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Physisorption and Chemisorption Trends in Surface Modification of Carbon Black

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ABSTRACT:

Carbon black has been an economical conventional reinforcing agent for a range of applications like catalysis, electrical conduction, pollutant adsorption, mechanical or optical materials. To enrich these properties, carbon black surface has been modified through either chemisorption or physisorption. This review contains latest literature to compare both these modifications in connection to particular applications, where first method despite of high yield is ineffective for thermally unstable materials, and second method despite of its effectiveness for thermally unstable materials is delicate due to easy desorption.

Keywords: Porous Carbon Black; Surface chemistry; adsorbent; Physisorption, Chemisorption, Surface modification.

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1. INTRODUCTION:

Carbon black (CB) is a natural allotrope of carbon in amorphous form, which is obtained through anaerobic combustion of carbon materials. It is not a solitary artifact but is a bunch of products, with applied technical reputation due to far-reaching applications [1-5].

CB is elemental carbon in the form of a fine powder (90-99% elemental carbon) with a large surface area; refers to a prime group of products most widely used material with dimensions in nanometers (nm). CB at its smallest level consists of spherical primary particles, which quickly form aggregates. Primary carbon particles fuse together permanently, in a randomly branched chain like structure, which is known as aggregate. The aggregate can have a small number or hundreds of primary spherical particles, as per method used to prepare. Thermal black aggregates consist of single spheres rather than chains. These chains like structures are used to grip fluids and reinforce materials. The aggregates can fix with each other through van der Waals forces to form feebly joined agglomerates [5].

CB presents good electrical conductivity, admirable thermal stability with low thermal expansion coefficient, decent chemical and weathering resistance. Altering CB surface chemistry has been an utmost desire since ages, not only to improve its dispersion but also to boost its mechanical, electrical and optical characteristics. CB surface modification anchors modifier molecules on CB surface through physical week forces (physisorption) or chemical covalent bonding (chemisorption). CB functionalization, whichever physisorption or chemisorption, is carried out by two distinctive approaches regarding energy source for reaction, i.e. thermal or photochemical. Both methodologies cultivate CB surface functionalities to enhance its characteristics. Either method has precise positive influences. Thermal functionalization is timeworn and diverse in application; whereas photochemical modification is simple, vigorous and versatile. Both thermal and photochemical tactics can successfully refine CB structure as well as its surface chemistry [6]. CB modification, for whatever purpose is done, must improve its dispersion in solvents/matrices used, to makes it behave as reinforcing agent, by vitalizing properties of final product. The most common commercial use of CB is as filler in composites. CB surface functionalities hook up with matrix components, for

reinforcement [7]. Various factors of CB, particularly higher concentration and smaller particle size, have been reported to affect lifetime of composites [8].

2. CB Surface Chemistry:

Surface chemistry of CB plays an important role in defining its reactivity. Subject to the preparatory process a range of oxygen functionalities, i.e. phenolic, carboxylic, quinonic or lactonic, on the periphery of commercial CBs has been reported [9, 10]. Oxidation is the most widely used classical way to enhance surface chemistry of CBs [11-13]. CB surface chemistry is directly related to its surface energy, which regulates "filler-filler" or "filler-medium" interactions [14]. Considering this fact, plasma treatment has also been tried for CB surface modification [15].

3. CB Modification:

Surface chemistry of CB is modified with different molecules which link either physically or chemically to the surface functionalities. Hence two distinct phenomena have been spotted, broadly classifying CB surface modification into, physisorption and chemisorption.

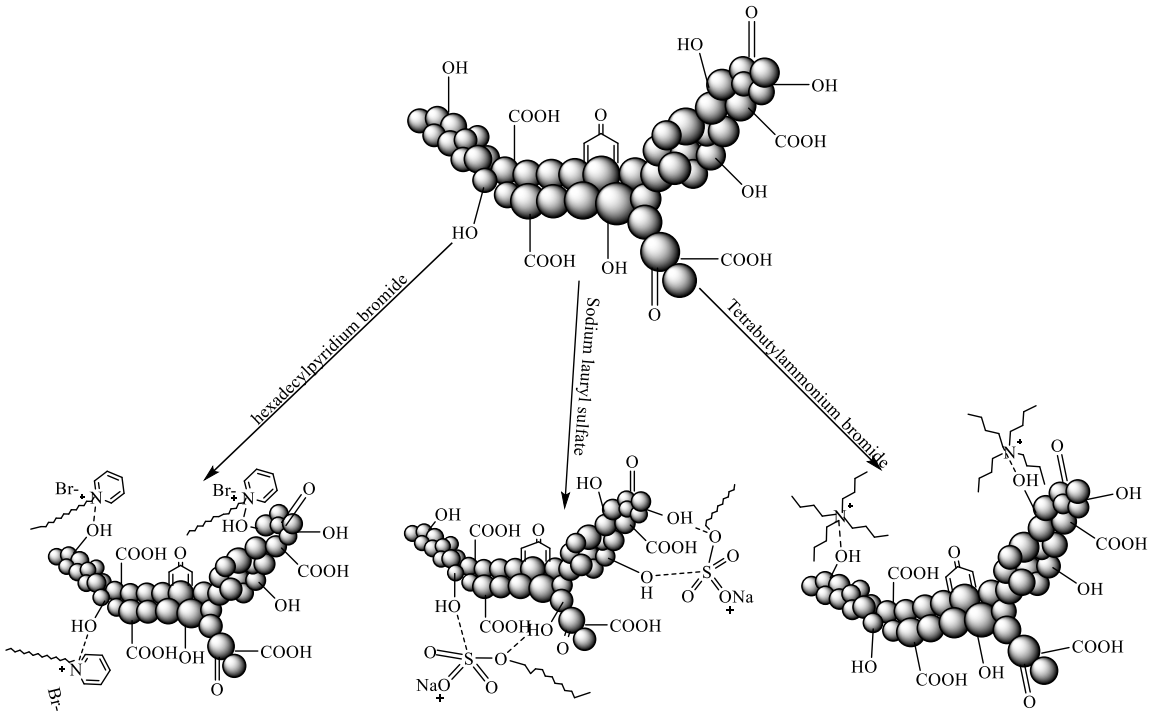
3.1. Physisorption:

To comprehend workability of CBs in various applications, precise estimation of micro-pores is crucial, as it controls physisorption. A physical interaction through which adsorbable molecule (*the adsorptive*) is either adsorbed onto (*surface physisorption*) or into (*intercalation*) the CB (*adsorbent*), through van der Waals forces [16]. Physisorption on the surface or in the core of CB is a reversible reaction. Desorption requires very low energy, so physisorption can not resist high temperature [17]. Basically, CB physisorption has been divided into monolayer, multilayer or capillary action phenomenon [18]. Nonporous carbons are particularly reported for monolayer or multilayer physisorption, whereas porous carbons show capillary action as well [19].

Physisorption, as interaction of adsorbate with CB, can broadly be categorized into three types. The most classic one is pure physical adsorption, which is depicted with complete recovery of adsorbate either with temperature rise or decrease in surrounding concentration. It is low temperature phenomenon, as rise in temperature weakens the interactive forces. Second category is activated adsorption, which is portrayed with partial recovery of adsorbate due to complex formation. It is high temperature process,

which grasps equilibrium on a certain temperature, above that temperature complexes decompose. Third category is solution, with no recovery of adsorbate due to dissolution in adsorbent core, through diffusion. It is slow process. Data has been reported on physisorption of gases onto and into CB for their utilization in environment [20-22] and sustainable energy proficient hydrogen fuel-cell based vehicles [23]. This physisorption process critically depends on pore size in CB. Fan *et. al.*, [24] reported a realistic model for the study of pore size on complex structure of CBs, in contrast to conventional models of pore with tubular shape having both ends in gaseous environment. This model studied adsorbent-adsorbate connectivity through gaseous physisorption on porous CBs. This study was made to evaluate heterogeneous energy changes with gas physisorption on CB. Simulation data has been reported not only to determine adjacent pore associations but also for surface description and performance of CBs. Gas adsorption studies utilize CB as emphasized exemplary adsorbent. Estimation of physisorbed chemicals is frequently used as a typical CB characterization procedure. Literature [25] has reported that carbon structure ties compounds at its surface through physical adsorption that do not resist high temperature, so as per its instability we can say that entire physisorbed materials do not augment desired properties.

Surfactant adsorption on CB surface (Scheme 1) has been reported for amphiphilic [26], ionic [27, 28], non-ionic [29, 30] surfactants. Significance of physisorbed amount of surfactants has been highlighted. It has been reported that use of non-polar solvent or long-time storage may effect CB dispersion, by causing desorption of material from CB surface.



Scheme 1: Physisorption of surfactants on CB surface

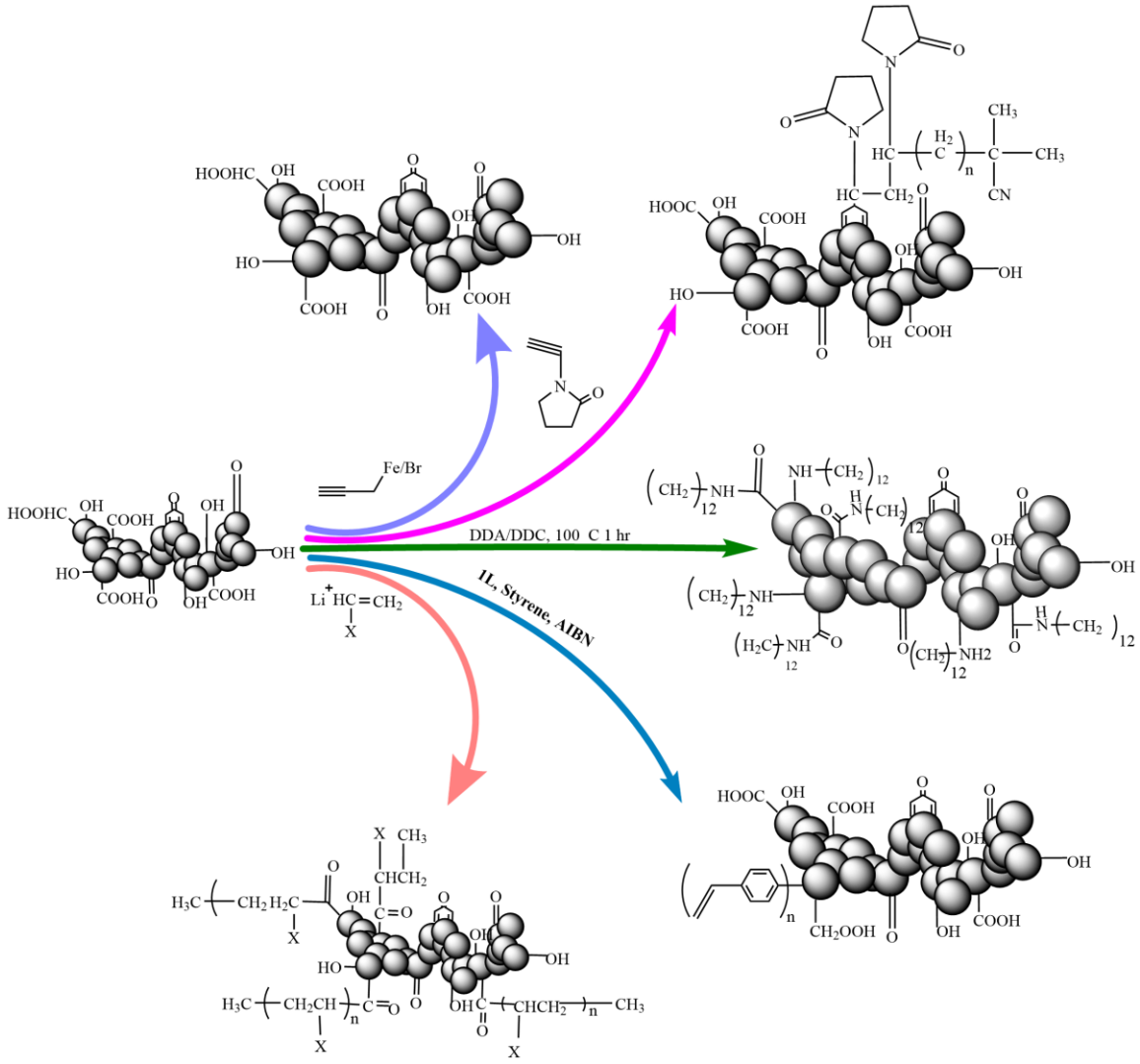
Activated carbons (ACs), because of porous structure with hydrophobic interior and hydrophilic exterior, are well-known adsorbents for metals, gases and liquids. The metal adsorbing behavior of CB has been extensively utilized either in removal of metallic pollutants [31] or in catalysis [32]. Researchers [33] reported that oxidative treatment of ACs enhanced cadmium ions adsorption from waste water. Carboxylic group, out of all oxy functionalities, has been reported with excellent metal adsorption. On the basis of reaction enthalpy, this study categorized metallic adsorption in reversible and irreversible phenomena. Irreversible adsorption has been related to carboxylic cation exchange, whereas reversible phenomenon has been attributed to hydrogen bonding between oxygen surface sites and hydrated metal ions. In another study Rich *et al*., [34] utilized amorphous carbon for catalysis, modified with 4-aminomethylpyridine (4AMP) to uptake Pt. The process has been reported with enhanced catalytic activity as well as catalyst durability. Physisorption of 4AMP was detected with thermal analysis. Similar type of result has been reported by Park *et al*., [35], where CB has been employed as a support for electrochemical catalyst enclosing Pt nanoparticles. Reported data states that

physisorption of polyethyleneimine on CB enhanced the stability of electrochemical catalyst for polymer electrolyte membrane fuel cell.

Different types of CBs have been reported for their different adsorption behavior, that leads to a broad range of CB characteristics and consequently their implementation in different applications. For example, graphitic carbon has its application in areas where effective adsorption on well-organized structures is required [36]; thermal CBs, prepared through high temperature thermal treatments of raw material like wood, bones or any waste, are important for their nonporous surface [19]; Glassy CBs are used in electrochemical applications due to their extraordinary chemical inactivity [35]. ACs being porous are useful in gas or liquid adsorption thus utilized in pollution control, heterogeneous catalysis, gas-electrical energy storage [37]. Quantitative estimation of physisorbed material has been reported theoretically [38] as well as through different experimental techniques including electrochemical methods [39] magnetic suspension balance method [40], gravimetric and volumetric methods [41].

3.2. Chemisorption:

Contrary to physisorption, chemisorption is an adsorption process that involves a chemical bond formation between a modifier molecule (*the adsorptive*) and a surface (*the adsorbent*). Chemisorption takes place either by ionic phenomenon [42, 43] or through radical processes [44-46]. Embedding CB exterior with various functionalities convalesce its surface features. Considerable data has been reported with improved dispersion [47-50], promising electrochemical behavior [51], better mechanical aspects of composites [52] and photo-thermal properties of modified CB [53]. Few commercially important chemisorption tracks have been reviewed (Table 1).



Scheme 2: Protocols for chemisorption on CB surface

3.2.1. Oxidation:

Oxidation is extensively used chemisorption approach since ages. Cheng *et. al.*, [54] has reported CB oxidation through different acids. The work was aimed at enriching metal absorption capacity of CB, to expand its utilization in wastewater treatment. Various instrumental analysis verified cyclic ether like structural moieties that repositioned to ether like arrangements in poly-aromatic spheres [31]. Oxygen chemisorption on CB surface by acidic thermal treatment has also been reported by others. [31, 55]

Table 1: Chemisorption strategies for CB surface modification

Modification	Reagents/Modifiers	Reaction Conditions	Observations	Application	Ref
Oxidation	HCl (4M)	Thermal & chemical treatment	92.9 wt% carbon obtained	Rubber Formulations	[1]
	Orthophosphoric acid (H_3PO_4)	PQ curve linear from 0.4 -2.0 mgL^{-1}	Limit detection and quantification it is 0.19mgL^{-1}.	Environmental and Food chemistry	[56]
	1. HNO_3 2. H_2SO_4 3. Oxidizing agents.	1. 65% acid 150mL volume 1.1 20% acid with 1.58% $KMnO_4$ 2. 50% by volume (150mL) 3. Non acidic	1. Cu II adsorption 30.15 $mg.g^{-1}$ 1.1 Cu II adsorption 48.92 $mg.g^{-1}$ 2. Cu II adsorption 5.47 $mg.g^{-1}$ 3. Cu II adsorption is 12.33 $mg.g^{-1}$	Adsorption of Metal ion (Waste-water treatment)	[54]
	1. Phosphoric acid (H_3PO_4) 2. Iron oxide (FeO_2)	Pyrolysis at 450ºC, Freundlich isotherm constant n >1	NH_4^+ retention of CB increased 30%.	Waste water treatment, dairy form, agricultural soil	[55]
	Silica, Fe_3O_4	Reaction times 2, 4 and 24hrs	Heavy metal adsorption at pH>2.5 CO_2 adsorption enhanced up to about 20 mg/g Ethanol and n-butanol detection at atmospheric pressure/RT in the concentration range 0–100 ppm.	Waste water treatment CO_2 capture Bio-sensors	[57]
	H_2O_2, Cetyltrimethylammonium bromide (CTAB)	Hexachloroplatinic acid /H_2O (1.93 mM), $NiCl_2/H_2O$ (33.66 mM), 3000 rpm/1hr, 80°C/24hrs	Large BET surface area of 388 m^2/g Remarkable catalytic activity and high stability	ORR reactions	[58]
	98% H_2SO_4	1.0mol L^{-1}	14-16nm increase in CPs size	Nano-oil reporter	[59]
Halogenation	Choloroacetic acid (CAA) (≥ 99%),	1. Waste: CAA mass ratio (1:3) 2. CAA:H_2SO_4 molar ratio (0.1:0.01).	Composite conductivity ($2.07\times10^{-4}\Omega^{-1}cm^{-1}$) increased comparative to matrix ($4.91\times10^{-9}\Omega^{-1}cm^{-1}$)	Electrically conductive composites	[7]
	Triflouroacetic acid (TFA)	Mixed with Phosphoric acid (H_3PO_4)	high interfacial area	Elastomers and rubber	[60]
	Vaporized Bromine (99.98%)	Gas flow rate 0.5-10 g L^{-1}	Chemosorbed Bromine 0.4 - 2.2 mmol g^{-1}) Diethylamino grafting (0.3 to 1.7 mmol g^{-1})	Gaseous pollutant adsorbent Hg /NO_2 /CO_2	[61]
	PCl_5 or PBr_5	100mM Grignard reagent	15.98 % Cl and 8.59 % Br addition	Biosensors and Electronics	[62]
	Fluorine doped CB catalyst	NR	oxygen reduction reactions	Catalysis in fuel cell	[63]
	1. Direct Fluorination: F_2 2. Controlled Fluorination: TbF_4	1. T_F 380℃-440℃ 2. T_F 320℃ -480℃	1. C/F ratio 0.3-0.82 2. C/F ratio 0.37-0.83	Electrode (lithium batteries), Lubricants	[62]
	Hydrogen tetracholoroaurate ($HAuCl_4.3H_2O$) 99.9% purity	Direct reaction upon CB	Electrode with (100 times) improved sensitivity in range of 0.12-0.25µmolL^{-1}	Capacitors or storage devices	[64]
Polymer Grafting	L-Histidinemonohydrochloride monohydrate ($C_6H_{12}ClN_3O_3$).	Optimized concentration 0.5g	Dispersion improved with isotonic point at 3.78	Dye wool fabrics	[3]
	Acetic acid (AA) ($C_3H_4O_2$)	5.16-6.54%	Improved dispersion	Water based inks and pigments	[65]
	Polyvinyl pyrrolidone (PVP, K-30).	5mL,10wt% used with 136mL/100g oil absorption number	Better dispersion in aqueous media	Used in ink jets	[66]
	4-Sodium Styrene-sulphonate	PNASS-CB: 87.13 m^2/g ,	lowered free surface energy to 71.62mJ/m in	Rubber composites	[67]

	($C_8H_7NaO_3S$) (PNaSS)	CBs:107.18m^2/g	comparison to CBs: 96.14m^2/g		
	Polyethylenimine	2 wt. %, 4hrs/50°C	Maximum capacity at 29.40 mg/g 60% aspirin removal/2hrs/pH 3/RT	Drug (Aspirin) removal	[68]
	Poly (styrene-co-butadiene)	90°C/8min/65rpm 2mm Teflon molds 70°C/3min/8MPa	Increased modulus/tensile strength	Composites	[69]
	Poly-acrylic acid (PAA)	Carbonization at 1000°C	Larger BET surface area of 83.8 m^2/g and 356.7 m^2/g for carbonized fibers High thermal stability	Vanadium redox flow batteries	[70]
	Polypyrrole	Sonication mixing (1hr)	High sensitivity of 0.5405 $\mu A \mu M^{-1} cm^{-2}$ and ultra-low limit of detection of 22.9nM at neutral pH	Hydroquinone sensor	[71]
	Polysaccharide, epichlorohydrin	Alginate (1%), 200µL 1% glutaraldehyde (GA), 1hr sonication,	Linear PQ curve from 0.4 to 2.0 mg/L, Detection (0.06mg/L) and quantification (0.19mg/L)	Paraquat treatment	[56]
	Polyethylene terephthalate (PET)	laser engraved cutting (5mm/sec speed, 22KHz frequency)	Dispersibility, sensitivity and selectivity enhanced	Wearable H_2S gas sensor	[72]
	Poly(melamineformaldehyde) copolymer	Reaction temperature 95°C	Adsorption of 1 kg CO_2 (96%) in 4hrs	CO_2 adsorption	[73]
	Polycrystalline platinum, hexadecyltrimethylammonium bromide (CTAB), $H_2PtCl_6 \cdot 6H_2O$	160°C (1hr)	Catalytic ability increased	ORR reactions	[74]
	Polyethylene glycol (PEG)	120°C (24hrs)	Improved 300% elongation, abrasion resistance, wet grip, ice-traction and tire rolling resistance	Tire composites (green tire technology)	[75]
	Syringic acid (SA, 4-hydroxy - 3,5-dimethoxy benzoic acid) ($C_9H_{10}O_5$)	1mM	0.42 and 5.4 $nA\mu M^{-1}$ sensitivity in detection range of 20-100 and 100-1000µM, respectively, with 639nM detection limit.	Electroanalytical applications	[76]
	Poly (Acrylic acid) (PAA) $(C_3H_4O_2)_n$	0.5g, 6.9mmol 24h, 50% PAA grafted on CB	improved absorption/desorption kinetics	Gas sensors, Ethanol Vapour Sensor	[77]
	Polyvinyl alcohol (PVA) $(C_2H_4O)_X$	Degree of polymerization 1750; Alcoholysis degree higher than 98%.	85% increased resistance.	Dew Sensor	[78]
	1. Azobisisobutyronitrile (AIBN) ($C_8H_{12}N_4$) 2. Vinyl aniline (C_8H_9N)	0.1g used as molecular grafting	Better charge control improved 540ms fast switching	Electronic papers	[79]
	Polypyrolene maleic anhydride	2.16 kg with 0.8 wt % PPMA, MFI = 32 g/min at 230℃	Electrical conductivity 7.8S/m.	Flame Retarder	[80]
Thiolation	Mercaptopropyl trimethoxy silane (MPTS) ($C_6H_{16}O_3SSi$)	CB:MPT Mass ratio 4:1, 5-10 wt% incorporation occurred	Photochemical thiolation (2.5–7%) and silanization (3.3–10.8%)	Electronics	[5]
	Sublimed sulphur (S > 99.5%).	30-65%	At 50% S, 424 $mAhg^{-1}$ & 271.2 $mAhg^{-1}$ discharge specific capacity at 0.5C and 2C rate, respectively	Rechargeable batteries Sulphur, re-neutralization batteries	[81]
	SO_2	Pre-treatment 1000°C-2700°C	Surface mediation	Adsorption of SO_2 in flue	[82]

				gases	
	Pristine Sulphur		Conductivity	Lithium sulphur batteries	[83]
Salinization	Mercaptopropyl trimethoxy silane (MPTS) ($C_6H_{16}O_3SSi$),	MPTS:NaOH 1:3 mole ratio	Dispersion	Used in composite Material	[5]
	3mM Dodecyltrichosilane (DTS) ($C_{12}H_{25}Cl_3Si$), Hydrophillic behaviour of CB converted to hydrophobic		Decreased efficiency 59% (Pt/CB) at 0.6V and Pt/DTS-CB (17%) after corrosion	Electrochemical corrosion fuel cell	[84]
	3-glycidoxypropytrimethoxy silane (GPTMS, purity = 98%)	1 wt% toulene solution incorporated 5.43% Si	Increased hydrophilicity	Adsorbents	[85]
	1. Poly 3-(triethoxysilyl) propyl methacrylate (PMPS) 2. bis(3-(triethoxysilyl)-propyl)-tetras(TESPT)	9.5g in 200mL dry toluene	Tensile strength (4.5MPa) and elongation break (211%)	Rubber industry	[86]
	3-aminopropyltriethoxysilane,	Salinization at 80°C for 5hrs	High removal of Ni(II) 139 % and Pb(II) 38 %	Adsorbent for heavy metals	[87]
	3-octanoylthio-1-propyltriethoxysilane, 3-mercaptopropyl-di (tridecan-1-oxy-13-penta ethylene-oxide-ethoxy-silane) (V), Bis-triethoxy-silylpropyl-tetrasulfide (S)	Salinized for 2min, discharge temperature 97°C	Increased abrasion resistance, fatigue crack growth and side force coefficient	Tyres	[88]
	3-aminopropyl-triethoxy-silane, tetra-ethoxy-silane	H_2PdCl_4 at 130°C/2hr	Catalytic activity enhanced	Catalyst for cyclohexene hydrogenation	[89]
	3-[methoxy(polyethyleneoxy)$_{6\text{-}9}$ propyl]trimethoxysilane (90%), PEG200	CB-ox:SiPEG (1:1) refluxed at 150°C/24hrs.	High dispersion stability Decreased friction coefficient (35%) and specific wear rate (67%)	Lubrication	[90]
Phosphorylation	CB, N,N-Dimethylformamide (DMF)	$NaH_2PO_2{\cdot}H_2O$: FeO_x/SP (20:1, w/w)	High specific capacities (1518 mAh/g at 0.2°C) and rating performance (728 mAh/g at 5°C)	Lithium-Sulfur batteries	[91]
Hydrogenolysis	5-Methylfurfural (99%), 2,5-Bis (hydroxymethyl)furan (98%), 5-Methyl-2-furanmethanol (97%), 2,5-Dimethyltetrahydrofuran,	1 - 2 wt. % $RuCl_3.xH_2O$	Catalytic conversion of 5-hydroxymethylfurfural (HMF) into 2,5-dimethylfuran (DMF) (69.5%)	Catalyst	[92]
Nitration	Pyrazinamide	Pt/C	High density of 371mWm^{-2} with COD 73% removal	Microbial fuel cell wastewater treatment	[93]
	Hydrazine monohydrate (80%),	H_2PdCl_4	Increased Pd dispersion (23.60%) and surface area (1057m^2/g)	Catalyst	[94]

Pd-deposition	3-Hexyne, phenylacetylene (98%),	$[PdCl_2(NH_3)_4].H_2O$	Decreased mobility Enhanced selectivity and activity	Catalyst for Hydrogenation of Alkynes to Alkenes	[95]
Carboxylation	1,4-benzenedicarboxylic acid (99%)	$FeCl_3.6H_2O$, $ZnCl_2$ (99%) at 170°C for 24hrs	Better magnetic separation and reusability	Adsorbent for TCN removal	[96]
Sulfonation	2-methylfuran (99 %), furfural (99 %), Phloroglucinol dihydrate (98%)	4-amino-benzenesulfonic acid (99 %), graphene oxide, $KMnO_4$ at 60°C for 6hrs	Improved catalytic condensation activity	Catalyst	[97]

An alternative approach for CB oxidation is ozone treatment [98]. Kim *et al.* [99] have reported oxidation of CBs through ozone treatment. Escalation in oxygen functionalities on CB surface has been reported with rise in ozone concentration or reaction time. Instrumental analysis confirmed the formation of oxygen functionalities on CB surface. This reaction augmented the tensile strength of epoxy. Increase in epoxy tensile strength has been credited to better dispersion of CB which reinforced crosslinking.

Liu *et al*., [100] reported H_2O_2 oxidation of CB to prepare solar energy devices. These modified CBs has been reported with excellent capacity to store solar energy (38-545 g^{-1} dm^2), and has been utilized in renewable energy applications.

Though utilization of UV for surface modification of fillers is a documented method [101-105], yet it is rather new for implanting CB surface with functional molecules. So, availability of literature, in the field, is not appreciably ample. Tominaga *et al*., [106] reported ultraviolet oxidation of CB to improve its efficiency in heterogeneous electron transfer reactions. CB, owing to its poly-condensed aromatic structures, is considered to be a strong radical scavenger [107, 108], hence is conceivable to have radical reactions on its surface by exploiting its radical scavenging nature. Radical approach effectively engages all kinds of CB without any severe pretreatment.

3.2.2. Halogenation:

Halogenated CBs have numerous utilizations including carbon-based electrodes, capacitors and energy storage devices (ultra-capacitors). These ultra-capacitors are employed in wide range of applications from cell phones to hybrid vehicles [64]. Moreover, halogenated CBs conspicuously affect vulcanization kinetics, resulting in enormously crosslinked resins [60].

Diyuk *et. al.,* [61] have reported CB high temperature (200–500 °C) vapor bromination, resulted in 0.4-2.2 mmol g^{-1} of surface functionalization. A thermogravimetric kinetic study revealed 300-500 °C as optimal temperature for bromine chemisorption. The reaction has been found to occur in two distinctive kinetic boards: a fast reaction occurred at surface and made 65-80 mass% chemisorbed bromine, whereas a slow process occurred on the surface of tight micropores.

Minh *et. al.*, [109] have reported chemisorbed chlorination of AC by HCl, which decreased surface area and increased pore size. The chlorinated AC have been reported with

reduced Cd(II) sorption, due to acyl- or alkyl chloride groups formation. Chemisorption of chlorine has been reported through addition and substitution reactions. Another study [63] has reported fluorination of CB for catalysis in fuel cell. Using a facile approach, two types of CB were produced, fluorinated CB (328 m^2g^{-1} surface area) and fluorine-nitrogen added CB (206 m^2g^{-1} surface area), for economical and workable electro-catalyst in oxygen reduction reactions (ORR). ORR value for Fluorine-nitrogen-CB (-0.17 V) and fluorinated CB (-0.20 V) has been found better than Pt/C, suggesting microbial fuel cells as their potential application. Both the modified CBs have been found with excellent methanol as well as sulfide-tolerance.

Ahmed *et. al.*, [62] have reported plasma treatment method to fluorinate CB either with pure fluorine or with TbF_4. Analysis revealed that CB crafted by TbF_4 had better thermal stability as well as tribologic characteristics. Whereas pure fluorine decorated CB showed superior electrochemical behavior for lithium-ion batteries. Both procedures follow specific fluorine chemisorption protocols and produce specific C-F bonds. Instrumental analysis has been done to study bond nature along with structure and texture of CBs produced. Reported data confirmed chemical linkage between fluorine and peripheral or external carbon atoms.

Lockett and Smith [110] worked on solution based radical initiated halogenation of CBs, by 100mM PX_5/benzene solution with minute quantity of benzoyl peroxide. After vacuum drying brominated CBs were tailored with different Grignard reagents, including dodecyl-magnesium bromide, fluorinated decyl-magnesium iodide and methoxy PEG magnesium bromide.

3.2.3. Polymer Grafting:

Chemisorption is usually considered to graft polymers on CB surface, and two different approaches are utilized for this phenomenon, i.e., “graft onto” and “graft from”. First approach exploits surface functionalities of CB to implant macromolecules. Surface chemistry sometimes obstructs the contact of approaching molecules causing an inadequate reaction exposure. Second approach initiates polymer progression from CB surface. This approach allows maximum grafting density, as small monomer molecules diffuse faster than polymers. In this regard, diverse range of functional moieties has been reported, including: amine [59], acrylic acid [111], Polyvinylpyrrolidone [112], hyper-

branched polymers [113].

He *et. al.*, [67] have reported radical-polymerization of sodium 4-styrenesulfonate on CB to obtain water-dispersible particles (90 nm). Results confirmed reduced agglomeration tendency within modified particles, and excellent dispersion of filler in rubber. Reduced filler-filler and superior filler-matrix connectivity, yielded excellent tensile stress bearing capacity in rubber. Covalent link between polymer and filler allows stress redistribution in order to control strain, hence resist any destruction in polymeric chains. So, modified particles have appreciably enhanced the mechanical strength of composites.

Jiang *et. al.*, [65] have reported electron beam irradiated synthesis of polyacrylic acid implanted CB to augment its dispersion in water. Analysis proved chemisorbed covalent linkage between polymer and CB. The modified CB has been found with reduced aggregate size and better dispersion in water. The modification method was performed in air as well as in nitrogen, and no meaningful variance in degree of grafting has been noticed.

Yuan *et al.*, [66] have reported an economical and environment friendly, low temperature CB modification method through plasma treatment. CB nanoparticles, after oxidation, were grafted with Polyvinyl pyrrolidone (PVP), and utilized as pigment in ink. Modified CB ink showed comparable characteristics to that of commercial inks.

Al Dine *et al*. [76] reported an electrochemical method for covalent modification of CB, by grafting carbon electrode sub-monolayers with propargyl bromide and ethynyl ferrocene. Electrochemical grafting is easy to handle at low temperature, in short time, without catalyst or additive requirement. Cyclic voltammetry confirmed chemisorbed covalent linkage.

Sundaram *et al.*, [114] have reported CB modification with antioxidant. The method has been reported for precise and exact electrochemical estimation (0.04 V vs Ag/AgCl) of bio-molecules, i.e. L-cysteine, by using syringic acid planted CB. The composite CB (639 nM detection limit) reduced 0.42 $nA.\mu M^{-1}$ and 5.4 $nA.\mu M^{-1}$ L-cysteine in 20–100 μM and 100–1000 μM detection range, respectively. The study has also discovered structures of intermediates through instrumental analysis.

Wang *et. al.*, [115] synthesized CO_2 adsorbents with quinonic functionalization of CB through Friedel–Crafts scheme. A calculation, for hydroquinone coated CB, showed

58.7% higher separation of CO_2/N_2 than pristine CB, and quinone coated CB showed 28.4% higher separation of CO_2/CH_4. The optimal CO_2 adsorption reported for modified CB was 3.46 mmol g^{-1} (298K , 1atm). The prepared CB has been suggested for dealing with flue gas and purification of natural gas. Quinonic moieties as per their electron transfer capability have been tried as mediators in biofuel cells.

Poly(p-chloromethylstyrene) (PCMS) grafting on CB surface via self-condensing atom transfer radical polymerization (SC-ATRP) has been reported by two distinctive approaches[116]. In first technique, CBs were oxidized with acid to get COOH functionality, which were then esterified with ATRP initiators. In second approach, azido and bromo bearing ATRP initiators were attached to CB surface through nitrene chemistry. ATRP initiators have been utilized to anchor PCMS and grafting density varied with reaction time. Polymers grafted on the surface of CB were tailored to get ammonium hydroxide. These tailored materials have been reported for excellent capacity to absorb and desorb CO_2 from air, proposing a novel trend[117].

Surface modification of CB with polymers have been implemented in various applications; some of which include electrical conductivity[118], ethanolic vapor sensors[119], dew sensors[78], electronic papers [79] and flame retarders[80].

3.2.4 Thiolation:

CB and Sulfur interaction is of practical interest, not only because of rubber industry but also for Li rechargeable batteries [120]. The reactions of sulfur or its derivatives have been reported in the literature, either by ionic methods [121-123] or by radical reactions [124, 125].

Tendency of CB to fix sulfur on their surfaces is long since known [126, 127]. Till that time, sulfur insertion was confused to be capillary condensation, physisorption or chemisorption. Afterward, Puri *et. al.* [128] discovered, sulfur is fixed on CB surface either by addition at unsaturated sites or by substitution with oxygen and hydrogen-containing groups. Papirer *et. al.*, [129] studied formation of sulfur containing functional groups on CB surface by P_2S_5 reaction with CB in temperature range of 60-500^oC and reaction time up to 4 hours. In another study thiols and thio-esters have been incorporated on CB surface using thermal methods.

Recently [83] a composite with increased surface area and ordered structure of sulfur and carbon has been reported for rechargeable lithium sulfur batteries. This unique material

presents extraordinary discharge capacity due to better sulfur reutilization. Lithium sulfur batteries have been a source of inspiration in recent era [81, 130].

3.2.5. Silanization:

Silanization is another very popular method to improve CB dispersion in media. Silane coupling agents react with hydroxide-rich surfaces [5]; moreover, they are widely available with a large variety of end groups. Thus, by selecting the appropriate silane groups, the compatibility and interaction of the filler can be improved. Silane coupling agents have been applied to natural fibers [131], titanium oxide particles, clay nanoparticles [132], carbon nanofibers (CNFs) [133] and carbon nanotubes (CNTs) [134].

Silanization of CB has been studied to see its impact on vulcanization of rubber or plastic matrices, through covalent bond formation between alkoxy group of organosilane and oxidized CB [135]. Reported data states that composite samples prepared with silane modified CB gave higher cross linkage, improved elasticity modulus and tensile strength. Another study [136] has reported that CB silanization speeds up curing rate of epoxy matrices, which has significantly reduced curing time at low temperature.

Lee *et. al.*, [84] has reported that silanization of CB escalates its resistance to electrochemical corrosion in fuel cells. Data reports superb performance and durability of these cells due to the formation of hydrophobic coating of dodecyltrichlorosilane (DTS) on CB surface, which reduces the chances of water contact with CB.

CBs are well known adsorbents in numerous applications. Out of these, one application is adsorbent in cigarette filter, which has a problem of wet feeling. It has been reported recently, that silanization of CB with 3-glycidoxypropyltrimethoxy silane has resolved the issue [85].

CB silanization affects the behavior of conducting polymers [137]. Noriman and Ismail [138] while working on silanized CB have reported an increase in tensile strength of styrene butadiene/acrylonitrile-butadiene rubber due to better interaction of CB-Silica-polymer. Miller *et al.*, [139] have worked on silanization of amorphous carbon membranes, which are preferred substrate in transmission electron microscopy as per their better imaging quality, flexibility and durability of thin films and decent conduction to reduce charging.

Various approaches have been utilized time to time, to compare the effects of CB and silane on composite properties, without any chemical connection between the two.

Mahata *et. al.,* [86] has studied in parallel the mechanical aspects of silanized or CB-natural rubber composites. Shang *et. al.,* [140] has modified the approach by using dual filler system, containing both CB and silane agent, in different weight ratios.

4. CONCLUSION:

CB signifies a family of traditionally spent materials that are easy to obtain, economical and moderately benign with established industrial importance. CB surface modifications either by physisorption or by chemisorption, bring changes to its interfacial properties like surface chemistry and particle size. Adjusted surface functionalities and controlled particle size lead to a number of research directions, be conquered, including: novel electrochemical applications like protein reduction, sophisticated catalytic reactivity and stability of fuel cells, energy storage devices, sensors, solar cells, super-capacitors, bioelectronics materials or medicinal tools.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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