# Influence of the Zeta Potential on the Dispersability and Purification of Single-Walled Carbon Nanotubes

**Hui Hu, Aiping Yu, Eric Kim, Bin Zhao, Mikhail E. Itkis, Elena Bekyarova, and Robert C. Haddon\***

*Center for Nanoscale Science and Engineering, Departments of Chemistry and Chemical and Environmental Engineering, University of California, Riverside, California 92521-0403*

We report a systematic study of the purification of nitric acid treated single-walled carbon nanotubes (SWNTs) by centrifugation at constant pH. The progress of the purification procedure was followed by estimating the purity by solution-phase near-infrared spectroscopy, and it was found that the sediment obtained by centrifugation at pH 2 had the highest purity. The stability of the aqueous dispersions of SWNTs and carbonaceous impurities (CIMP) after nitric acid treatment was investigated by measuring their $\zeta$ potential and the concentration of acidic sites. We found that, at lower pH, the CIMP has a higher $\zeta$ potential than nitric acid treated SWNTs, and it is this factor that allowed the separation of the carbonaceous impurities via centrifugation and the concomitant purification of the SWNTs.

## Introduction

The purification of carbon nanotubes is of great importance since most carbon nanotube applications require materials of high quality. Nitric acid is a common reagent for purification of carbon nanotubes and has constituted the first step in many different purification schemes. Nitric acid treatment is usually employed to remove metal catalysts, together with some of the amorphous carbon,[1,2] but it can also oxidize carbon atoms at the ends and at defect sites of carbon nanotubes. Refluxing or sonicating carbon nanotubes in nitric acid opens the ends of the carbon nanotubes[3] and thereby introduces carboxylic acid groups at the ends or at defect sites of carbon nanotubes.[4–10] The carboxylic acid groups play an important role in SWNT chemistry as they can be further reacted with a variety of organic molecules.[11] Recently we reported a systematic study on the use of refluxing nitric acid as a purification treatment for electric arc produced (EA) single-walled carbon nanotubes (SWNTs).[12] In addition to removing metal catalyst, we found that nitric acid destroys SWNTs to produce carbonaceous impurities. The removal of the acidified amorphous carbon can be achieved via centrifugation;[1,3,13,14] however, the mechanism of this process and the role played by centrifugation has not been systematically studied.

The as-prepared SWNTs exist in bundles between 1 and several tens of nanometers in diameter, but nitric acid treatment exfoliates the SWNT bundles.[12] The average bundle size of the nanotubes after the nitric acid treatment is between 1 and 6 nm, and thus they behave as colloidal particles. The $\zeta$ potential is an index of the magnitude of the electrostatic interaction between colloidal particles and has already been used to discuss the density of acidic sites on the surface of multiwalled carbon nanotubes (MWNTs) and the stability of the MWNT/water colloidal system.[15–21] The stability of the MWNT/water colloidal system is increased by introducing polymers,[20,21] which leads to an increase of the absolute value of the $\zeta$ potential or a shift of the isoelectric point. The $\zeta$ potential of shortened MWNTs

in water has also been measured,[18] and it was found that the carboxylic acid groups introduced in the shortening step led to charges on the surface of MWNTs.

In this paper, we report the purification of nitric acid treated SWNTs by centrifugation as a function of pH. The mechanism of the separation of the carbonaceous impurities from SWNTs was studied by measurement of the concentration of acidic sites and the $\zeta$ potential of the carbonaceous constituents in aqueous dispersion. SWNTs give rise to colloidal solutions, and because the stability of such dispersions depends on the balance between the repulsive electrostatic charges on the colloidal particles and the van der Waals attraction, it is clear that the $\zeta$ potential is a useful parameter for understanding SWNT dispersability.

## Experimental Section

As-prepared (AP) SWNTs and purified SWNTs were obtained from Carbon Solutions Inc. (www.carbonsolution.com). Other chemicals were purchased from Aldrich and used without further treatment. The near-IR spectra were obtained on a Varian Cary 500 spectrophotometer. Scanning electron microscopy (SEM) images were taken with a Philip XL-30 microscope. The $\zeta$ potentials of the SWNT samples were measured at a concentration of 0.05 mg/mL with a Zetaplus analyzer (Zetaplus, Brookhaven, USA). The pH values of the SWNT solutions were adjusted from 2.0 to 10.0 by adding 0.05 M hydrochloric acid or 0.05 M sodium hydroxide solution.

The $\zeta$ potential was calculated by use of the Smoluchowski equation (eq 1), which is appropriate as an average particle size of 500 nm was found in light scattering measurements using the same instrument (Zetaplus, Brookhaven). With these assumptions, the $\zeta$ potential can be directly calculated from the electrophoretic mobility ($\mu$):

$$\mu = \frac{\zeta \epsilon V}{4\pi \eta d} \qquad (1)$$

where $\epsilon$ is the dielectric constant of the medium, $V$ is the applied

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* Corresponding author: haddon@ucr.edu.

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voltage, $\eta$ is the viscosity of the suspension, and $d$ is the electrode separation.

In a general purification procedure, AP-SWNTs (10 g) were refluxed in 1500 mL of 7 M nitric acid for 6 h.[12] After cooling to room temperature, the black mixture was centrifuged at 3500 rpm for 15 min and the brown transparent supernatant was decanted. Water was added and mixed thoroughly with the sediment (1 g/200 mL). The black mixture was then centrifuged at 3500 rpm for 15 min. The upper layer was decanted, and water was added to the sediment. The weight of the resulting product (paste) was 6.5 g. The paste was divided evenly into four portions, and each portion was used in three cycles of the resuspension/centrifugation/decantation procedure at pH values of 2, 3, 7, and 10. In each step of the cycle, 200 mL of water was added to the sediment and mixed thoroughly and the pH of the mixture adjusted by using 1 M HCl and a Corning 445 pH meter. Then the mixture was centrifuged at 3500 rpm for 15 min and the supernatant decanted and collected via membrane filtration; the resulting sediment was used in the next resuspension/centrifugation/decantation cycle. The carbonaceous purity of the sediments and supernatants was evaluated by solution-phase near-IR spectroscopy in dimethylformamide (DMF), and the relative purity (RP) of all samples was referenced to the standard sample R2;[22] the final yield and relative carbonaceous purity (RP) of each product is shown in Figure 3. The purity evaluations were carried out on dilute dispersions of SWNTs in DMF where light scattering is insignificant.[27]

The titration of the acidic sites in carbonaceous materials is based on previously reported methods.[8,23,24] The carbonaceous materials were stirred in water for 2 days under argon and collected via filtration to remove residual nitric acid. In a typical experiment, 7 M/(6 h) nitric acid treated SWNTs (109.77 mg) were stirred in 50.00 mL of 0.05 M NaOH aqueous solution under argon for 48 h. Prolonged stirring was required to allow the solid SWNTs to equilibrate with the NaOH solution. The mixture was filtered through a 1.2 $\mu$m pore-size membrane, and the SWNTs collected on the membrane were washed with DI water to remove residual NaOH. The combined filtrate and washings were titrated with 38.90 mL of 0.05 M aqueous HCl solution to reach neutrality (pH = 7.00), as monitored by a pH meter (Corning pH meter 445). Thus the amount of acidic sites in the SWNT sample is 0.56 mmol, while the amount of carbon in the SWNTs is estimated to be 9.15 mmol assuming that the SWNTs are solely composed of carbon (after correction for metal residue)[12] and therefore the mole percentage of acidic sites in the SWNT sample is 6%.

To analyze the usefulness of a purification procedure, the content of SWNTs in the purified material should be evaluated by reference to a 100% pure SWNT sample. However, an analytically pure SWNT sample is not available, and we have previously utilized an arbitrary high purity sample as reference (R-SWNT = R2), to evaluate relative purities (RP) by use of solution phase near-IR spectroscopy.[22] Apart from the purity of the product that is obtained from the purification process, it is important to evaluate the fraction of the desired material that is recovered in the product. Thus it is convenient to define a purification recovery factor (PRF), which provides a measure of the fractional quantity of the product that is recovered after the purification; while the purity of the final material (product, SWNT) is important, a process that destroys most of the desired product during the process is of doubtful utility. Assuming that a measure of the absolute purity (P) is available, then PRF = [*P*(product)/*P*(starting material)] × Y, where Y is the yield of
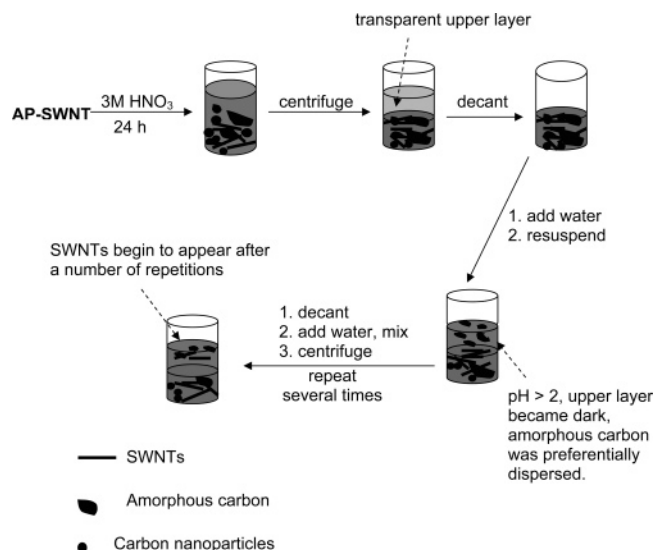


**Figure 1.** Schematic diagram of the resuspension/centrifugation/decantation procedure.

product after purification; clearly an ideal purification process would exhibit P ≡ PRF ≡ 1. In the case of SWNTs where the only available measure of purity is RP,[22] we write P = Z × RP, where Z is a presently unknown factor with a value greater than unity;[25,26] in the present case in which the starting material is the AP-SWNTs and the product is the purified SWNTs (P-SWNT), we have

$$PRF = [P(\text{P-SWNT})/P(\text{AP-SWNT})] \times Y$$
$$= [RP(\text{P-SWNT})/RP(\text{AP-SWNT})] \times Y$$

As before,[22] the relative purity of a SWNT sample X is given by

$$RP(\text{X-SWNT}) = [AA(S, \text{X-SWNT})/AA(T, \text{X-SWNT})]/$$
$$[AA(S, \text{R-SWNT})/AA(T, \text{R-SWNT})]$$

in which the areal absorption values (AA) are obtained by integration of the near-IR spectra between the spectral cutoffs of 7750 and 11750 cm$^{-1}$ (chosen to capture the $S_{22}$ interband transition in electric arc produced SWNTs). AA(T, X-SWNT) and AA(T, R-SWNT) are the total integrated areas of the X-SWNT and R-SWNT samples, whereas AA(S, SWNT) and AA(S, R-SWNT) are the areas of the X-SWNT and R-SWNT samples under the $S_{22}$ absorptions after baseline correction.[12,22,25,26] It is important to note that the value of PRF is independent of Z and therefore does not depend on the purity of the arbitrary reference sample R2.

## Results and Discussion

In our previous report, we found that nitric acid treatment destroys SWNTs to produce carbonaceous impurities.[12] The key to obtaining high-quality SWNTs from this procedure is to find an appropriate process for removing the carbonaceous impurities remaining in the sample after the nitric acid treatment.

In the present work we evaluated the use of a centrifugation method to remove the carbonaceous impurities. In the example given in Figure 1, refluxing the SWNTs in 3 M nitric acid for 24 h, followed by centrifugation at 3500 rpm for 15 min, led to precipitation of the carbonaceous materials as sediment. The upper supernatant layer of the mixture was brown and transparent, and this was decanted and water added and mixed thoroughly with the sediment. The resuspension/centrifugation/decantation cycle was repeated several times (Figure 1); when
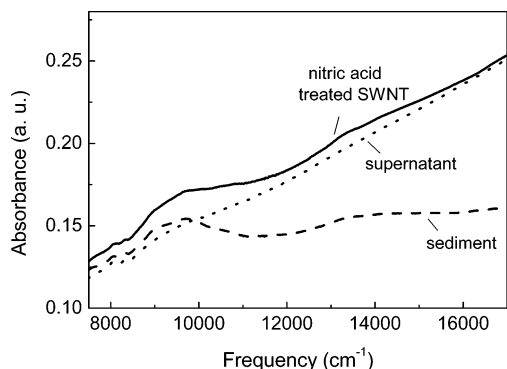
**Figure 2.** Vis−near-IR spectra of nitric acid treated SWNTs: (solid line) SWNTs refluxed in 3 M HNO$_3$ for 24 h (relative carbonaceous purity, RP = 30%); (dashed line) sediment (RP = 45%) and (dotted line) supernatant (PR = 8%) obtained after centrifugation. The relative carbonaceous purity (RP) is evaluated against reference sample R2.[22]
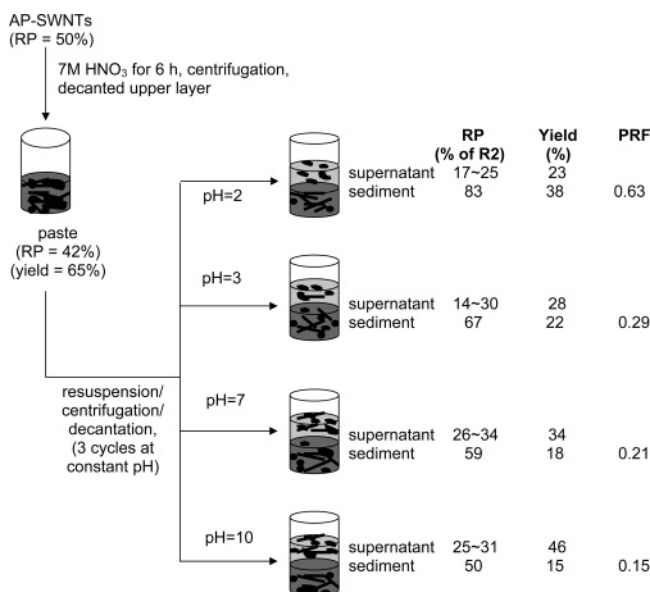


**Figure 3.** Schematic diagram of the SWNT purification procedure by centrifugation at constant pH, where RP is the relative carbonaceous purity and PRF is the purification recovery factor.

the pH of the aqueous mixture became higher than 2, the upper layer remained black and opaque after centrifugation. This phenomenon is consistent with previous reports,[13,14] where the supernatant and sediment were separated by microscale filtration and examined with electron microscopy and it was found that the sediment was enriched in SWNTs.

To analyze the content of the materials after the resuspension/centrifugation/decantation treatment discussed above, we measured the relative carbonaceous purity of the sediment and the supernatant by using solution-phase near-IR spectroscopy. After nitric acid treatment, it was found that the purity of the SWNTs mixture was RP = 30%; after the centrifugation treatment the sediment and the supernatant had relative carbonaceous purities of RP = 45 and 8%, respectively (Figure 2). It is therefore apparent that the carbonaceous impurities are more easily dispersed than the SWNTs that largely remain in the sediment. Thus the centrifugation procedure can serve to purify nitric acid treated SWNTs.

To optimize this purification method, we investigated centrifugation under a range of different pH conditions. The as-prepared SWNTs were refluxed in 7 M HNO$_3$ for 6 h as a first step in the purification procedure.[12] As illustrated in Figure 3, after decantation of the transparent upper layer, the initial paste
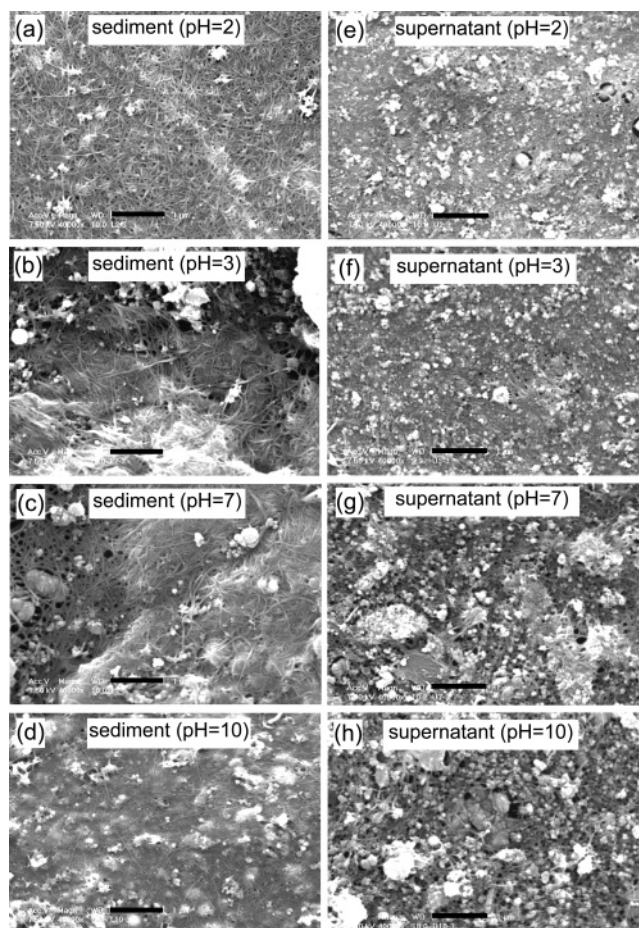


**Figure 4.** SEM images of sediments obtained at pH = (a) 2, (b) 3, (c) 7, and (d) 10 and the corresponding supernatants at pH = (e) 2, (f) 3, (g) 7, and (h) 10. The scale bar is 1 $\mu$m.

was divided into four portions, and the resuspension/centrifugation/decantation cycle was repeated three times at constant values of pH 2, 3, 7, and 10, and both the sediment and the supernatant were analyzed.

It was found that the purity of the sediment was dependent on the pH of the aqueous suspension. At a pH of 2 the sediment had a purity of RP = 83%, and both the purity and the yield of sediment decreased with increasing pH. Thus it is clear that at low pH the carbonaceous impurities (CIMP) have a higher dispersibility in water than SWNTs. As the pH is increased, more SWNTs appear in the supernatant and this decreases the purity of the sediment—at a pH of 10 the purity of the sediment had fallen to RP = 50% and the yield was lowered to 15%.

The purification recovery factor (PRF) for purification at values of pH 2, 3, 7, and 10 is 0.63, 0.29, 0.21, and 0.15, respectively. This emphasizes the importance of pH in the separation, and at pH 2 it is possible to recover more than 60% of the SWNTs originally present in the AP-SWNTs, which is twice as high as that for the purification run at pH 3. This suggests that when pH = 2, the functionalized amorphous carbon (CIMP) is preferentially dispersed in water, whereas most of the SWNTs remain in the sediment; this interpretation is supported by measurements of the concentration of acidic sites and the $\zeta$ potentials of these materials which are reported below.

SEM images of the supernatant and sediment are shown in Figure 4, and it is apparent that the sediment separated at pH 2 contains high-purity SWNTs, whereas the sediments collected at values of pH 3, 7, and 10 only contain a small amount of SWNTs. All of the supernatant fractions, which showed
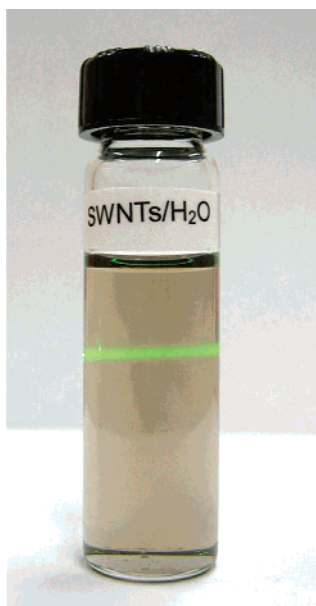
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**Figure 5.** Tyndall effect for an aqueous dispersion of SWNTs at a concentration of 0.05 mg/mL (see text).



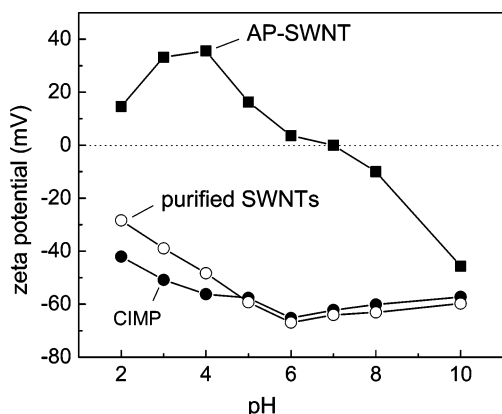**Figure 6.** $\zeta$ potential of AP=SWNT, purified SWNTs, and carbonaceous impurities (CIMP) as a function of pH, in aqueous solutions at a concentration of 0.05 mg/mL.

**TABLE 1:  Concentration of Acidic Sites**

| sample | conc of acidic sites (mol %) | sample | conc of acidic sites (mol %) |
|---|---|---|---|
| CIMP | 8 | 7 M/(6 h) SWNT | 6 |
| 3 M/(24 h) SWNT | 6 | 7 M/(12 h) SWNT | 11 |
| 3 M/(48 h) SWNT | 10 | | |

carbonaceous purities from RP = 14−34%, contain a large amount of amorphous carbon and carbon nanoparticles.

To interpret the centrifugation purification experiments, we measured the $\zeta$ potential and the concentration of acidic sites of the samples. These measurements are of interest because they provide information on the dispersability of SWNTs, which is related to the ionization of carboxylic acid groups introduced by nitric acid treatment (SWNT−COOH → SWNT−COO⁻ + H⁺) and adsorption of ions such as H⁺ or OH⁻ from the aqueous suspension and leads to the presence of a net charge on the surface of the SWNTs. The net charge on the SWNT or CIMP surface leads to the formation of an electrical double layer that is an ionic volume a few angstroms in thickness which prevents the particles from aggregating and thereby stabilizes the suspension. The charge density on the SWNTs is dependent on the pH of the dispersion as this affects the extent of ionization
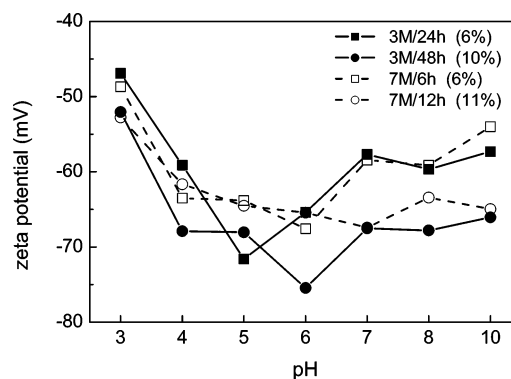


**Figure 7.** pH dependence of the $\zeta$ potential of nitric acid treated SWNTs, as a function of acid treatment (concentration of acidic sites).

and adsorption and in turn the stability of the dispersion. As discussed below, the present purification is successful because the CIMP apparently contain a higher concentration of surface charges and are therefore more dispersable than the SWNTs at certain pH values.

Colloidal solutions give rise to the Tyndall effect, in which a light beam passing through a colloidal solution leaves a discernible track as a result of scattering. Figure 5 shows the passage of a light beam from a laser pointer through an aqueous suspension of SWNTs, and the path of the beam can be clearly seen through the homogeneously dispersed SWNTs. However, studies of the near-IR absorption spectroscopy of SWNT dispersions have established that scattering has a negligible effect on transmission experiments on well-dispersed samples.[27]

Figure 6 shows the $\zeta$ potential as a function of pH of dispersions of AP-SWNTs, purified nitric acid treated SWNTs, and CIMPs. For AP-SWNTs, the absolute value of the $\zeta$ potential is smaller than 30 mV, and the isoelectric point is around pH = 7. This is in accord with the low dispersability of AP-SWNTs in water that is clearly a result of the low surface charge on AP-SWNTs, which is insufficient in preventing AP-SWNT aggregation and precipitation.

Nitric acid treated SWNTs and CIMP have a high $\zeta$ potential value over a wide pH range (2−10), which indicates that they are fairly stable in water; at a pH value of 2, the $\zeta$ potentials of purified SWNTs and CIMP are −28 and −42 mV, respectively. Since the weight densities of amorphous carbon and SWNTs are comparable (1.2−1.4 g/mL),[28−30] the stability of the dispersions is largely determined by the electrostatic repulsion due to the surface charge. At pH 2, the CIMP have higher $\zeta$ potential than the SWNTs and thus the supernatant becomes enriched in CIMP at the expense of the SWNTs, whereas the SWNTs are preferentially concentrated in the sediment. This interpretation is supported by the purification procedure given in Figure 3, where it may be seen that the best separation is achieved at low pH values. The high $\zeta$ potential found for purified SWNTs suggests that it is the presence of the carboxylic groups and concomitant surface charges that enable the efficient dispersal of SWNTs in water. The strongest SWNT composite film yet to be fabricated made use of nitric acid treated SWNTs, with a $\zeta$ potential value of −80 mV.[31]

Nitric acid treatment introduces carboxylic acid groups at the open ends and the defect sites of the SWNTs, and the concentration of the acidic sites of SWNTs can be estimated by acid−base titration (Table 1).[8] The concentration of acidic sites on the SWNTs is increased by employing more vigorous nitric acid treatment, and this variation is reflected in the measured $\zeta$ potentials (Figure 7). At pH 3, the $\zeta$ potential values of the SWNTs decrease in the order 7 M/(12 h) > 3 M/(48 h)

> 7 M/(6 h) > 3 M/(24 h), and this is consistent with the decrease in the concentration of acidic sites on the SWNTs.

## Conclusion

Nitric acid treated SWNTs can be efficiently purified by centrifugation at constant pH, and at pH 2, the purified SWNTs reach a relative carbonaceous purity of 83%. The separation of carbonaceous impurities from SWNTs is based on their differential dispersability in water as demonstrated by measurement of the $\zeta$ potentials and the concentration of acidic sites.

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