RSC Advances

Supporting Information

Surface modification of ferrite nanoparticles with dicarboxylic acids for the synthesis of 5-hydroxymethylfurfural: A novel and green protocol.

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All the X-ray diffraction patterns were examined for phase identification and quantification (Rietveld refinement) with TOPAS – software package supplied with Bruker's D8 DISCOVER instrument.

Table S1. X-ray diffraction analysis – qualitative and quantitative (refinement analysis)

Sample id	Phases present (with Crystal system & Space group)	Tune cell Lattice parameters* (in A°)	Weight fraction* (in Weight %)	Crystallites size* (in A°)
Fe_3O_4-L1	Magnetite (Cubic system, Fd-3m(227)	a = 8.35316	0.4748	135.9
	Magnetite –surface coated DCA	a = 5.02946 c = 13.83656	0.5252	85.52
Fe_3O_4-L2	Magnetite (Cubic system, Fd-3m(227)	a = 8.36301	0.4532	138.0
	Magnetite –surface coated DCA	a = 5.04666 c = 13.83466	0.5468	80.6
Fe_3O_4-L3	Magnetite (Cubic system, Fd-3m(227)	a = 8.3433	0.4462	141.0
	Magnetite –surface coated DCA	a = 5.04272 c = 13.81214	0.5574	97.5
Fe_3O_4-L4	Magnetite (Cubic system, Fd-3m(227)	a = 8.34987	0.473	136.8
	Magnetite –surface coated DCA	a = 5.03878 c = 13.82828	0.527	77.4
Fe_3O_4-L5	Magnetite (Cubic system, Fd-3m(227)	a = 8.33673	0.1988	142.2
	Magnetite –surface coated DCA	a = 6.44435 b = 7.44496 c = 3.75293	0.8012	311.0

* Refinement parameters; All the refinement parameters were considered with GoF <5

Table S2. Stretching frequency of Infra Red Spectroscopy of surface modified MNPs

S.No	Stretching frequency	Ligand	Assignment
1	1000-1300 cm^{-1}	L1, L2, L3, L4	ν (C–C)
2	1415 cm^{-1}	L1-L5	ν (COOFe)
3	1576 cm^{-1}	L5	ν (C=C) aromatic
4	2925cm^{-1}	L1-L4	ν (C–H) of aliphatic
5	700-900 cm^{-1}	L5	ν (C–H) vibration of aromatic
6	3400cm^{-1}	L1-L5	ν (O-H)
7	1625-1630 cm^{-1}	L1-L5	ν (O-H) deformed bending mode
8	580 cm^{-1}	L1-L5	ν (Fe-O) stretching

Table S3: Synthesis of HMF using different heterogeneous catalysts.

Entry	Catalyst	Temperature (^{0}C)	Solvent	Time (min)	Conversion (%)	Selectivity (%)	Reference (main text)
1	sulfonic acid-functionalized MOF	120	DMSO	60	99	91	43
2	aluminium doped zirconium phosphate	135	Water	240	12	40	44
3	niobium catalysts	120	Water	180	92	52	45
4	sulphated zirconia	180	Acetone/ DMSO	5	93	73	46
5	sulfonic acid functionalized silica	100	DMSO	60	75	54	47a
6	Solid silica immobilized ionic liquid	100 (MW)	DMSO	4	100	74	47b
7	SnO_2–ZrO_2	120	DMSO	150	--	75	48a
8	WO_3/ZrO_2	130	water	240	60	40	48b
9	Sn-W oxide	80	DMSO	720	99	70	48c
11	Dowex-type ion-exchange resin	110	DMSO	300	100	85	49a
12	Ion exchange resin	90	Water/MIBK	1080	98	85	49b
13	Dowex-type ion-exchange resin	150	water	60	82	34	49c
15	Dowex-type ion-exchange resin	150 (MW)	Acetone/ DMSO	30	99.4	82	49d
16	Amberlyst 15 pellets	120	DMSO	120	100	92	50a
17	Amberlyst 15	80	[BMIM][Cl]	10	98.6	83.3	50b
18	HT/Amberlyst 15	100	DMF	180	99	76	50c
19	Amberlyst 15	80	[BMIM][PF6]/ DMSO	1440	--	80	50d
20	12-MPA	120	[BMIM][Cl]/ acetonitrile	180	99	98	51
21	Functionalized CNTs	80	DMF	480	75	99	52
22	Mg-NHCs	100	DMF	120	99	89	53
23	**Surface modified ferrites**	**80**	**Solvent free**	**60**	**96**	**89**	**In this work**

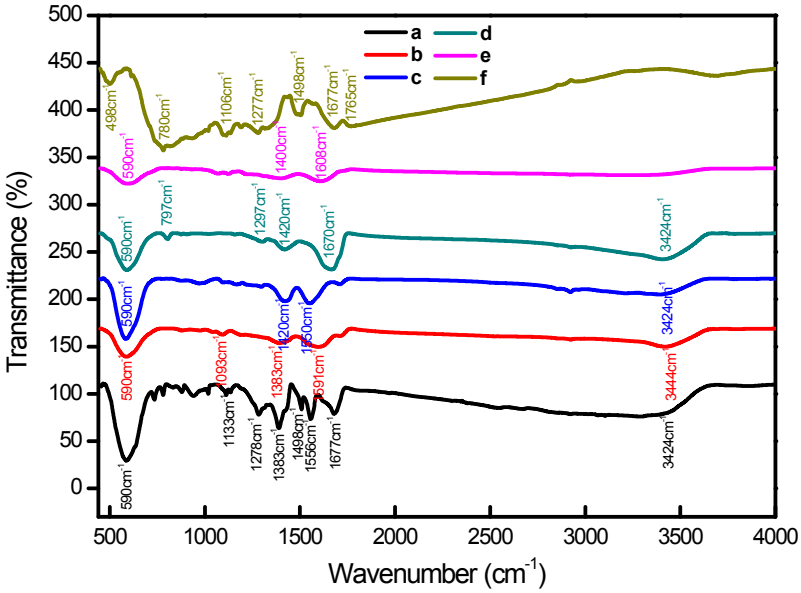


Fig. S1. FT-IR pattern of the (a) synthesized $CoFe_2O_4$ (b) $CoFe_2O_4@L_1$ (c) $CoFe_2O_4@L_2$ (d) $CoFe_2O_4@L_3$ (e) $CoFe_2O_4@L_4$ (f) $CoFe_2O_4@L_5$

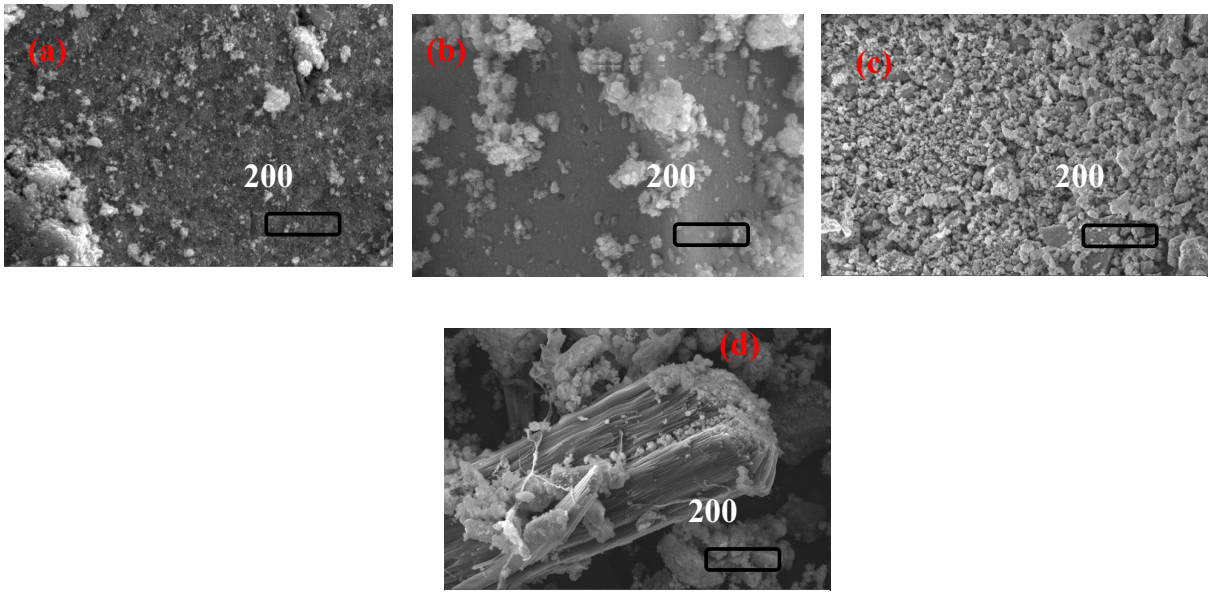


Fig. S2. SEM of surface modified MNPs with (a) L1 (b) L3 (c) L4 (d) L5

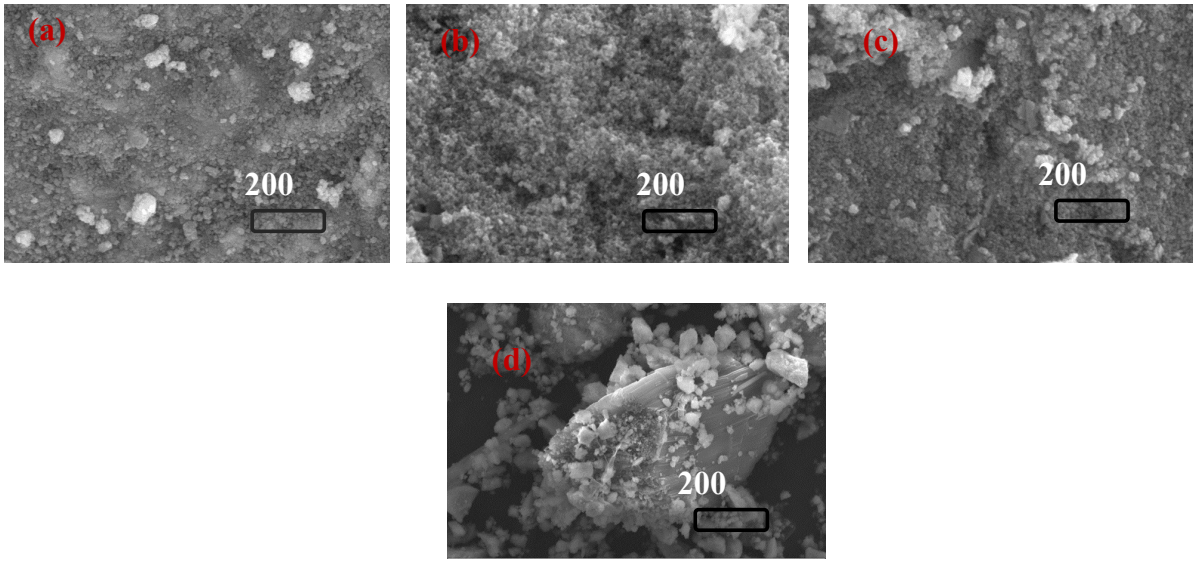


Fig. S3. SEM of surface modified cobalt ferrite NPs modified with (a) L1 (b) L3 (c) L4 (d) L5

2. Calculation of HMF Yield (%)

$$\text{Conversion (\%)} = \frac{Initial\ concentration\ of\ fructose - final\ concentration\ of\ fructose}{Initial\ concentration\ of\ fructose} \text{x100\%}$$

$$= \frac{Concentration\ of\ fructose\ at\ t = 0 - Concentration\ of\ fructose}{Concentration\ of\ fructose\ at\ a\ given\ time} \text{x100\%}$$

$$\text{Selectivity (\%)} = \frac{HMF\ concentration}{Fructose\ concentration} \text{x100\%}$$

3.1. The Spectrophotometric method

After completion of the reaction, 0.5µl reaction mixture was diluted up to 50 mL with HPLC water followed by the addition of 0.5 mL of Carrez solution I and 0.5 mL of Carrez solution II. Aliquots of 5 mL were put into 2 tubes; 5 mL of deionized water was added to one tube (sample solution); 5 mL of sodium bisulfite solution 0.2% was added to the second (reference solution). The absorbance (determined using a Lambda 25 double beam spectrophotometer UV/Vis, Shimadzu) of the aqueous reaction sample at 284 nm (A284) was determined versus reference solution, in order to avoid the interference of other components at that wavelength. The absorbance at 336 nm (A336) was read to subtract the background absorbance. The HMF was quantified by using the proposed formula of the original White method.

HMF(mg) = (A284 − A336) × 149.7 × 5*/W,* where W is the weight of the fructose, the factor 149.7 is a theoretical value linked to the molar extinction coefficient of HMF at 284 nm, which is 16830. In this work we studied the experimental extinction coefficient of HMF to check the correspondence with the theoretical behaviour of HMF.

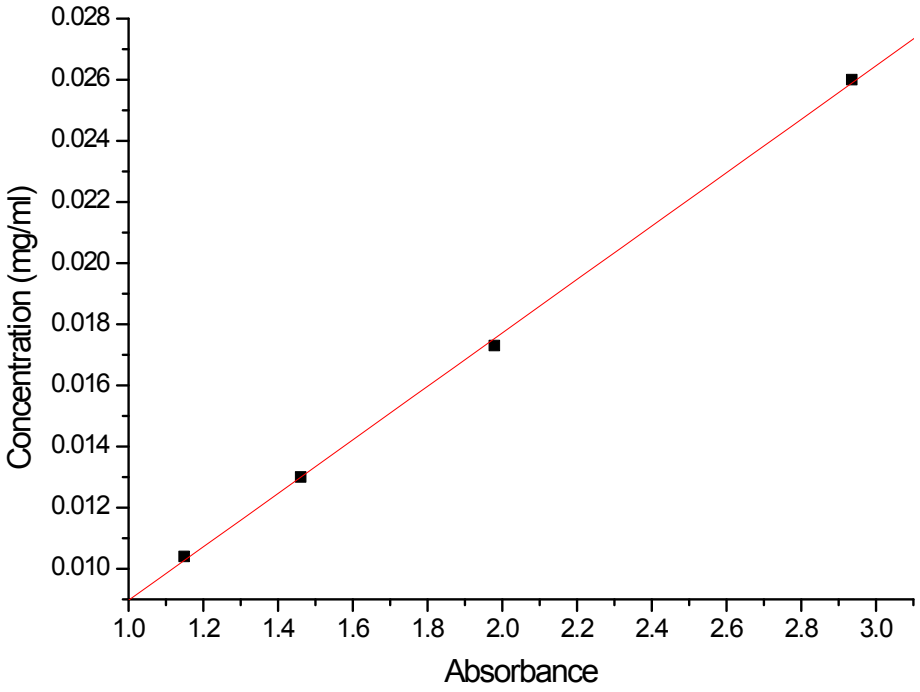


Fig. S4. Calibration Curve for the HMF using UV-spectrometer.

$$\mathbf{Y = (87.4 \times 10^{-4})\ (X) + 2.264 \times 10^{-4}}$$

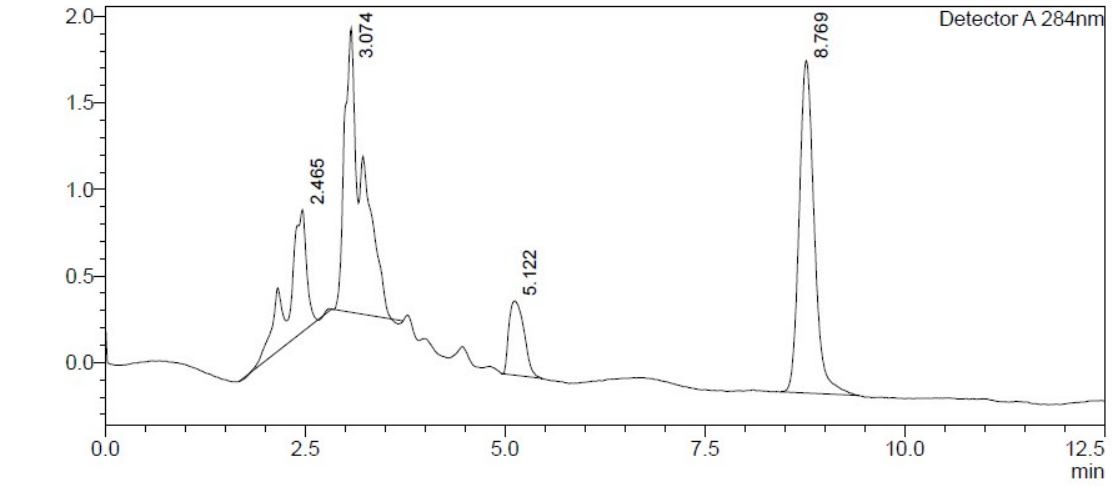
3.2. HPLC analysis report

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Ferrite-Oxalic Acid

<Chromatogram>



<Peak Table>

Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
2.465	11684	707	17.074	15.054
3.074	25901	1641	37.849	34.933
5.122	5617	429	8.208	9.128
8.769	25231	1921	36.869	40.884
	68434	4698	100.000	100.000

Fig.S5. HPLC analysis of MNPs treated with oxalic acid catalyzed dehydration of fructose.

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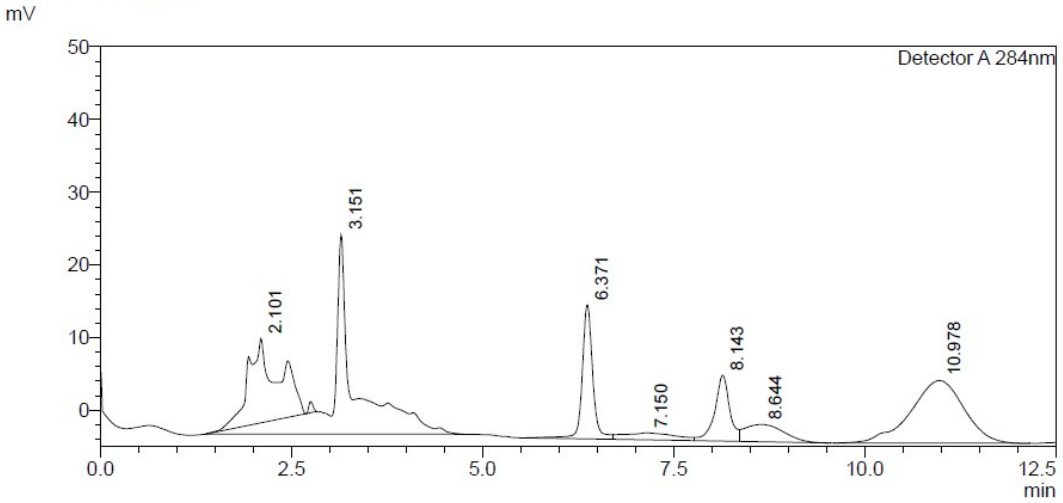
SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

, Ferrite- Succinic Acid

<Chromatogram>



<Peak Table>

Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
2.101	326744	11588	18.469	14.768
3.151	596192	27425	33.700	34.950
6.371	176033	18421	9.950	23.475
7.150	46369	964	2.621	1.228
8.143	122277	9082	6.912	11.573
8.644	84431	2388	4.772	3.044
10.978	417092	8601	23.576	10.961
	1769139	78469	100.000	100.000

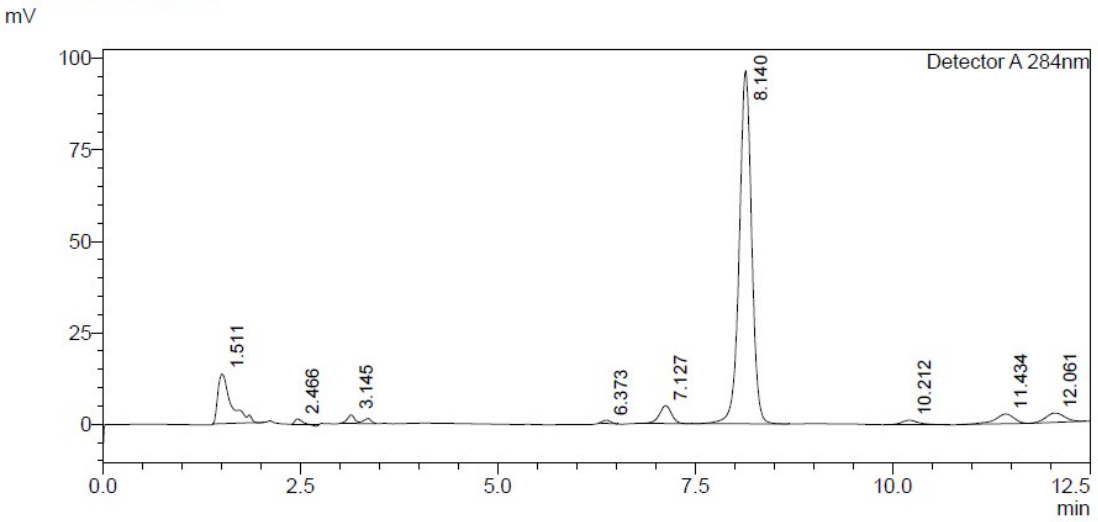
Fig.S6. HPLC analysis of MNPs treated with succinic acid catalyzed dehydration of fructose.

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Ferrite-Malic Acid

<Chromatogram>



<Peak Table>

Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
1.511	159761	13528	11.416	10.756
2.466	6165	1394	0.441	1.109
3.145	24110	2297	1.723	1.826
6.373	6128	852	0.438	0.677
7.127	52371	4875	3.742	3.876
8.140	1046197	96391	74.758	76.641
10.212	17255	1183	1.233	0.941
11.434	44714	2669	3.195	2.122
12.061	42746	2581	3.055	2.052
	1399446	125769	100.000	100.000

Fig.S7. HPLC analysis of MNPs treated with malic acid catalyzed dehydration of fructose.

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SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	:Fe3O4-TA		
Sample ID	:Fe3O4-TA		
Data Filename	:Fe3O4-TA		
Method Filename	: melatonine.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 9/30/2015 3:07:28 PM	Acquired by	: System Administrator
Date Processed	: 9/30/2015 4:08:10 PM	Processed by	: System Administrator

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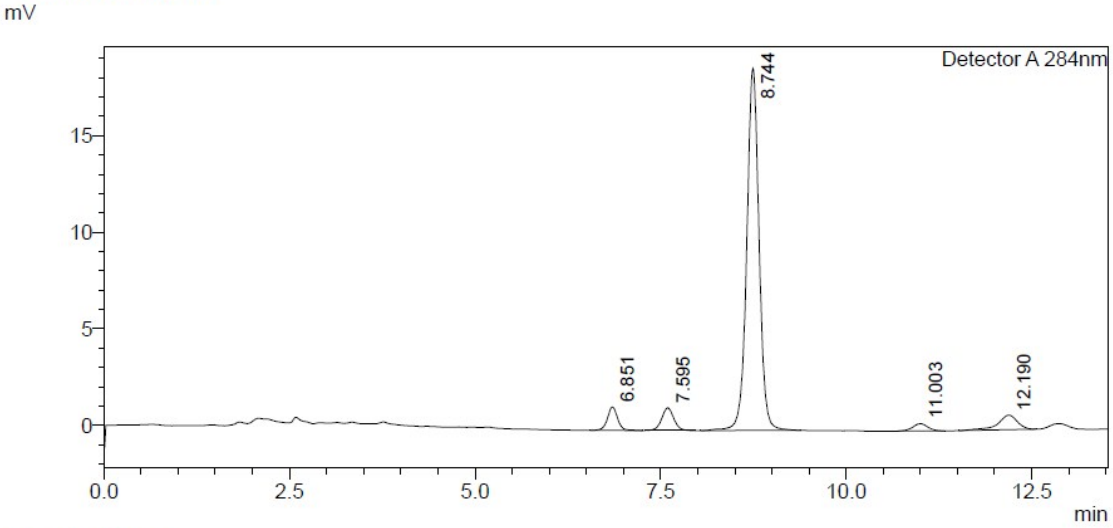

<Peak Table>

Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
6.851	11567	1215	4.438	5.459
7.595	13315	1171	5.108	5.262
8.744	216554	18739	83.079	84.194
11.003	5413	380	2.076	1.709
12.190	13811	751	5.298	3.376
	260659	22258	100.000	100.000

Fig.S8. HPLC analysis of MNPs treated with tartaric acid catalyzed dehydration of fructose.

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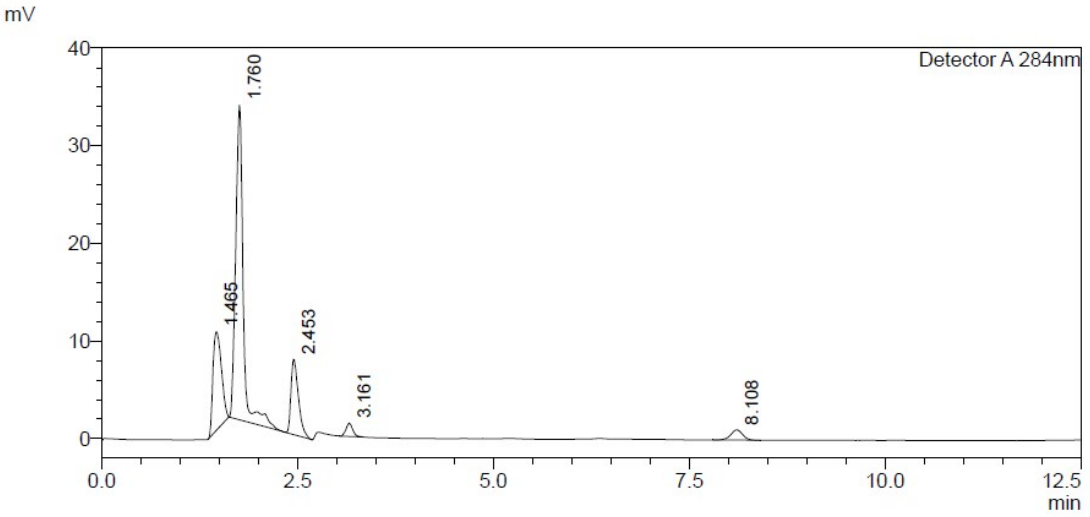
<Chromatogram>



<Peak Table>

Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
1.465	76130	10087	21.142	19.229
1.760	214102	32271	59.458	61.517
2.453	50785	7714	14.103	14.705
3.161	7995	1345	2.220	2.563
8.108	11079	1042	3.077	1.986
	360092	52459	100.000	100.000

Fig.S9. HPLC analysis of MNPs treated with terepthalic acid catalyzed dehydration of fructose.

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: CoFe2O4-TA		
Sample ID	:CoFe2O4-TA		
Data Filename	:CoFe2O4-TA		
Method Filename	: melatonine.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 2 uL		
Date Acquired	: 9/30/2015 5:08:05 PM	Acquired by	: System Administrator
Date Processed	: 9/30/2015 5:27:46 PM	Processed by	: System Administrator

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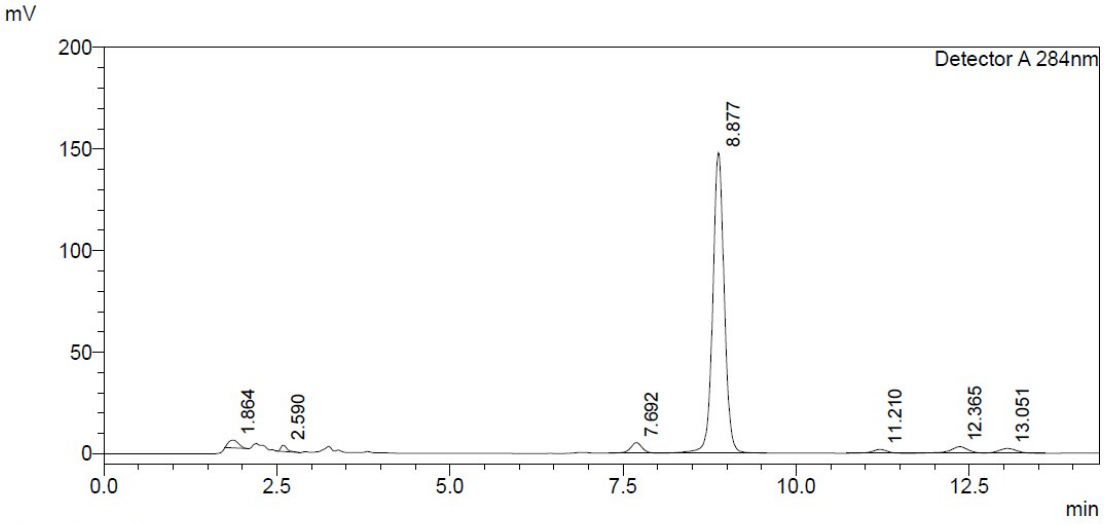

<Peak Table>

Detector A 284nm

Ret. Time	Area	Height	Area%	Height%
1.864	38643	3857	1.983	2.302
2.590	19642	3127	1.008	1.866
7.692	58733	5091	3.013	3.039
8.877	1702685	148047	87.360	88.371
11.210	27550	1855	1.414	1.107
12.365	59102	3178	3.032	1.897
13.051	42686	2374	2.190	1.417
	1949041	167529	100.000	100.000

Fig.S10. HPLC analysis of $CoFe_2O_4$ treated with tartaric acid catalyzed dehydration of fructose.