ASM Sc. J., 14, Special Issue 1, 2021 for ICSTSS2018, 86-92

Study of Dispersants for Fabrication of MWCNTs-PANi Film in Deionised Water Medium

Nor Hamizah Eleas[1], Intan Syaffinazzilla Zaine[2*], Nurul Nazwa Mohammad[2] and Abd Hakim Hashim[3]

[1]*Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, Selangor, Malaysia*

[2]*Department of Applied Sciences, Universiti Teknologi MARA, Cawangan Pulau Pinang, Malaysia*

[3]*Advanced Materials Research Center, SIRIM Bhd. Kulim Hi-Tech Park, Kulim, Kedah, Malaysia*

Multiwall carbon nanotubes-polyaniline (MWCNTs-PANi) films were fabricated through electrophoretic deposition (EPD) by using crystal violet (CV) and safranin (SAF) as the dispersant. EPD was conducted in deionised water as a suspension medium. The analysis and comparison of the experimental data for CV and SAF conveyed the influence of dyes in the deposition of MWCNTs-PANi. It was discovered that CV and SAF both can be used as a dispersant for EPD of MWCNTs-PANi via in-situ polymerisation. Both dyes were co-deposited on MWCNTs-PANi as it can be observed through FESEM images supported by the FTIR result. Contrariwise, CV appears to co-deposit dominantly compared to SAF. MWCNTs-PANi electrodes were analysed with active mass loading in the range of 7.0 - 7.4 mg cm^{-2} of the nickel foil current collector for electrochemical supercapacitor application. The highest specific capacitance achieved for CV was at 15.94 F g^{-1} and SAF was at 21.32 F g^{-1}, respectively. Meanwhile, charge-discharge curve analysis for MWCNTs-PANi in CV and SAF as the dispersant were evaluated with power density of 12.26 x 10^{4} W kg^{-1} and 37.40 x 10^{4} W kg^{-1}, respectively. The organic dyes are the promising dispersant to deposit MWCNTs-PANi composite materials. Nonetheless, the effect of organic dyes used must be taken into consideration since it may influence the material ability to perform as a supercapacitor electrode.

Keywords: crystal violet; dispersant; electrophoretic; multiwall carbon nanotubes; safranin

I. INTRODUCTION

Up to date, the use of carbon as electrode material for supercapacitor is rising due to their cost-efficient and ability to enhance supercapacitor performance (Hao *et. al.*, 2017; Liu *et. al.*, 2017; Zhou *et al.*, 2018). Carbon material has been engineered to various type of structures such as porous carbon, wire-like carbon, onion-like carbon and carbon nanotubes in order to enhance supercapacitor performance (Liu *et. al.*, 2017; Shaibani *et. al.*, 2017; Zhou *et al.*, 2014, 2018). Strategies include engineered carbon materials or by creating carbon composite materials were commonly done by researchers (Wang *et al.*, 2016). One of the engineered carbon materials is multiwall carbon nanotubes (MWCNTs). MWCNTs are acclaimed to have a high aspect ratio which facilitates the charging process while ions transport in the electrochemical process. MWCNTs as the supercapacitor electrode material element used to associate with other related elements such as polymer was done to produce powerful material in providing more reliable supercapacitor electrode material. Many types of conducting polymer (CP) found can be used to create MWCNTs composite material in supercapacitor application especially polypyrole and polyaniline (PANi) (Dhibar & Das, 2014; Eising *et. al.*, 2017; Guo *et. al.*, 2015; Online *et. al.*, 2013; De Souza *et. al.*, 2014; Su & Zhitomirsky, 2015).

In order to develop a method in creating MWCNTs-CP composite, several studies showed, the use of organic dyes efficiently fabricated MWCNTs-CP composite (Chen *et. al.*, n.d.; Fahdil *et. al.*, n.d.; Njuguna *et. al.*, 2015; Su & Zhitomirsky, 2013). Previous work had published that the

---

*Corresponding author's e-mail: intan.zaine@uitm.edu.my

use of safranin (SAF) and crystal violet (CV) as the organic dye material used to fabricate MWCNTs-CP material. The approach used to produce MWCNTs-CP material was done by using electrophoretic deposition (EPD) method. SAF and CV are able to disperse MWCNTs well in aqueous solution (Hasnida *et al.*, 2018). Furthermore, the use of organic dyes were the easiest, reliable and effective way to create MWCNTs-CP composite.

The used of SAF and CV as dispersant reagent have been proven to disperse MWCNTs in aqueous solution. However, the effects of using both types of dyes in achieving good supercapacitor properties remain as a gap to be studied. This study focused on the effects of using organic dyes to fabricate MWCNTs-PANi for supercapacitor electrode. The deposition of MWCNTs-PANi using SAF and CV were successfully done. The chemical structure of SAF and CV were shown in Figure 1. Both dispersants had cationic charged group.

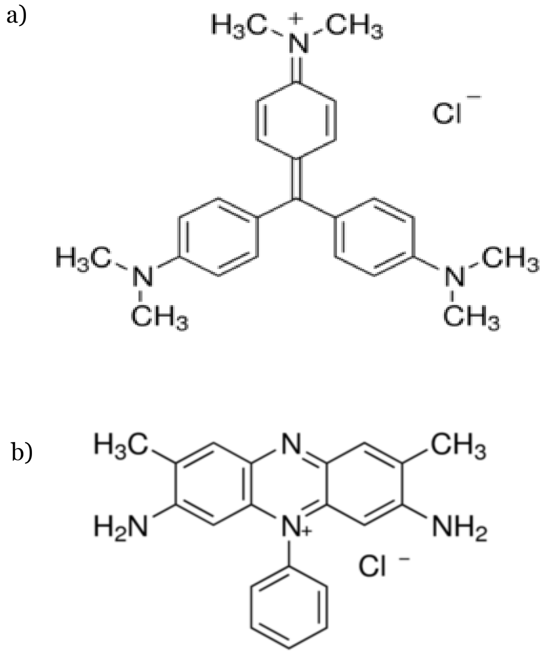


Figure 1. Structure of (a) crystal violet and (b) safranin

II. FABRICATION OF ELECTRODES

SAF and CV used as MWCNTs dispersant in deionised water. Both dye powders containing 15 weight % of MWCNTs were dispersed in deionised water and ultrasonically agitated for 7 hours. Aniline was added to the suspensions with 10 volume % respectively to fabricate MWCNTs-PANi composite. Since aniline was used as monomer, in-situ polymerisation method took place in order to polymerise the aniline. In-situ polymerisation also allows MWCNTs-PANi to be fabricated simultaneously in the polymerisation process. The in-situ polymerisation was conducted for 6 hours with titration of aluminium persulphate (APS) at the earlier 30 minutes. Nickel foil was used as a substrate to deposit the MWCNTs-PANi composite. The film deposition preparation was fabricated according to EPD general procedure. The procedure of the electrodes fabrication was simplified in Figure 2.

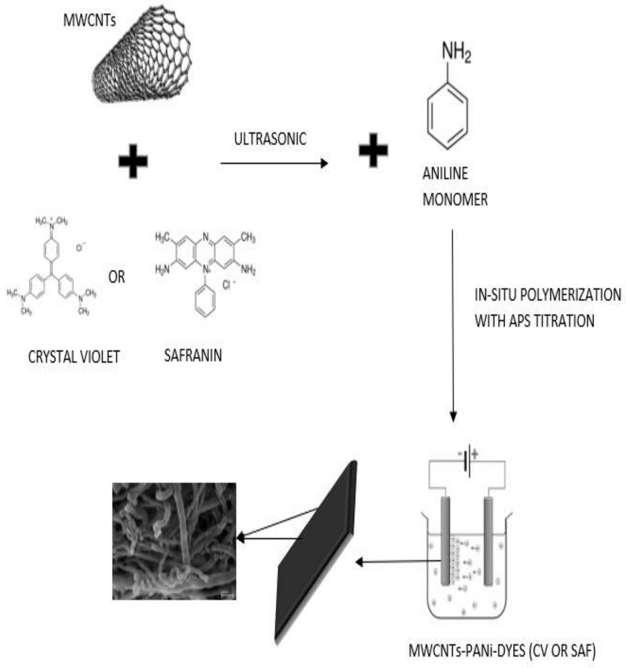


Figure 2. Framework of MWCNTs-PANi electrode fabrication

After several attempts of EPD, the films were found deposited at cathode using parameter as shown in Table 1.

Table 1. Optimum parameter for EPD of MWCNTs-PANi films using SAF and CV as dispersant

Parameters	**Value**
Voltage (V)	8
Deposition time (minute)	10

III. RESULTS AND DISCUSSION

Figure 3 compares the microstructures of MWCNTs-PANi deposited using CV and SAF as dispersant. The FESEM images of MWCNTs-PANi showed agglomerates of dyes particles with PANi. The agglomeration of dyes or PANi seems hard to be distinguished since the agglomeration of dyes covered likely the whole part of MWCNTs-PANi especially in CV. The size of agglomerates was about 40-50 nm for MWCNTs-PANi in CV and 20-40 nm in SAF. This result indicated the amount of SAF was less agglomerated compared to CV coated MWCNTs-PANi.

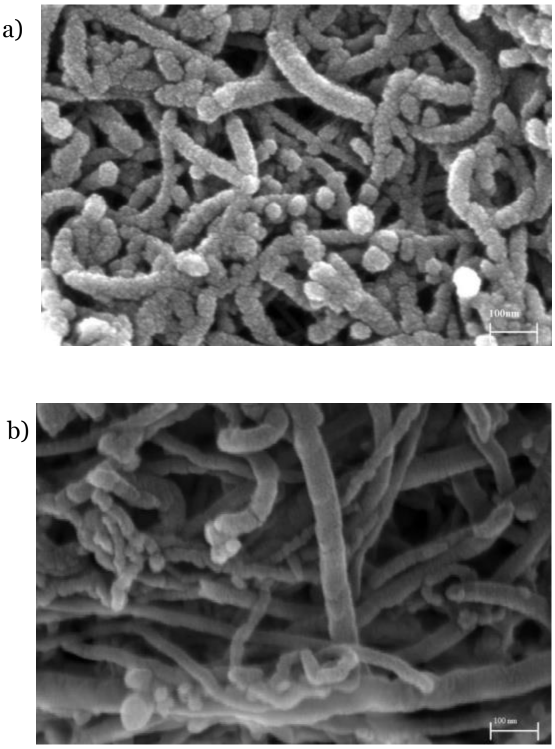


Figure 3. Comparison of MWCNTs-PANi deposited usingn(a) CV and (b) SAF as dispersant

Uncoated MWCNTs still can be seen in the FESEM image of MWCNTs-PANi in SAF. However, as for MWCNTs-PANi in CV, all surfaces were covered by CV. The formation mechanism of CV and SAF coated MWCNTs involved hydrophobic interaction of CV and SAF with dispersed MWCNTs-PANi (Barsan *et. al.*, 2015; Wang *et. al.*, 2012; Zare *et al.*, 2015). The amount of dyes coated influence the capacitance amount through MWCNTs-PANi. This result showed, too much agglomeration of dye will agitate the amount of capacitance as the properties of MWCNTs-PANi was distracted.

The FTIR spectra for MWCNTs-PANi in CV and SAF as dispersant were shown in Figure 4. The MWCNTs-PANi structure properties change can be seen in the FTIR spectra. CV and SAF molecular structure were shown in Figure 1 as a reference. The electrical charge of CV is related to two C-N and C=N ligans, whereas the charge of SAF is attributed to two C=N and two C-C. Both dyes containing redox active C-N+ groups which reacted via electrochemical reaction with MWCNTs-PANi in deionised water (Arshadi *et. al.*, 2016; Shi & Zhitomirsky, 2015; Zare *et al.*, 2015). This electrochemical reaction is accountable in resulted to the agglomeration of both dyes to MWCNTs-PANi (Maiaugree *et. al.*, 2012; Online *et al.*, 2013). The interaction of MWCNTs-PANi with the redox active from both dyes was sketched in Figure 5. The appearance of C-N stretching for both CV and SAF were shown in the FTIR spectra of the variable absorption band in the range of 2000 cm^{-1} to 2407 cm^{-1} and 1977-2355 cm$^{-1,}$ respectively (Cheriaa *et. al.*, 2012; Sahu *et al.*, 2015). This variable band may also pointed to PANi amine group (Roy *et al.*, 2018). This result also explains how agglomeration of dyes and PANi are hard to be distinguished. The chemical structure related to the redox active reaction towards MWCNTs-PANi was also shown in Figure 5.

Nonetheless, the broad absorption band at 3286 cm^{-1} in CV FTIR spectra may shows O-H stretching which also revealed CV dominantly interact with MWCNTs-PANi compared to SAF. Benzoid ring with N+ chemical structure can be seen on the FTIR data in the variable of the wavenumber in the range between 3000–4000 cm^{-1} of amine group from both types of dispersant, CV and SAF (characteristic of primary amine group).

The stretching of C-C for MWCNTs-PANi in CV and SAF appeared to be shifted to the lower wavenumber of 1018 cm^{-1} and 938 cm^{-1}, respectively. This is due to resonance of C-C and C=N from CV and SAF structure. The resonance structure occurred when a single bond and double bond characters were introduced into C=N of MWCNTs-PANi base on their chemical structure. These results show MWCNTs-PANi was successfully deposited by using both dyes. However, the fingerprint of PANi in CV was unseen since CV had annihilated the PANi properties. Whereas, as for SAF the fingerprint of MWCNTs-PANi was not dilated much. This result also explained that the agglomeration of CV lowers the capacitance value as CV submerged the MWCNTs-PANi properties.

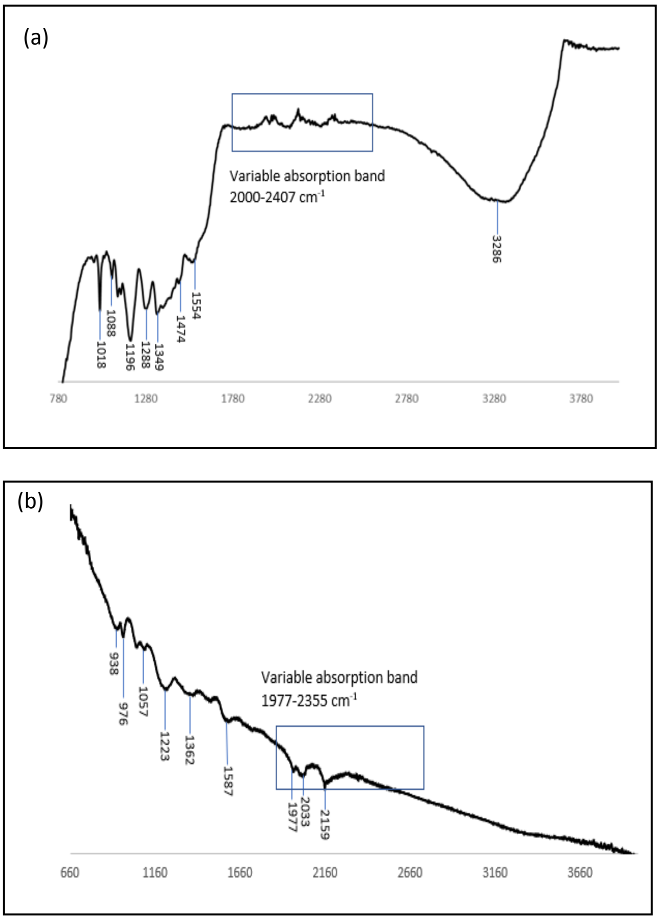


Figure 4. FTIR spectra of MWCNTs-PANi deposited using (a) CV and (b) SAF as dispersant

Figure 5. Schematic structure of MWCNTs-PANi interaction with dyes used

Mobilised MWCNTs-PANi was influenced by direct current applied with electric field of 8 V. Both dispersants, SAF and CV had resulted the deposition formed on the negative electrode. Thus, the chemical reaction of MWCNTs-PANi and suspension occurred on negative electrode. When current passed through the electrode, the electrochemical reaction at cathode surface involved with the reductions reaction of N+, H_2O and O_2 in dyes ions containing solution (Ata *et. al.*, 2018; Salavagione *et al.*, 2014). The chemical reaction related to the schematic structure in Figure 5 was shown as below;

The suspension contains deionised water resulted the possible reaction involving water:

$2H_2O + 2e$ -----------$H_2 + 2OH^-$ (1)

In the presence of H_2O and O_2 together, another possible reaction was also occurred:

$O_2 + 2H_2O + 2e$ -------- $2OH^- + H_2O_2$ (2)

All reactions produced hydroxyl ions (OH^-) at the cathodic surface:

$N^+ + OH^-$ -------------- NOH (3)

OH^- produced at the CNTs surface by the electrochemical reaction, would react with the N^+ which are the functional group contain in both dyes and in PANi. This chemical reaction equation points out the agglomeration occurred due to the electrochemical reaction resulted at redox active group. This result also explains why it is hard to differentiate between the agglomeration of PANi and dyes on MWCNTs as shown in Figure 3.

Figure 6 shows cyclic voltammogram at 2 mV s^{-1} for MWCNTs-PANi electrodes. The MWCNTs-PANi fabricated by SAF clearly shows a larger area of cyclic voltammogram compared to MWCNTs-PANi fabricated by CV as the dispersant. The larger area of cyclic voltammogram was resulted by higher capacitance. The capacitance exhibited by CV and SAF were then calculated to obtain the specific capacitance value.

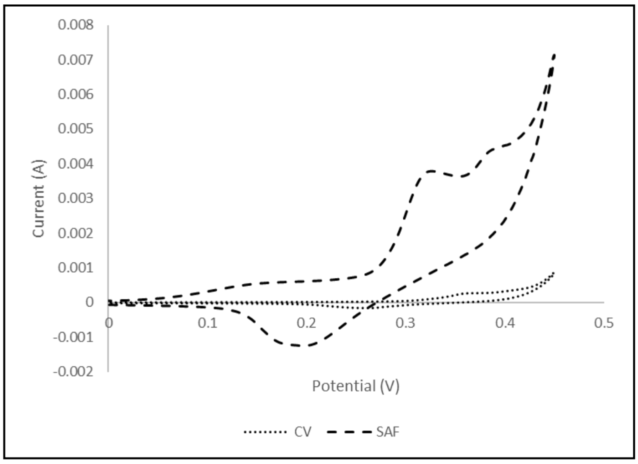
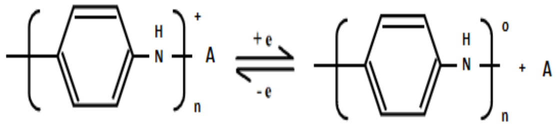


Figure 6. Cyclic voltammogram for MWCNTs-PANi using CV and SAF as dispersant

The highest specific capacitance of MWCNTs-PANi deposited via CV and SAF as dispersants were achieved at 15.94 F g^{-1} and 21.32 F g^{-1}, respectively through cyclic voltammogram. The measured properties were strongly contributed from the pseudo-capacitance due to electrochemical redox reaction provided by PANi at the electrode-electrolyte interface. The redox reaction shows in Equation (4).



(4)

Figure 7 presents the charge discharge curves of MWCNTs-PANi in CV and SAF. The time taken for charge discharging process shows that the MWCNTs-PANi cycling was much longer than the MWCNTs-PANi in CV compared to MWCNTs-PANi in SAF. The discharging time was used to evaluate the power density. The power density calculated was 12.26 x 10^4 W kg^{-1} and 37.40 x 10^4 W kg^{-1} for CV and SAF, respectively. This result pointed out the influence of using dyes as dispersant for fabrication of MWCNTs-PANi supercapacitor electrode. The specific capacitance was significantly different as CV was dominantly agglomerated on MWCNTs-PANi compared to SAF which had changed the properties of MWCNTs-PANi. The co-deposited dyes affect the properties of MWCNTs-PANi since the electrochemical reaction appears to be overlapped with dyes in macromolecule compound.

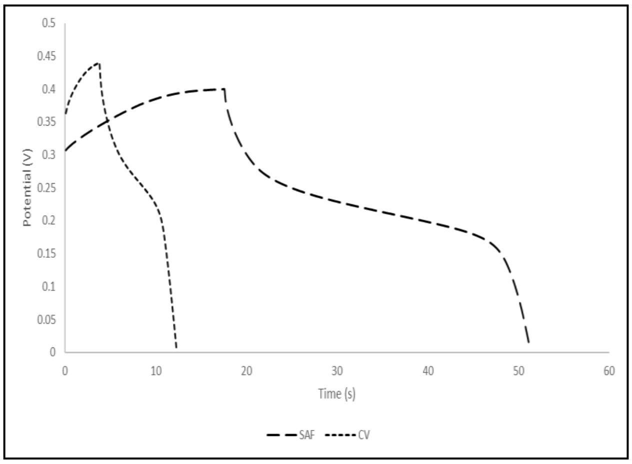


Figure 7. Charge-discharge curve of MWCNTs-PANi using CV and SAF as dispersant

The chemical reaction involved was notified in the Equation (1)-(4). All calculations were evaluated using Equation (5)-(7). The specific capacitance, C_s (F g^{-1}) can be calculated by using Equation (5):

$$C_s = \frac{I}{mS} \qquad (5)$$

where I represents average current that can be obtained from cyclic voltammetry graph, S is the scan rate (mV s^{-1}) and m is the mass of deposited film (g). Energy density, U (W h kg^{-1}) of the deposited film was calculated using Equation (6):

$$U = \frac{1}{2} C_s V^2 \qquad (6)$$

where V is the potential window (V). The power density, P (W kg^{-1}) can be calculated using Equation (7):

$$P = \frac{U}{\Delta t} \qquad (7)$$

where Δt is the time of discharging range.

Table 2 summarised all calculated values of electrochemical properties including mass of deposited film on 1 cm^2 of nickel foil.

Table 2. Mass, specific capacitance and power density of MWCNTs-PANi film

Properties	**Dispersants**	
	CV	**SAF**
Mass (mg)	7.4	7.0
Specific capacitance (F g^{-1})	15.94	21.32
Power density (W kg^{-1})	12.26 x 10^4	37.40 x 10^4

IV. CONCLUSION

The used of CV and SAF allow the dispersion of MWCNTs-PANi in deionised water and electrophoretically deposited on nickel foil. The presence of CV and SAF dyes microstructure influence the result of MWCNTs-PANi for electrode supercapacitor application. MWCNTs-PANi in SAF resulted higher specific capacitance compared to MWCNTs-PANi in CV due to the lower amount of SAF co-deposited on MWCNTs-PANi as shown in FESEM and FTIR result. On the other hand, previous work showed that CV has better stability and reliable to disperse MWCNTs compared to SAF. Nevertheless, the tendency of CV to agglomerate with MWCNTs-PANi could distract the properties of MWCNTs-PANi in electrode supercapacitor application. The use of CV was believed to be reliable if the amount of CV coated on MWCNTs-PANi can be controlled. Strategy to control the amount of CV coated MWCNTs-PANi will be carried out in further research work.

V. ACKNOWLEDGEMENT

The authors would like to thank the Ministry of Education, Malaysia that supports this work through Race Acculturation Colloborative Efforts grant (600-RMI/RACE 16/6/2(5/2014).

VI. REFERENCES

Arshadi, M, Faraji, AR, Moaddeli, A, Khalafi-Nezhad, A & Firouzabadi, H 2016, 'Nanostructured cobalt ions for the adsorption of an organic dye: mechanism and electrochemical study in the presence of carbon nanotubes', Chem. Eng. Res. Des., vol. 109, pp. 707–719.

Ata, MS, Poon, R, Syed, AM, Milne, J & Zhitomirsky, I 2018, 'New developments in non-covalent surface modification, dispersion and electrophoretic deposition of carbon nanotubes', Carbon N. Y., vol. 130, pp. 584–598.

Barsan, MM, Ghica, ME & Brett, CMA 2015, 'Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: A review', Anal. Chim. Acta, vol. 881, pp. 1–23.

Chen, H, Muthuraman, H, Stokes, P, Zou, J, Liu, X, Wang, J, Huo, Q, Khondaker, SI & Zhai, L 2007, 'Dispersion of carbon nanotubes and polymer nanocomposite fabrication using trifluoroacetic acid as a co-solvent', Nanotech., vol. 18, no. 41, pp. 415606.

Cheriaa, J, Khaireddine, M, Rouabhia, M & Bakhrouf, A 2012, 'Removal of triphenylmethane dyes by bacterial consortium', Sci. World J., vol. 2012, pp. 1-9.

De Souza, VHR, Oliveira, MM & Zarbin, AJG 2014, 'Thin and flexible all-solid supercapacitor prepared from novel single wall carbon nanotubes/polyaniline thin films obtained in liquid-liquid interfaces', J. Power Sources, vol. 260, pp. 34–42.

Dhibar, S & Das, CK 2014, 'Silver nanoparticles decorated polyaniline/multiwalled carbon nanotubes nanocomposite for high-performance supercapacitor electrode', Ind. Eng. Chem. Res., vol. 53, no. 9, pp. 3495-3508.

Eising, M, Cava, CE, Salvatierra, RV, Zarbin, AJG & Roman, LS 2017, 'Doping effect on self-assembled films of polyaniline and carbon nanotube applied as ammonia gas sensor', Sensors Actuators B Chem., vol. 245, pp. 25-33.

Fahdil, S, Khalid, SH, Yusof, AM, Mokhtar, M, Alias, AN & Zaine, IS 2016, 'Electrophoretic deposition of functionalised multi-walled carbon nanotubes (f-MWCNTs)-polyaniline (PANi)', Key Eng. Mater., vol. 701, pp. 33-41.

Guo, F, Mi, H, Zhou, J, Zhao, Z & Qiu, J 2015, 'Hybrid pseudocapacitor materials from polyaniline@multi-walled carbon nanotube with ultrafine nanofiber-assembled network shell', Carbon N. Y., vol. 95, pp. 323–329.

Hao, Y, Xu, F, Qian, M, Xu, J, Zhao, W & Huang, F 2017, ‘Low-cost and massive preparation of nitrogen-doped porous carbon for supercapacitor application’, RSC Adv., vol. 7, no. 18, pp. 10901–10905.

Hashim, RHR, Hashim, AH, Yusof, AM & Zaine, IS 2018, 'The effects of dispersants on electrochemical supercapacitor properties of MWCNTs film prepared by AC-EPD technique', ESTEEM Aca. J., vol. 14, no. June, pp. 93–105.

Liu, T, Zhang, F, Song, Y & Li, Y 2017, ‘Revitalising carbon supercapacitor electrodes with hierarchical porous structures’, J. Mater. Chem. A, vol. 5, no. 34, pp. 17705–17733.

Maiaugree, W, Pimanpang, S, Towannnang, M, Rutphonsan, P, Laupa, S, Jarernboon, W & Amornkitbamrung, V 2012, 'Co-electrophoretic deposition multiwall carbon nanotubes/Pt counter electrodes for dye-sensitised solar cell', Jpn. J. Appl. Phys., vol. 51, no. 10s.

Njuguna, J, Vanli, OA & Liang, R 2015, 'A review of spectral methods for dispersion characterisation of carbon nanotubes in aqueous suspensions', J. Spect., pp. 1-11.

Roy, A, Ray, A, Saha, S & Das, S 2018, 'Investigation on energy storage and conversion properties of multifunctional PANI-MWCNT composite', Int. J. Hydrogen Energy, vol. 43, no. 14, pp. 7128–7139.

Sahu, MK, Sahu, UK & Patel, RK 2015, 'Adsorption of safranin-O dye on CO2 neutralised activated red mud waste: process modelling, analysis and optimisation using statistical design', RSC Adv., vol. 5, no. 53, pp. 42294–42304.

Salavagione, HJ, Díez-Pascual, AM, Lázaro, E, Vera, S & Gómez-Fatou, MA 2014, 'Chemical sensors based on polymer composites with carbon nanotubes and graphene: the role of the polymer', J. Mater. Chem. A, vol. 2, no. 35, pp. 14289–14328.

Shaibani, M, Smith, SJT, Banerjee, PC, Konstas, K, Zahari, A, Lobo, DE, Nazari, M, Hollenkamp, AF, Hill, MR & Majumder, M 2017, 'Framework-mediated synthesis of highly microporous onion-like carbon: energy enhancement in supercapacitors without compromising power', J. Mater. Chem. A, vol. 5, no. 6, pp. 2519–2529.

Shi, K & Zhitomirsky, I 2013, 'Polypyrrole nanofiber-carbon nanotube electrodes for supercapacitors with high mass loading obtained using an organic dye as a co-dispersant', J. Mater. Chem. A, vol. 1, pp. 11614–11622.

Shi, K & Zhitomirsky, I 2015, 'Influence of chemical structure of dyes on capacitive dye removal from solutions', Electrochim. Acta, vol. 174, pp. 588–595.

Su, Y & Zhitomirsky, I 2013, 'Cataphoretic assembly of cationic dyes and deposition of carbon nanotube and graphene films', J. Colloid Inter. Sci., vol. 399, pp. 46–53.

Su, Y & Zhitomirsky, I 2015, 'Influence of dopants on performance of polypyrrole coated carbon nanotube electrodes and devices', J. Electrochem. Soc., vol. 162, no. 5, pp. A5013–A5019.

Wang, S, Ng, CW, Wang, W, Li, Q & Hao, Z 2012, 'Synergistic and competitive adsorption of organic dyes on multiwalled carbon nanotubes', Chem. Eng. J., vol. 197, pp. 34–40.

Wang, W, Yan, J & Fan, Z 2016, 'Carbon materials for high volumetric performance supercapacitors: design, progress, challenges and opportunities', Energy Environ. Sci., vol. 9, no. 3, pp. 729–762.

Zare, K, Gupta, VK, Moradi, O, Makhlouf, ASH, Sillanpaa, M, Nadagouda, MN, Sadegh, H, Shahryari-ghoshekandi, R, Pal, A, Wang, Z, Tyagi, I & Kazemi, M 2015, 'A comparative study on the basis of adsorption capacity between CNTs and activated carbon as adsorbents for removal of noxious synthetic dyes: a review', J. Nanostructure Chem., vol. 5, no. 2, pp. 227–236.

Zhou, W, Zhou, K, Liu, X, Hu, R, Liu, H & Chen, S 2014, 'Flexible wire-like all-carbon supercapacitors based on porous core-shell carbon fibers', J. Mater. Chem. A, vol. 2, no. 20, pp. 7250–7255.

Zhou, Y, Jin, P, Zhou, Y & Zhu, Y 2018, ‘High-performance symmetric supercapacitors based on carbon nanotube/graphite nanofiber nanocomposites’, Sci. Rep., vol. 8, no. 1, pp. 1–7.