Electronic Supplementary Material (ESI) for RSC Advances.

Novel Sensor for the determination of CA 15-3 in Serum of Breast Cancer patients based on Fe-Gallic Acid complex doped in modified Cellulose polymer thin film

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S1.1. FTIR

Investigation of the functional groups in Modified CMC membrane was carried out compared to its neat polymer using FTIR analysis

S1.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetric analysis of Modified CMC membrane was carried out in comparison with its neat polymer (~ 5 mg in sealed Al-pan) using Differential Scanning Calorimeter device (Shimadzu DSC –50, Japan) in the temperature range from 20–300 ^{o}C at a heating rate of 10 ^{o}C/ min under nitrogen flow (30 ml/min).

DSC experiments were used to finalize the thermal characterization as presented in S1.2. The findings were in good alliance with what have been previously reported in the literature. Some modifications in both endothermic/exothermic peaks were noticed between the components of the membrane and their locations. The thermogram exhibited an outside endothermic peak near 100 °C, most probably due to the membrane's moisture content release. The ability of the membrane to hold onto moisture molecules could account for the rise in the endothermic peak. Exothermic peaks were observed between 205 and 240 °C as a result of the breakdown of the pyranose ring of the glucose unit along the polymer chains. After activation, the peak shift to a higher temperature suggested an elevation in the new derivative's thermal stability

S1.3. Raman spectroscopy analysis

The micro-Raman scattering spectra were recorded with a Renishaw Raman RM1000 equipped with the 532 nm laser line, an electrically refrigerated CCD camera, and a notch filter to eliminate the elastic scattering. The spectra shown here were obtained by using a 25× microscope objective. The output laser power at the samples was about 0.2 mW. The spectral resolution was 4 cm^{-1}. The spectral scanning conditions were chosen to avoid sample degradation.

Raman spectroscopy analysis of CMC and its epoxy derivative is shown in Fig. 7. Two samples show characteristic polysaccharide asymmetric and symmetric O–H stretching vibration bands at 3275 and 3401 cm^{-1}; A C–H stretching at 2983 cm^{-1} will show a stretching vibration of CH_2 at 2833 cm^{-1} as it will show a bending vibration at 1400-1422 cm^{-1}. The carboxylate ion (COO−) appeared at 1610-1740 cm^{-1} and near 1315-1435 cm^{-1}. The C-O-C stretching vibration range was demonstrated at 890 cm^{-1}, while the C-C bond was shown at 540 cm^{-1}. Introducing the epoxy group with epichlorohydrin generates significant peaks such as the –CH deformation of the epoxy ring at 804 cm^{-1}, the in-plane C-H epoxy deformation at 1198 cm^{-1} and the methylene vibration at 2899 cm^{-1} [1-3].

[1] M. Choucair, P. Thordarson and J. A. Stride, Nat. Nanotechnol., 2009, 4, 30–33.

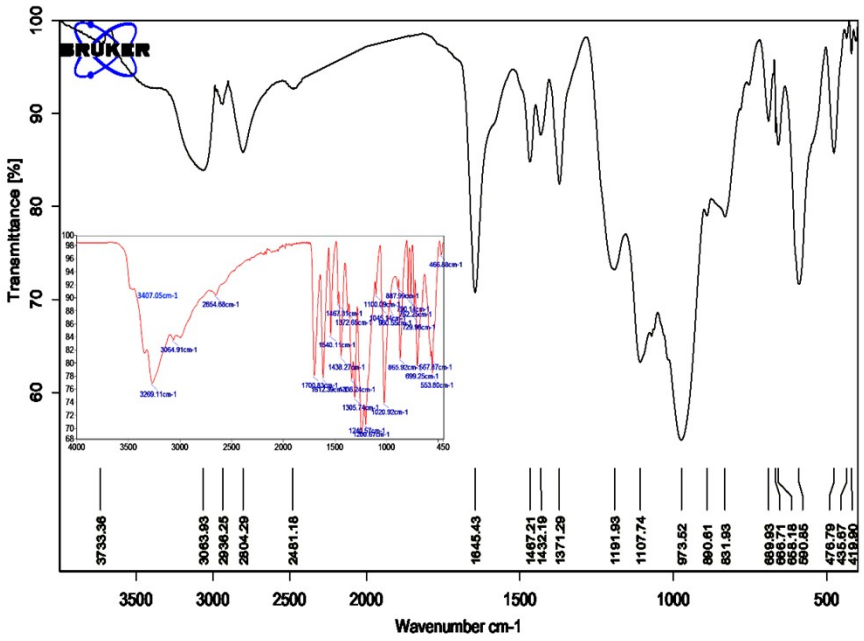
[2] K. Sadowska, K. P. Roberts, R. Wiser, J. F. Biernat, E. Jabłonowska and R. Bilewicz, Carbon, 2009, 47, 1501– 1510.

[3] H. L. Wang, J. Liu and D. J. Qian, Synth. Met., 2012, 162, 881–887.

S1.4. Surface roughness measurement

The surface roughness measurements of the Modified CMC membrane were compared with its neat polymer utilizing surface roughness tester (model: SJ- 201P), made in Japan. Briefly, samples with an approximate dimension (4cm×5cm) were mounted on a double-sided glass slide. Additionally, all results are the average of six measurements.

S1.5.FTIR of Fe-Gallic acid



S1.5. FT-IR of GA (inset) and Fe-GA MOF

S2.1 : XPS Survey scans

Name	Peak BE	FWHM, eV	Area (P) CPS., eV	Atomic, %
O1s	533.2	3.72	185924.3	34.8
C1s	286.04	3.71	120574.5	57.58
S2p	169.76	3.55	13297.49	3.6
Fe2p	711.92	6.37	32864.01	4.02

S2. 2: XPS Fe2p scan

Name	Peak BE	FWHM, eV	Area (P) CPS., eV	Atomic %
Fe2p	710.66	3.27	2001.67	46.21
Fe2p Scan A	723.96	2.69	669.17	15.61
Fe2p Scan B	718.14	3.37	314.58	7.3
Fe2p Scan C	725.59	2.2	197.36	4.61
Fe2p Scan D	714.38	3.37	904.92	20.95
Fe2p Scan E	728.24	3.37	227.2	5.32

S2. 3: XPS O1s scan

Name	Peak BE	FWHM eV	Area (P) CPS., eV	Atomic %
O1s	531.73	1.71	8021.71	41.97
O1s Scan A	533.12	1.84	5248.4	27.48
O1s Scan B	532.69	3.16	5835.65	30.55

S2. 4: XPS C1s scan

Name	Peak BE	FWHM, eV	Area (P) CPS., eV	Atomic %
C1s	284.75	1.72	8348.15	68.73
C1s Scan A	286.38	1.51	2146.95	17.69
C1s Scan B	288.60	2.17	1645.54	13.57

S2. 5: XPS S2p scan

Name	Peak BE	FWHM, eV	Area (P) CPS., eV	Atomic %
S2p	168.89	2.18	1497.2	100

S2. 6: Details of XPS analysis peaks of the Fe(III)-GA-MOF

XPS Survey scans																
Name	Start BE	Peak BE	End BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) KE^0.6	Atomic %	Peak Type	Q	SF Al Scof	TXFN	Backgnd	PP Height CPS	PP Hgt (N)	PP At. %
O1s	540.58	533.2	524.08	44803.42	3.72	185924.31	1034.86	34.8	Standard	1	2.93	1	Smart	48736.37	59.68	36.76
C1s	296.08	286.04	277.08	26422.21	3.71	120574.52	1712.41	57.58	Standard	1	1	1	Smart	28991.92	90.58	55.8
S2p	175.08	169.76	163.58	3477.95	3.55	13297.49	106.98	3.6	Standard	1	1.67	1	Smart	3892.77	6.89	4.24
Fe2p	730.08	711.92	706.08	4304.06	6.37	32864.01	336.97	4.02	Standard	1	16.42	1	Smart	5525.74	1.37	0.84
XPS Fe2p scan																

Fe2p	734.98	710.66	706.48	564.02	3.27	2001.67	2.25	46.21	Fitted	1	16.42	1	Smart	555.69	0.62	22.18
Fe2p Scan A	734.98	723.96	706.48	229.6	2.69	669.17	0.76	15.61	Fitted	1	16.42	1	Smart	536.15	0.61	21.61
Fe2p Scan B	734.98	718.14	706.48	86.26	3.37	314.58	0.36	7.3	Fitted	1	16.42	1	Smart	259.36	0.29	10.41
Fe2p Scan C	734.98	725.59	706.48	82.96	2.2	197.36	0.22	4.61	Fitted	1	16.42	1	Smart	422.92	0.48	17.08
Fe2p Scan D	734.98	714.38	706.48	248.13	3.37	904.92	1.02	20.95	Fitted	1	16.42	1	Smart	373.51	0.42	14.95
Fe2p Scan E	734.98	728.24	706.48	62.3	3.37	227.2	0.26	5.32	Fitted	1	16.42	1	Smart	340.4	0.39	13.77
XPS O1s scan																
O1s	537.28	531.73	528.28	4334.2	1.71	8021.71	44.61	41.97	Fitted	1	2.93	1	Smart	6126.49	17.03	35.48
O1s Scan A	537.28	533.12	528.28	2635.12	1.84	5248.4	29.21	27.48	Fitted	1	2.93	1	Smart	5285.24	14.71	30.63
O1s Scan B	537.28	532.69	528.28	1712.68	3.16	5835.65	32.47	30.55	Fitted	1	2.93	1	Smart	5848.97	16.27	33.89
XPS C1s scan																
C1s	292.18	284.75	281.68	4474.01	1.72	8348.15	118.48	68.73	Fitted	1	1	1	Smart	4891.29	34.71	61.24
C1s Scan A	292.18	286.38	281.68	1311.18	1.51	2146.95	30.5	17.69	Fitted	1	1	1	Smart	2107.22	14.97	26.4
C1s Scan B	292.18	288.6	281.68	701.38	2.17	1645.54	23.4	13.57	Fitted	1	1	1	Smart	985.2	7	12.36
XPS S2p scan																
S2p	172.68	168.89	161.48	634.45	2.18	1497.2	12.04	100	Fitted	1	1.67	1	Smart	676.56	4.08	100

S2. 7: Details of XRD analysis peaks list of the Fe(III)-GA-MOF

Pos.[°2Th.]	Height [cts]	FWHMLeft[°2Th.]	d-spacing [Å]	Rel. Int. [%]
9.24(5)	12(6)	2.1(2)	9.56029	40.00
11.84(5)	55(6)	2.7(5)	7.79815	74.16
16.8(5)	11(6)	2.3(3)	7.2151	66.00
20.1(3)	12(4)	2.1(5)	5.9214	48.14
23.0(1)	11(6)	2(1)	4.2451	34.58
26.5(3)	22(4)	2(1)	3.24292	12.46
29.88(1)	11(7)	0(1)	2.98816	22.89
56.44(5)	10(6)	0.2(2)	1.62891	20.31
58.63(5)	9(6)	0.1(2)	1.57330	16.64
61.45(9)	12(3)	0.6(5)	1.50762	12.82