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Interactions between Multiwall Carbon Nanotubes and Poly(dially dimethylammonium) Chloride: Effect of the Presence of a Surfactant

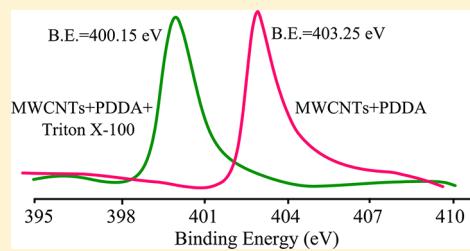
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ABSTRACT: The interactions between multiwall carbon nanotubes (MWCNTs) and poly(dially dimethylammonium) chloride (PDDA) have been studied in the presence of different ionic and nonionic surfactants, such as sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), Tween 20, 40, 60, and 80, and Triton X-100. On the basis of scanning electron microscopy (SEM) results, the MWCNT/PDDA sample treated with Triton X-100 has been observed to show good dispersion of nanotubes. This is due to the $\pi-\pi$ stacking between the benzene ring of Triton X-100 and the hexagonal carbon rings of nanotubes and better coating of PDDA on MWCNTs, as is confirmed by the Raman studies. Energy dispersive X-ray (EDX) spectroscopic data shows the presence of higher oxygen content in the MWCNTs/PDDA/Triton X-100 sample. The maximum upshift in the C1s peak position and down-shift in the N1s peak position for the MWCNTs/PDDA/Triton X-100 sample has been observed from X-ray photoelectron spectroscopy (XPS) results and is due to the intermolecular charge transfer from carbon in MWCNTs to nitrogen in PDDA. The presence and nature of a surfactant in the MWCNTs/PDDA system has been found to affect their interactions. The above results suggest that the MWCNTs/PDDA/Triton X-100 system is suitable as a metal-free electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells.



INTRODUCTION

The versatile properties of carbon nanotubes (CNTs) have attracted the attention of the scientific community worldwide, which led to their applications in many important fields such as hydrogen storage, field emission, electronic devices, composites, etc.^{1–4} It is well-known that CNTs are formed by rolling up a graphene sheet. In the graphitic surface of CNTs, a π bond is present along the z -axis which is responsible for the interaction of various chemical groups on their surface via $\pi-\pi$ stacking interactions. This interaction is actually responsible for the strong van der Waals forces between them, and due to this reason, CNTs generally exist in the bundled form. The inert nature and insolubility of pristine CNTs in different solvents limits their usefulness for many applications. However, their dispersion and functionalization with suitable functional groups helps to overcome these problems. The dispersion of CNTs with various surfactants has already been widely reported and hence will not be discussed in detail here.^{5–17} The surface modification of CNTs with various surfactants assists in overcoming the strong van der Waals forces between them as well as in the selective adsorption of various chemical groups on their walls and at end-caps. The cationic and anionic surfactants have electrostatic interactions with CNTs. However, there are no charge interactions between CNTs and nonionic surfactants and in this case the steric hindrance of the chemical moieties prevents the agglomeration of nanotubes. The concentration,

chemical nature, and structure of a surfactant along with the dimensions (average diameter and length) of CNTs are some of the key factors which control their dispersion behavior. Various polymers and biomolecules like DNA have also been reported to act as dispersing agents for CNTs.^{18–24}

The functionalization of MWCNTs with a polyelectrolyte, poly(dially dimethylammonium) chloride (PDDA), has recently been reported to enhance their dispersion.²⁵ It has been confirmed by XPS and PA-FTIR spectroscopic studies that $\pi-\pi$ interactions exist between MWCNTs and PDDA. The polyelectrolyte coats the graphitic surface of MWCNTs with positive charge (from N^+ of PDDA), which is responsible for the dispersion of MWCNTs. The CNTs/PDDA system is being actively studied at present due to its application as a metal-free electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells.^{26,27} These materials have the potential to replace the conventional Pt/C based electrocatalysts in fuel cells. Being corrosion resistant and having surface active sites for the adsorption and desorption of reaction products, CNTs can act as an efficient electrocatalyst. Because of its strong electron-withdrawing ability, PDDA creates a net positive charge on carbon atoms in the CNTs via intermolecular charge

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transfer. These positively charged carbon atoms can easily attract electrons from the anode of the fuel cell and enhance the ORR. The carbon nanomaterials (mainly CNTs and graphene) doped with various heteroatoms like B, S, P, I, and Se have also been reported to act as metal-free electrocatalysts.^{28–32}

So far, only few research groups have made efforts for the development of carbon nanomaterials based metal-free electrocatalysts, which are reported to be very promising candidates for fuel cell technology. However, still, there is considerable scope for the further improvement in their performance. Keeping this in mind, we have studied the interactions between MWCNTs and PDDA in the presence of different surfactants. In the present work, we have examined whether the presence of a surfactant in the MWCNTs/PDDA system leads to an enhanced coating of PDDA on MWCNTs, and how the presence of a surfactant affects the interactions between PDDA and MWCNTs.

The effect of the presence of different ionic (cationic, anionic) and nonionic surfactants on the interactions between MWCNTs and PDDA has been investigated by SEM, EDX, Raman, and XPS studies.

■ EXPERIMENTAL SECTION

MWCNTs (CNT M95, Carbon Nanomaterial Technology Co. Ltd., South Korea) with a diameter of 5–15 nm, length 10 μm , and >95% purity, Triton X-100 (Sigma Aldrich), PDDA (Sigma Aldrich), Tween 20, 40, 60, and 80, SDS and CTAB (sdfine) have been used as received in the present study. We prepared eight different samples (A1–A8) of MWCNTs functionalized noncovalently with PDDA. The codes and ionic nature of different surfactants used in these samples have been listed in Table 1. In all the samples (A1–A7), the same amount of

Table 1. The Sample Codes and the Ionic Nature of Different Surfactants Used

sample code	MWCNTs/PDDA + surfactant	ionic nature
A1	SDS	anionic
A2	CTAB	cationic
A3	Tween 20	nonionic
A4	Tween 40	nonionic
A5	Tween 60	nonionic
A6	Tween 80	nonionic
A7	Triton X-100	nonionic
A8		

MWCNTs, PDDA, and surfactant has been used, whereas, in sample A8, no surfactant has been used. The detailed protocol followed for the preparation of these samples is given below:

An 80 mg portion of MWCNTs was taken in a conical flask, and 200 mL of deionized (DI) water was added to it. To this solution, 2.6 wt % (0.0302 mg) of surfactant and 0.5 wt % (1 mL) of PDDA was added. This mixture was then ultrasonicated for 120 min at room temperature (10 min on and 3 min off basis). Upon ultrasonication, a homogeneous black solution was obtained which indicates the complete dispersion of a sample. In order to extract nanotubes from this solution, the sample was given multiple washings via centrifugation using DI water (at 7000 rpm, 5 times for 15 min each run). The retrieved MWCNTs were then dried in an oven overnight at 60 °C.

In order to examine the size and distribution of MWCNTs for all the samples, scanning electron micrographs were

obtained with a Hitachi S-4800 field-emission SEM at an acceleration voltage of 0.5–30 kV. The specimens for high-resolution imaging were coated with osmium (Os). Energy dispersive X-ray (EDX, X-Max 50011, Horiba) spectra were recorded to determine the elemental composition of different samples at 16 kV and 15 μA . The Raman spectroscopy measurements were carried out at room temperature using a Raman spectrometer FRA 106/S (BRUKER OPTIK GMBH, Germany) with a 1006 nm Nd:YAG laser having a 4 cm^{-1} resolution in the 500–4000 cm^{-1} wavenumber range. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech ESCALAB 201 using a monochromic Al X-ray source (Mg (1253.6 eV)/Al (1486.6 eV), 0.5 eV).

■ RESULTS AND DISCUSSION

The SEM images of some representative samples (A1–A3, A6–A8) are shown in Figure 1a. The SEM image of pristine MWCNTs has also been included in Figure 1b for the purpose of comparison. The bundles present in pristine MWCNTs have been observed to be well dispersed only in samples A3, A6, and A7. In these three samples, Tween 20, Tween 80, and Triton X-100 have been used, respectively, and all of these surfactants are nonionic in nature (Table 1). Among these three samples, A7 (treated with Triton X-100) shows the best dispersion results and this is due to the presence of π – π interactions between the benzene ring of Triton X-100 and hexagonal rings of carbon atoms on the graphitic surface of MWCNTs.⁶ The wrapping of PDDA on MWCNTs should also result in an increase in their average diameter, and this was verified by measuring the diameters of MWCNTs in different samples using SEM images. The diameter values are also shown in Figure 1a. An increase in diameter for a sample as compared to pristine MWCNTs indicates the wrapping of PDDA on its graphitic surface. On the basis of these diameter values, again the samples A3, A6, and A7 have been observed to show better wrapping of PDDA on MWCNTs. The samples A1 and A2, which contain ionic surfactants, and sample A8, which does not contain any surfactant (Table 1), show very less dispersion. This suggests that the nature of a surfactant affects the dispersion of MWCNTs. The surfactants assist in unzipping the bundled MWCNTs during the ultrasonication process. Triton X-100 has already been reported to be a very good dispersant for the CNTs.⁶ On the other hand, SDS, CTAB, and Tween surfactants have been reported to result in relatively poor dispersion of CNTs.¹¹ The debundling of MWCNTs also helps in an improved coating of PDDA on CNTs.

The MWCNTs used in the present work are >95% pure, so there is a possibility of the presence of some residue catalytic elements such as Fe, S, and Al in small amounts. This was checked by EDX studies, and the wt % and at % contents of different elements present in all the samples are listed in Table 2. The oxygen content is very high in samples A3–A7, and its value is highest for sample A5, which was treated with Tween 60 (Table 2). On the other hand, if we look at the chlorine content, its value is lowest for sample A5. This decrease in the chlorine content is due to the reaction of Cl^- (from PDDA) with H^+ and its loss as HCl gas.²⁷ The chloride in PDDA changes to hydroxide, and the presence of –OH groups also contributes to a higher content of oxygen in a sample. An increase in oxygen content and a corresponding decrease in chlorine content have been observed for all the samples (see Table 2).

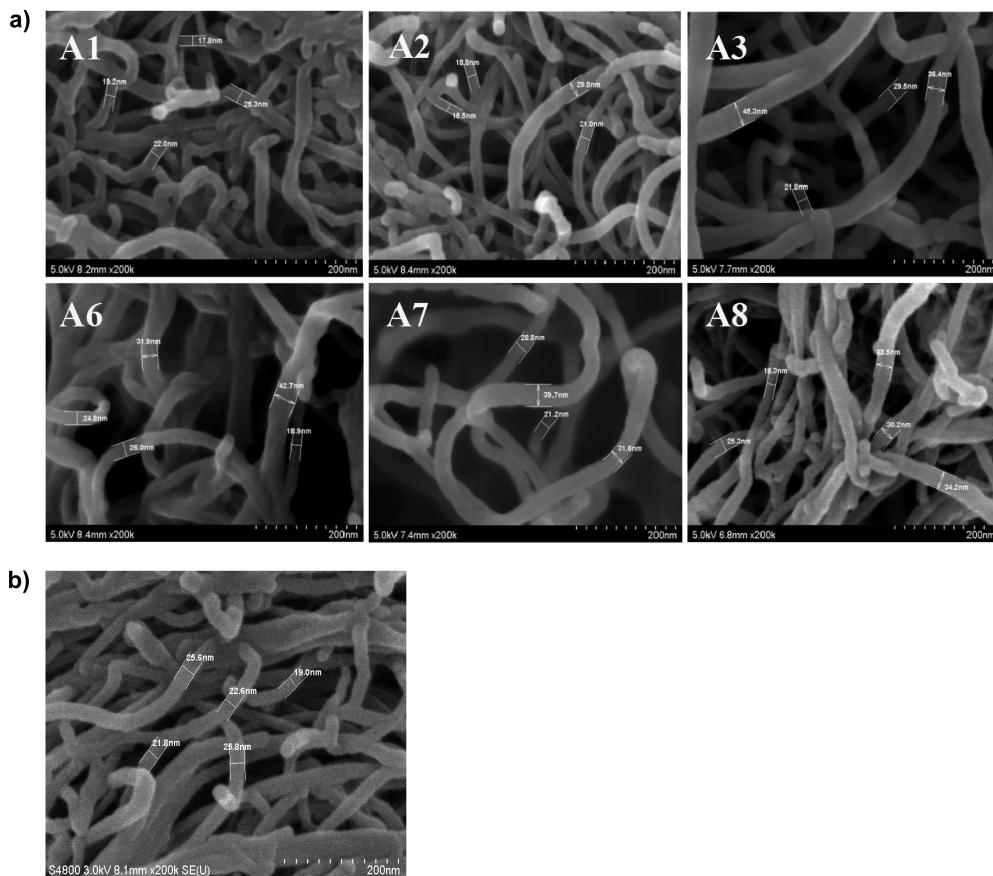


Figure 1. (a) SEM micrographs of some selected samples. (b) SEM micrograph of pristine MWCNTs.

Table 2. EDX Data for Different Samples

element	C		O		Al		S		Cl		Fe	
sample	wt %	at %	wt %	at %	wt %	at %	wt %	at %	wt %	at %	wt %	at %
A1	85.78	90.30	10.57	8.35	0.63	0.29	1.88	0.74	0.42	0.15	0.73	0.17
A2	89.26	92.54	8.64	6.73	0.65	0.30	0.12	0.05	0.38	0.13	0.77	0.17
A3	71.34	77.86	26.0	21.31	0.74	0.36			0.19	0.07	1.72	0.40
A4	72.86	78.33	26.61	21.48	0.22	0.10			0.05	0.02	0.26	0.06
A5	69.25	75.15	30.27	24.66	0.26	0.13			0.04	0.02	0.18	0.04
A6	76.37	81.67	22.23	17.85	0.59	0.28			0.15	0.06	0.65	0.15
A7	77.09	82.55	20.83	16.75	0.77	0.37			0.24	0.09	1.07	0.25
A8	86.15	90.62	10.40	8.21	0.87	0.41	0.30	0.12	0.96	0.34	1.33	0.30

The Raman spectra of all the samples are shown in Figure 2. The presence of a peak near 1287 cm^{-1} (D-band) has been assigned to the disorder and structural defects, whereas a peak near 1596 cm^{-1} (G-band) has been assigned to the planar vibrations of carbon atoms on the graphitic surface of MWCNTs. The extent of imperfections and defect concentration in MWCNTs can be estimated from the intensity ratio (I_D/I_G) of D and G peaks. The positions of D and G peaks as well as the I_D/I_G ratio for different samples have been determined from Figure 2, and the respective values are listed in Table 3. The I_D/I_G ratio is lower for the samples A1 and A7 as compared to all other samples (Table 3). As this ratio is an evaluation of defect concentration in MWCNTs, it shows that PDDA coverage on MWCNTs is the best for samples A1 and A7. PDDA coats the walls of nanotubes, which leads to the coverage of some defects and imperfections in them, and as a result, fewer defects are detected. It shows that the presence of

a surfactant assists in enhanced wrapping of PDDA on MWCNTs. It also shows that noncovalent functionalization of PDDA on MWCNTs is less destructive as compared to their covalent functionalization with strong acids and bases, which creates more defects and imperfections.³³

The chemical changes resulting from the interactions between MWCNTs and PDDA in the presence of different surfactants have been studied by XPS. In the MWCNTs/PDDA system, carbon, oxygen, and nitrogen are the main elements present. Thus, the XPS spectra for all the samples in relevant narrow binding energy ranges have been plotted separately for C1s, O1s, and N1s peaks, and are shown in Figures 3, 4, and 5, respectively. In the C1s spectra (Figure 3), in addition to the main binding energy peak, some other peaks are also present in some of the samples at higher binding energy values. These indicate the presence of other functional groups containing carbon, e.g., alcohol, epoxy, aldehyde, etc.³⁴

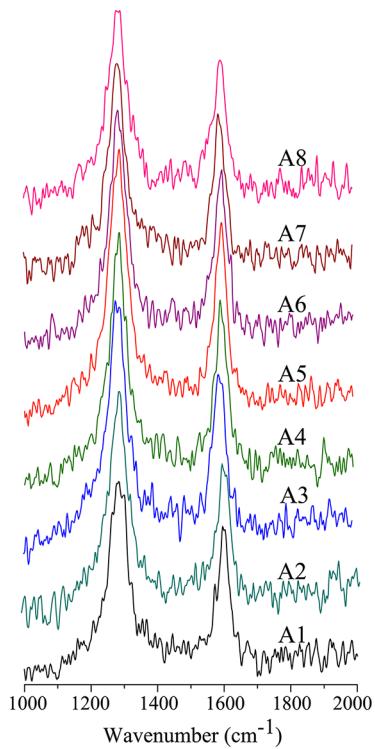


Figure 2. Raman spectra for all samples.

Table 3. Raman Data for Different Samples

sample	position of G-band (in cm^{-1})	position of D-band (in cm^{-1})	I_D/I_G
A1	1596	1284	1.247
A2	1593	1288	1.410
A3	1593	1279	1.380
A4	1595	1288	1.327
A5	1600	1288	1.342
A6	1601	1283	1.308
A7	1592	1284	1.281
A8	1598	1293	1.310

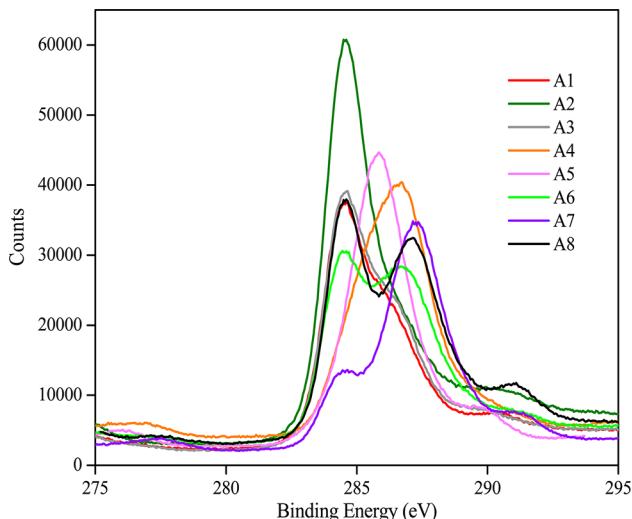


Figure 3. XPS spectra of the C1s peak for all samples.

For sample A7, peak binding energy (287.24 eV, Table 4) is significantly higher as compared to all other samples. For the

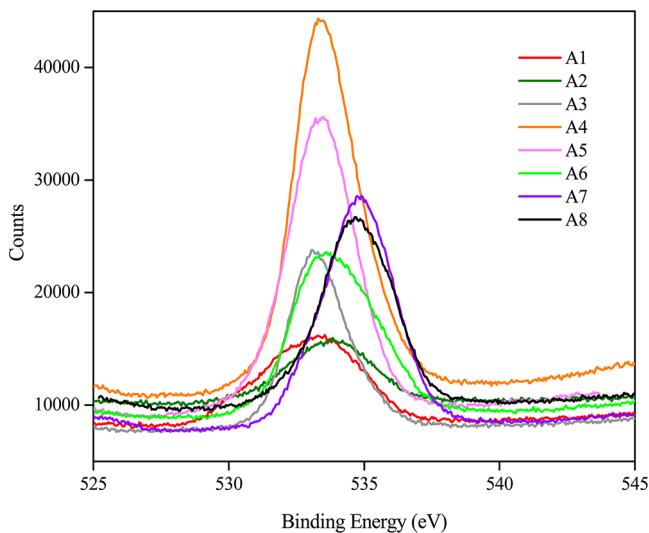


Figure 4. XPS spectra of the O1s peak for all samples.

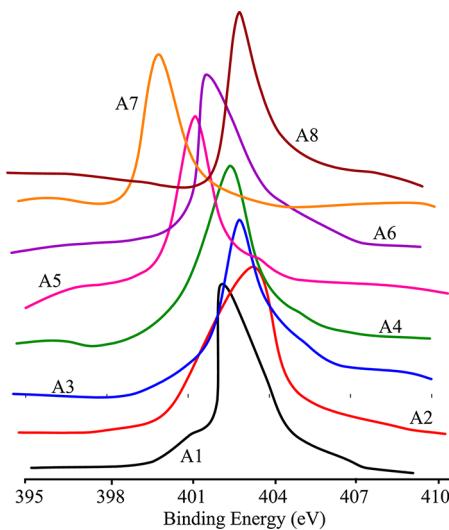


Figure 5. XPS spectra of the N1s peak for all samples.

Table 4. Peak Binding Energy Values of C1s, O1s, and N1s for Different Samples

sample	C1s B.E. (in eV)	O1s B.E. (in eV)	N1s B.E. (in eV)
A1	284.55	533.34	403.05
A2	284.57	533.81	403.25
A3	284.56	533.12	403.05
A4	286.66	533.39	402.05
A5	285.83	533.46	401.15
A6	284.5	533.61	401.9
A7	287.24	534.78	400.15
A8	284.56	534.67	403.25

samples A1, A2, A3, and A6, peak binding energy values are comparable to sample A8 (MWCNTs/PDDA). However, samples A4, A5, and A7 show enhanced peak binding energy values as compared to sample A8 (Table 4). An upshift in the C1s peak position is generally taken as evidence of charge transfer from carbon in MWCNTs to nitrogen in PDDA. The O1s peaks for all the samples are shown in Figure 4, and their respective peak binding energy values are listed in Table 4. For sample A7, the O1s peak binding energy is higher as compared

to the rest of the samples, and the value is 0.11 eV higher (Table 4) as compared to sample A8 (MWCNTs/PDDA). A significant amount of oxygen in the functionalized MWCNTs is probably due to the physically adsorbed oxygen and in addition, they are functionalized with PDDA which also contains oxygen.³⁴ In PDDA, the chloride changes to hydroxide and a large amount of water of hydration is also contained by PDDA around itself, which leads to a large oxygen content in these samples.²⁵

The N1s peaks for all the samples are shown in Figure 5, and their respective peak binding energy values are listed in Table 4. The presence of the N1s peak in XPS spectra, which comes from PDDA, confirms the functionalization of MWCNTs with PDDA. For sample A8, which does not contain any surfactant, the N1s binding energy peak is at 403.25 eV, which is attributed to the positively charged nitrogen (N^+) in PDDA.²⁵ As is observed from Figure 5, the binding energy peaks shift toward lower values for samples A1 and A3–A7 as compared to sample A8. The down-shift in the N1s peak binding energy value corresponds to the charge transfer from MWCNTs to the positively charged N^+ center of PDDA. As compared to sample A8, all other samples (except A2) show enhanced charge transfer in them. It is to be noted that the down-shift in the binding energy value is significantly high and is maximum for sample A7 (see Table 4).

CONCLUSIONS

The MWCNTs have been noncovalently functionalized with PDDA in the presence of different ionic and nonionic surfactants. The presence of a surface-active agent has been observed to greatly affect the interactions between PDDA and MWCNTs. The MWCNTs/PDDA samples have been observed to be dispersed in the presence of different surfactants. The sample A7, which has been treated with Triton X-100, shows the best dispersion results, as is revealed by the SEM studies. EDX data confirms the presence of a higher oxygen content in the samples treated with surfactants. The I_D/I_G ratio determined for all the samples from Raman data shows that there are less defects in the sample treated with Triton X-100. It is due to the better PDDA wrapping on MWCNTs for this sample. An upshift in the C1s peak position and down-shift in the N1s peak position in XPS spectra have been observed in all the samples which contain surfactants. However, the shift in peak positions is highest for the sample treated with Triton X-100. An upshift in the C1s and down-shift in the N1s peak positions show that the intermolecular charge transfer process takes place from carbon in MWCNTs to nitrogen in PDDA. These results could lead to better performance of the MWCNTs/PDDA system as a metal-free electrocatalyst for the ORR in fuel cells. However, further studies are needed to optimize the performance and testing of these materials in actual fuel cells.

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Notes

The authors declare no competing financial interest.

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