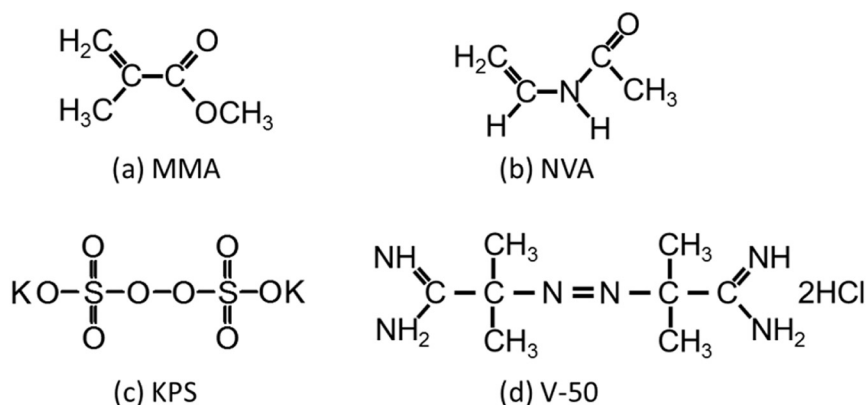
Next, 2 mL of the hydrophilic MWCNT colloid was added to 2 mL of the PMMA colloid upon stirring at 400 rpm for 2 h to promote the adsorption of the PMMA particles on the hydrophilic surface of the MWCNTs. A filtration was also performed to remove the excess of PMMA particles from the bulk. Hence, the MWCNTs coated with PMMA particles were obtained and dispersed again in 2 mL of water.

The morphologies of the MWCNTs in the suspensions were observed by field emission scanning electron microscopy (JSM-7500FA, JEOL). The SEM samples were prepared as follows: a small amount of the solution was sampled from the bottle, and a drop was then placed on a freshly cleaved mica plate. The specimen was dried, and then coated with a thin osmium film by chemical vapor deposition (Osmium Plasma Coater OPC60A, Filgen).

The zeta potential of the synthesized colloids was measured using a Zetasizer Nano-ZS (Malvern Co., Ltd) after diluting the sample with deionized water.

To measure the amounts of the adsorbed polymers on the MWCNTs, the samples were dried at room temperature, and then their weight change was detected using a thermal gravimetric analyzer (TG, DTG-60AH, Shimadzu) operated at a heating rate of 10 °C/min to heat the sample up to 500 °C. To evaluate the dispersion stabilities of the colloids, an UV-Vis spectrophotometer (V-650, Jasco Co.) was operated to measure the transmissivities of the colloids at a wavelength of 300 nm or 500 nm.

The MWCNTs were added to the various PNVA solutions upon dilution with water. The color of the colloids turned black, suggesting good dispersion stability in water. To study the adsorption of the PNVA polymers on the MWCNTs, their surface potentials were measured in water using a Zetasizer. The zeta potentials of all MWCNTs are shown in



**Table 2**  
Experimental conditions for the soap-free emulsion polymerization of MMA.

Water [g]	20
MMA monomer [mmol/L]	64
Initiator [mmol/L]	2.03
Temperature [°C]	70
Impeller rotation speed [rpm]	130

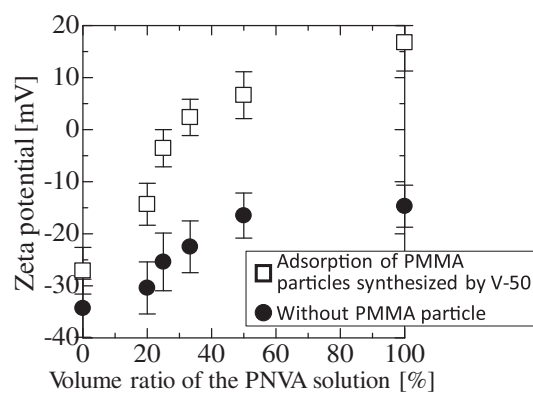


Fig. 2. Effect of the volume ratio of the PNVA solution on the zeta potentials of MWCNTs.

Fig. 2. Before the adsorption of the polymers, the zeta potential of the MWCNTs was found to be  $-38.7$  mV. This value was in agreement with previous results [16,17]. The surface potential decreased as the volume ratio of the PNVA solution increased. The reduction of the surface potential was attributed to the adsorption of the PNVA synthesized using the cationic initiator through electrostatic and hydrophobic interactions. However, the zeta potential remained negative.

Next, 3 mL of the hydrophilic MWCNT colloids and 1 mL of the PMMA colloids synthesized in the presence of KPS or V-50 were mixed, and the morphologies of the resulting MWCNTs after filtration are shown in Fig. 3. The surfaces of the MWCNTs were not covered with negatively charged PMMA particles due to KPS as a consequence of electrostatic repulsion. On the other hand, the positively charged PMMA particles enabled the surfaces of the MWCNTs to be covered due to their adsorption by electrostatic interactions.

The zeta potential of the MWCNTs after the surface modification with positive PMMA particles is also plotted in Fig. 2. It is clear that the zeta potential changed from negative to positive due to the adsorption of the PMMA particles bearing positive charges, by increasing the volume ratio of the PNVA solution. As the volume ratio of the PNVA solution increases, the surfaces of the MWCNTs are more easily coated with the PMMA particles. When the surface was not covered with PNVA, the surfaces of the MWCNTs were hardly covered with the PMMA particles because the change of zeta potential was very small.

Fig. 1. Chemical structures of the (a) MMA monomer, (b) NVA monomer, (c) KPS initiator, and (d) V-50 initiator.

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