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Complete List of Authors:	Mishra, Paridhi; Indian Institute of Technology (BHU) Varanasi, Ceramic Engineering KANDASUBRAMANIAN, BALASUBRAMANIAN; DIAT(DU), MATERIALS ENGINEERING

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ARTICLE

Nanostructured Microporous Polymer Composite Imprinted with Superhydrophobic Camphor Soot, for Emphatic Oil-Water Separation

Paridhi Mishra^a, Balasubramanian k.^{b*}

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Abstract

Pollution of water devastatingly affects the marine environment by physical smothering and intoxication. Therefore purification of water resources, especially fresh water reserves, is inevitable in the present age when there is inadequacy of potable water globally. Due to the ease of access and proficient performance, advanced sorbents are obligatory for the clean-up. Here, we report the oleophilicity of nanostructured superhydrophobic Camphor soot particles and their polymer composite, which absorbs oil up to 25 times its own weight. Camphor soot particles exhibit most consistent reusability after elimination of oil by burning in air, while the microporous composite gives superior absorption characteristics and facile handling. No surface oxidation, barrier less oleophilicity and faster rate of absorption, together make the material a potentially competent sorbent for oil-water separation.

Introduction

Discharge of industrial waste, leakage of oil from rigs and wells, and accidental oil spill into water, are acknowledged to be the roots for catastrophic blemish of water resources. In the present case scenario, when the environment is coping with severe repercussions of the burgeoning economy, awareness for environmental remediation is pressing. For the upkeep of water resources, numerous techniques including skimming, bioremediation, dispersant addition and sorption are universally used for the removal of oils¹, organic solvents and dyes, but sorption is an effortless and efficacious way out²⁻³. Commonly used absorbents including activated carbon⁴, zeolites⁵, and natural fibres⁶ suffer from low absorption capacity and separation selectivity² due to their weak affinity for oils/organics⁷. The advanced materials^{4, 5, 6}, developed to surmount these problems involve intricate processing, and expensive raw materials, while being a potent source of intoxication of water (e.g. manganese oxide nanowires) and lacking flexibility (e.g. metal meshes)⁷. Moreover, the sorbent should be flexible, environment friendly, cost effective, and should exhibit quick and easy absorption.

Camphor soot (CS) particles are catalyst free photoluminescent carbon nanoparticles derived from the combustion of camphor and exhibit diamond-like carbon nanostructure, with the presence

of hydrophobic functional groups imparting 'lotus leaf' like characteristics⁸⁻¹². Furthermore, these camphor soot particles form an interconnected network of carbon nanospheres having excellent absorption potential due to intrinsic porosity. Polyvinylidene fluoride (PVDF) is a pure thermoplastic fluoropolymer and frequently used porous membrane material², having low density, low melting point, and resistance to solvents, acids, bases and heat. A number of materials have been developed toward oil-water separation, such as activated carbon, clay, zeolite and organic-inorganic hydrids for separation and removal of organics or oils from water. Sun et al have fabricated reduced Graphene oxide coated cotton fabric for application of oil-water separation.¹³ By modification with polydimethylsiloxane (PDMS), superhydrophobic and Superoleophilic reduced graphene oxide cotton fabric was obtained, which shows a water contact angle of 152°, which exhibits absorption of organics and oils from water with an absorption capacity up to 11 to 25 times its weight. Similarly Gao¹⁴ et al, made Carbon soot (CS) made composite which has the advantages of cost effectiveness and production scalability over other carbons (i.e., graphene, CNTs) in their synthesis. They have demonstrated that a common daily waste CS can be used for developing a cost-effective absorbent (CS sponge) to remove oil contaminants from water. However, Sun et al. prepared a highly porous superhydrophobic activated carbon sponge which exhibits selective absorption of organics or oils from water.¹⁵ Earlier, it was reported that, activated carbon is one of the most important traditional absorbent materials for water purification.¹⁶⁻¹⁸ Due to its high surface area, abundant porosity, activated carbon has been widely used as a porous medium for the absorption of metal

^a Department of Ceramic Engineering, IIT (BHU)-Varanasi, Varanasi-221005, India; Tel: 08004336418; E-mail: paridhi.mishra.cer11@iitbhu.ac.in

^{b*} Department of Materials Engineering, Defence Institute of Advanced Technology(DIAT), Girinagar, Pune-411025, India; Fax: +91 (020) 2438-9509; Tel: +91 (020) 2438-9680; E-mail: meekbs@gmail.com

ions¹⁹ or toxic organic species²⁰ from water. However, the absorption performance of activated carbon is limited by its finite pore volume and hydrophilic nature. In particular, its hydrophilic nature makes it absorb both water and organics, resulting in poor selectivity and low efficiency, which lower its practicality for the removal of organics (especially weakly polar or nonpolar) from water.

In present study, a validation of the oleophilicity of extremely porous, superhydrophobic, incineration-proof, nanostructured CS particles was carried out and a simple formulation scheme for PVDF-camphor soot composite, for emphatic oil-water separation was employed. Combustion generated CS particles offer most consistent reusability as there is no further obliteration in the structure on subsequent burning. High porosity of PVDF foam imparts huge surface area for the absorption of oil, which gets amplified on further addition of camphor soot. The lightweight, benign composite, gives brilliant performance in terms of absorption, kinetics and post sorption handling, as there is no surface oxidation, barrier for oleophilicity and faster rate of response by quickly absorbing oil, up to 25 times its own weight, without settling down, thus facilitating easy removal. Easy availability of raw material and cost efficiency over materials like BN, graphene, carbon nanotubes, SiC etc., simple processing and proficient performance, together make the material a potentially competent sorbent.

2. Experimental Procedure

Materials

PVDF with MW of 2, 75, 000 was received from Sigma Aldrich, India and Camphor tablet of size of (7×5 mm) (C₁₀H₁₆O, 96%, Sigma-Aldrich) was used as source for carbon soot particles without any further.

Synthesis

For the synthesis of porous PVDF-camphor soot composite, we have opted for a facile non-solvent-induced phase separation method¹³. Succinctly, PVDF (0.5g) and coveted amount of CS (0.5, 2, 5, 8 and 10, wt %), were dissolved in a polar solvent (DMF), at 23°C for 1hr and homogenised by Sonication (Sonicator Model- EI-6LH-SP, Sl. No- 1209-122, India) at 20 kHz and 20W for 10 min, supplying uniform suspension of CS in the solution. This mixture was subsequently poured into 100ml deionised water, for the separation of phases. Further, precipitates of phase separation were treated in vacuum and dried in thermally controlled atmosphere at 70°C for 6 h for the removal of remnant moisture. The precipitation of PVDF-CS is attributed to the separation of phases, formed as a result of solvent-non solvent interaction, which followed adsorption of PVDF particles to the air-liquid interface, while unmodified CS particles remained inert¹⁴. It is a stupendous hydrophobic polymer, consequently making a mark in the domain of oil-water separation. Therefore, the hydrophobicity of camphor soot particles and PVDF, together may aid in fabricating superhydrophobic composites (Fig. 1).

Hence, an open-pore structure is generated when PVDF-CS separate as polymer rich phase, leaving the polymer-poor phase as cavities²¹. Scanning Electron Microscopy (SEM) revealed the nanostructure porous surface of the composite, imprinted with photoluminescent carbon nanospheres. On further examination,

the escalated amount of CS was observed to be sealing the pores, thereby closing the in-gates for diffusion of oil/solvent. De-ionized water was used for all the experiments, which was obtained from Millipore Milli-Q system.



Fig.1: Hydrophobicity of PVDF-CS composite is demonstrated by dripping water droplets on the surface of composite.

Test for oleophilicity of camphor soot

CS particles were tested with engine oil, paraffin oil, kerosene, toluene and ethylene glycol. Calculated amount of CS was drenched slowly with measured amount of oil, to compute the absorption capacity. After absorption, the wet CS particles were burned and reused for measuring absorption capacity.

Oil and organic solvent removal tests

Three different kinds of oils and two organic solvents, having different densities, were tested with the composite by keeping the composite with oil-water mixture in a Petri dish. Measurement of absorption capacity, (wt/wt) %, was done by weighing the dry and saturated composite, before and after absorption of oil/solvent, respectively, saturation of sample was ensured by soaking it for 3h. Evaporation of solvents from composite was avoided during weight measurements.

Characterisation

SEM Imaging was adopted on a Carl Zeiss FESEM, Germany. The samples were sputtered using Au-Pd for 75 seconds in 10 mA under the pressure of 0.6×10^{-2} Pa and were tested in 85 microscope at 5kV and the images were obtained under 25 KX and 50 KX, magnification. The thermogravimetric analysis (TGA) was carried out in a Perkin Elmer TGA, Pyris-1 analyzer. The soot samples (~10 mg) were heated from 200 to 800°C at a heating rate of 10°C min⁻¹ under continuous nitrogen flow. The specific surface area was determined by N₂ adsorption and calculated utilizing the Brunauer–Emmett–Teller (BET) method; the soot particles were out-gassed under vacuum (0.1 mm Hg) at 90°C overnight. BET analysis was carried using Costech Instruments Sorptometer Kelvin 1042, managed by Kelvin 1042 v.3.05 software. Surface wettability was measured by the sessile drop technique. The water contact angle (WCA) measurements were carried using a Krüss DSA25 (Germany) contact angle goniometer using deionised water at ambient temperature. 8 mL

DI water was delivered from a micro-syringe to form a sessile drop on the surface of the glass substrate coated with camphor soot and an average of an eight measurements were used for the analysis.

3. Result and Discussion

The porous features of the PVDF/CS composites were investigated with FESEM analysis and BET analysis. The FESEM of the composites exhibits the existence of a large number of mesopores. The surface area was found to be $45.9 \text{ m}^2 \text{ g}^{-1}$ by fitting the isotherm to the Brunauer–Emmett–Teller (BET) model. The pore size of the composites in the range of 40–100nm are illustrated in Fig. 2. The broad size of the pores suggests that the composites hold hierarchical pore structures. Generally, porous materials with simultaneous superhydrophobicity and superoleophilicity are considered as high capacity absorbers for the removal of oil spills and organic contaminants. The adsorption properties of the composites were varied for a range of organic solvents and oils. As shown in Fig. 2, when it came into contact with oil dispersed on the surface of water, composite surface immediately absorbed the oil layer around it, giving rise to the emergence of a transparent water surface.^{8, 22–25} At the same time the oil gradually shrunk and completely disappeared in a few minutes which illustrate superoleophilicity of the composite. The absorption capacities of the composites for different oils and solvents could be controlled by the existence of hierarchical porous network structure, the density and viscosity of the oils and organic solvents. Hence PVDF/CS composite has a superior adsorption ability compared with the PVDF which could be attributed to the hierarchical structure and large superhydrophobic surface area, as depicted in the FESEM images (Fig. 2). Furthermore, the adsorption of oils in the PVDF composites could be controlled dispersion of CS particle in the porous structure. The superoleophilicity characteristics nature of CS particles control capillary force of oil and water. Hence the concentration of CS particle in the PVDF composite could be controlled the adsorption capacity of the surface. Hence from above details, the conclusion can be arrived that porous size of the hierarchical structure, surface area of the PVDF composite, concentration of CS particle could control the oil/water separation.²⁶

The maximum water contact angle of 170° and high surface roughness of 90.57 nm suggests the superhydrophobic nature of the soot particles.⁸ Earlier Sahoo et al have reported the fabrication of superhydrophobic PVDF/CS composite using gelation technique which reveals water contact angle of 172° .²⁵ The maximum water contact angle for PVDF and PVDF/CS composite were 132° and 138° respectively. Similarly, sliding angle for PVDF and PVDF/CS composites were obtained as 8° and 12° respectively.

Absorption capacity of CS was computed by dosing known amount of CS with measured amount of oil/solvent (Fig.3). Wet CS particles were checked for reusability by burning in air and then reusing for the calculation of absorption capacity (Fig. 3c). Absorption of oil leads to soaking of CS particles, consequently sticking them together, increasing the packing and hence destroying porous nanotube structure (Fig.3d).

PVDF-CS composite responds rapidly in contact with oil-water mixture, by selectively absorbing oil and completely absorbing water (Fig.5) owing to its hydrophobicity

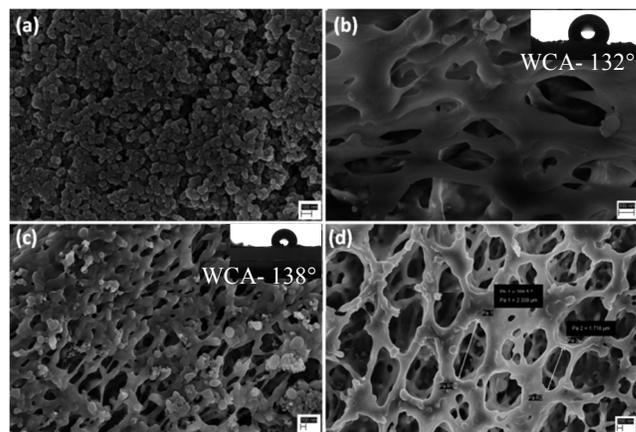


Fig.2: (a) The fractal-like interconnected network of carbon nanospheres inside camphor soot. (b) Porous nanostructure pure-PVDF foam. (c) Nano structured PVDF-CS foam imprinted with CS particles. (d) Microporous nature of the composite.

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Fig.3: (a) Crude CS before absorption. (b) Absorption of oil by CS. (c) burning of wet CS. (d) burnt CS

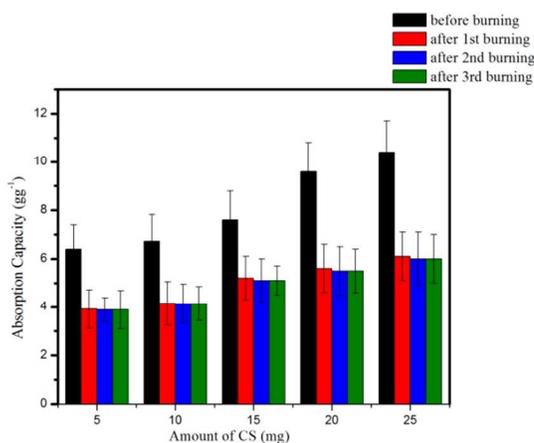


Fig.4: Reusability pattern of CS particles after burning.

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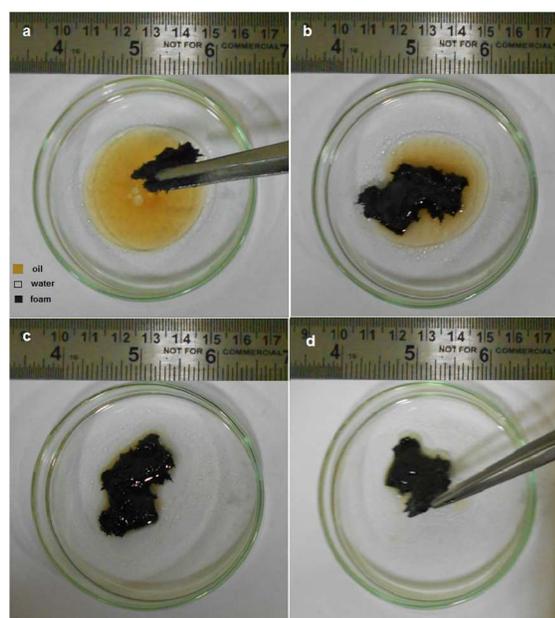


Fig.5: (a) Insertion of dry composite into oil water mixture. (b) Absorption of oil by composite. (c) Saturated composite. (d) Removal of composite after complete absorption of oil.

Therefore completion of first cycle i.e. elimination of oil, is accompanied by abrupt change in porous nanotube structure and packing of CS particles, consequently decreasing the absorption capacity. However, after second cycle there is trifling change in structure, so the absorption capacity remains constant henceforth (Fig.4). Camphor comprises three methyl (CH_3) and one carbonyl ($\text{C}=\text{O}$) group. The formations of nano sized camphor soot particles from the combustion of camphor in the absence of a precursor were obtained. The interconnected soot particles, were observed; this particle network can be easily broken. Soot particles with an average size of 25–60 nm agglomerated to form a chain of carbon nanospheres.⁸ However, not all carbon soot particles could be confirmed as carbon nanospheres. These camphor soot particles reveal superhydrophobicity, which shows water contact angle of 170° . The presence of C-H group illustrates the existence of superhydrophobicity, which was earlier reported by Sahoo et al. However, it was observed that camphor soot particles show partially absorbance of oil, which illustrates oleophilic property. The benefits of the incorporation of CS particles in the PVDF composite could be attributed to the controlled porous structure of the surface and the superoleophilicity of the CS particle. The presence of CS particle in the composite raises the adsorption capacity of engine oil and petrol which is revealed from Fig. 6. However for other oil, the incorporation of CS particle does not claim the adsorption property. The absorption capacities of PVDF-CS composite are promptly achievable and higher than pristine-PVDF foam (Fig.6).

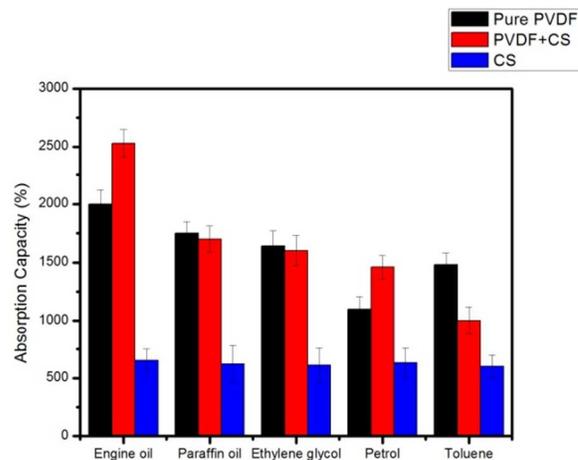


Fig.6: Comparison of absorption capacities of CS, pristine PVDF foam and PVDF+CS composite.

Different absorption values are an upshot of different density and viscosity of oils/solvents. The absorption is found to be higher than other contemporary materials, including super wetting nanowire membranes²⁷, collagen nanocomposites²⁸, commercial bulk BN¹ and activated carbon¹. High absorption values are attained due to the solvent entering the capillary and the polymer network and moving the network junctions away from each other. As these network junctions move away the chains attached to these junctions experience a stress due to the sorption of oil, hence causing swelling of composite. The stress is counteracted by the tendency of the polymer chain to return back to the relaxed state where the entropy is higher. A state is achieved where equilibrium is reached and the polymer composite refuses to accept any more solvent, this phenomenon determines the absorption capacity.

CS particles are interconnected through nanotubes, forming a fractal-like²⁹ network of carbon nanospheres. A single nanotube connects 4-8 nanoparticles, with 2-3 nanotubes growing from a single nanoparticle, thus denoting three dimensional network⁹. This three dimensional network of porous CS particles is analogous to a three dimensional capillary network, which has a propensity for absorption, owing to capillary pressure. Besides capillary pressure, surface diffusion on the porous composite plays a significant role in absorption. Surface diffusion of liquid molecules occur on the surface due to the adsorption of air in the porous cavities. The density and absorption capacity are functions of composition, i.e. the concentration of CS in the composite. With minor addition (0.5 wt %) of CS, the increase in the absorption capacity (Fig.7) indicates that intrinsically oleophilic CS particles enhance the oleophilicity of the pristine-PVDF foam. As revealed by Scanning Electron Microscopy (SEM) (Fig.2) of the composite, the interconnected network of nanotubes no more persist in the composite (Fig.2c) as in case of CS particles (Fig.2a), while augmentation in the amount of CS is found to be satiating the pores, consequently diminishing the porosity and thus hampering absorption.

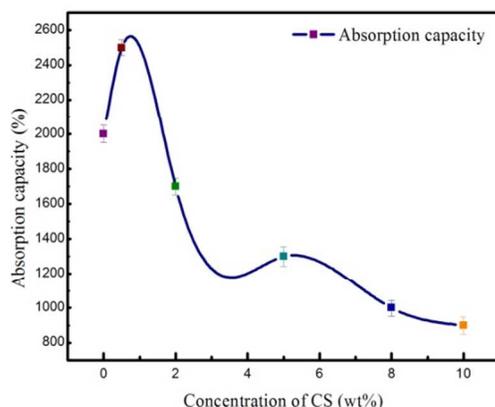


Fig.7: Absorption capacity curve, representing the optimum concentration of CS for maximum absorption of oil.

This suffusion is not evident in pristine PVDF foam (Fig.2b), and hence PVDF foam absorbs more oil than most of the composition which tend to fill the pores. The surface of the composite signifies diversified microporous topological structure (Fig.2d).

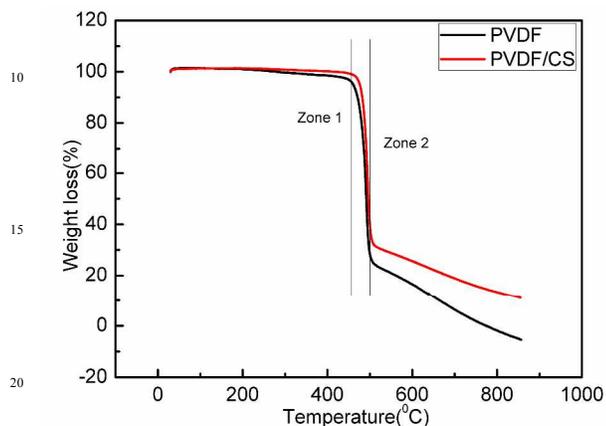


Fig. 8 TGA curves of PVDF and PVDF/CS composites

The thermal stability of PVDF and PVDF/CS (10 wt%) composites was examined with TGA. As exhibited in Fig. 8, the curve of PVDF and PVDF/CS can be divided into two major zones. The first zone (25–400°C for PVDF) displays minimal loss by the virtue of the removal of the absorbed moisture.^{30–31} However, no weight loss is displayed for PVDF/CS composites on in the first zone (25–440°C) due to the enhanced hydrophobicity of PVDF/CS as compared to pristine PVDF, and thereby reduction in retained moisture. As for the PVDF, the initial decomposition temperature occurs at 410°C, and it degrades completely by 500°C, which is ascribed to the thermal decomposition of the PVDF. In the case of the PVDF/CS composite, the thermal decomposition temperature shifts toward a higher temperature range in comparison to that of the pristine PVDF. This is a result of the strong interactions between the polymer and the CS hampering the movement of the polymer chains. The major weight loss in the range of 440–460°C derives from the elimination of a certain amount of the oxygen-

containing groups of the Carbon soot particles in the PVDF/CS composite. This suggests that the reduction degree is somewhat influenced by the incorporation of the Carbon soot particles in the composite.³² The ash content of PVDF/CS was found to be greater than PVDF by 20%, due to addition of Carbon soot as a filler which enhances the char yield, as compared to pristine PVDF.

4. Conclusions

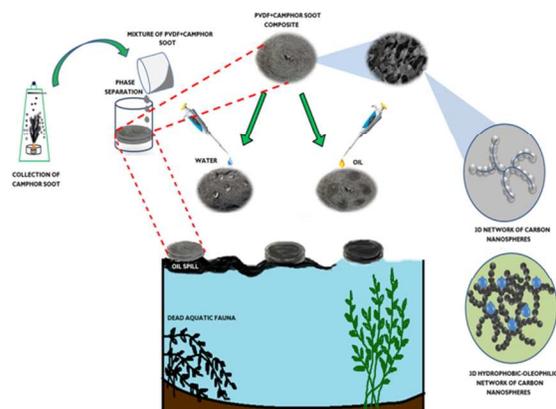
Summarily, the oleophilicity and superhydrophobicity of low-cost camphor soot were harnessed in fabricating a composite, by a facile, versatile and cost-effective approach. The composite being highly porous, gives superior performance in terms of absorption and handling, by absorbing oil up to 25 times (0.5 wt%) its own weight, without setting an alarm to the intoxication of water resources. The prepared composite has higher absorption capacity than pure-PVDF foam, as well as nascent CS. Camphor soot can also be used for absorption of oil, as it has got excellent recyclability and reasonable absorption capacity in addition to superhydrophobicity. Cost efficiency, simple procurability, easy handling, and superior absorption capacity of CS, as well as the composite, together provide an edge over the existing techniques.

References

- (1) W. Lei, D. Portehault, D. Liu, S. Qin, Y. Chen, *Nature Communications*, 2013, **4**, 1777.
- (2) D. Zha, S. Mei, Z. Wang, H. Li, Z. Shi, Z. Jin, *Carbon*, 2011, **49**, 5166.
- (3) Q. Zhu, Y. Chu, Z. Wang, N. Chen, L. Lin, F. Liu, Q. Pan, *Journal of Materials Chemistry A*, 2013, **1**, 5386.
- (4) A. Bayat, S.F. Aghamiri, A. Moheb, G.R. Vakili-Nezhaad, *Chem. Eng. Technol.*, 2005, **28**, 1525.
- (5) M. O. Adebajo, R. L. Frost, J.T. Klopogge, O. Carmody, S. Kokot, *J. Porous. Mater.*, 2003, **10**, 159.
- (6) G. Deschamps, H. Caruel, M. Borredon, C. Bonnin, C. Vignoles, *Environ. Sci. Technol.*, 2003, **37**, 1013.
- (7) L. Wu, J. Zhang, B. Li, A. Wang, *Polymer Chemistry*, 2014, **5**, 2382.
- (8) B.N. Sahoo, B. Kandasubramanian, *RSC Advances*, 2014, **4**, 11331.
- (9) H. M. Daly and A. B. Horn, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1069.
- (10) M. Knauer, M. E. Schuster, D. Su, R. Schlögl, R. Niessner and N. P. Ivleva, *J. Phys. Chem. A*, 2009, **113**, 13871.
- (11) J. O. Muller, D. S. Su, U. Wild and R. Schlögl, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4018.
- (12) K. Park, D. B. Kittelson and P. H. McMurry, *Aerosol Sci. Technol.*, 2004, **38**, 881.
- (13) H., Sun., Z. Zhaoqi, L. Weidong, Y. Baoping, Q. Xiaojuan, Z. Xinhong, P. Chunjuan, L. Peiqing, L. An, *RSC Adv.*, 2014, **4**, 30587.
- (14) G. Yang, Z. Shen, X. Wei, W. Mengmeng, F. Lisha, G. Hossein, Rabiee, J. Lijia, H. Wenjia, H. Xi, J. Lan, S. Francois, Y. Feng, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5924.

- (15) S. Hanxue, L. An, Z. Zhaoqi, L. Weidong, Z. Xinhong, L. Peiqing, D. Weiqiao, *Chem Sus Chem*, 2013, **6**, 1057.
- (16) P. Chingombe, B. Saha, R. J. Wakeman, *Carbon* 2005, **43**, 3132.
- 5 (17) H. Wang, Q. Gao, J. Hu, *J. Am. Chem. Soc.* 2009, **131**, 7016.
- (18) D. Lozano-Castell, J. M. Calo D. Cazorla-Amor, A. Linares-Solano, *Carbon* 2007, **45**, 2529.
- (19) E. Demirbasa, N. Dizgeb, M. T. Sulakb, M. Kobya, *Chem. Eng. J.* 2009, **148**, 480.
- 10 (20) P. J. M. Carrott, R. M. M. L. Carrott, T.S.C.Vale, L. Marques, V. J. M. P. Nabais, A.M. Mour. *Adsorpt. Sci. Technol.* 2008, **26**, 827.
- (21) T. Wu, Y. Pan, L. Li, *Coll. Surf. A: Physic Eng. Aspects*, 2011, **384**, 47.
- 15 (22) B. N. Sahoo, K. Balasubramanian, B. Sabarish, *Prog. Org. Coat.* 2014, **77**, 904.
- (23) B. N. Sahoo, K. Balasubramanian, *Mater. Chem. Phys.*, 2014, **148**, 134
- 20 (24) B. N. Sahoo, K. Balasubramanian, Sabarish, *Exp. Poly. Lett.* 2013, **7**, 900.
- (25) B. N. Sahoo, K. Balasubramanian, *J. Coll. Interf. Sci.*, 2014 DOI: 10.1016/j.jcis.2014.08.0312014,
- (26) B. N. Sahoo, K. Balasubramanian, *RSC Adv.*, 2014, **4**, 22053.
- 25 (27) J.C.H Wong, E. Tervoort, S. Busato, L. J. Gauckler, P. Ermanni, *Langmuir*, 2011, **27**, 3254.
- (28) N. Zhao, Q. Xie, L. Weng, S. Wang, X. Zhang, J. Xu, *Macromolecules*, 2005, **38**, 8996.
- 30 (29) J. Yuan, X. Liu, O. Akbulut, J. Hu, S. L. Suib, J. Kong, F. Stellacci, *Nature Nanotechnology*, 2008, **3**, 332.
- (30) C. Caibao, L. Run, X. Liming, Y. eyue, *RSC Adv.*, 2014, **4**, 17393
- (31) H. Hu, X. Wang, J. Wang, L. Wan, F. Liu, H. Zheng, R. Chen, C. Xu., *Chem. Phys. Lett.*, 2010, **484**, 247.
- 35 (32) P. Song, Z. Cao, Y. Cai, L. Zhao, Z. Fang, S. Fu, *Polymer*, 2011, **52**, 4001

Graphical Abstract

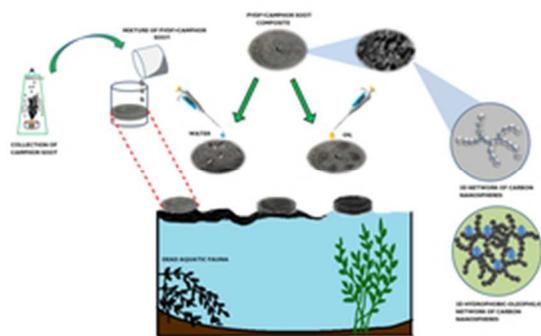


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