Dispersion solid-phase extraction of flavonoid with novel amphiphilic monomers N-vinyl pyrrolidone and 1H,1H,7H-dodecafluoroheptyl methacrylate based poly(styrene-divinylbenzene) and silica

Yuxin Ma[a], Dandan Han[b], Yingjie Lei[a] and Tao Zhu[a,*]

[a]*Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China*

[b]*Department of Preventive Medicine and Health Management, Hebei University, Baoding 071002, China*

Supporting Information

3.1 Characterization of materials

FT-IR was employed to examine the modification process and recognition of any changes on the PS-DVB and silica matrix after polymerization compounds (Supporting Information Figure S1). The broad bands at 3600 cm^{-1} and 2955 cm^{-1} correspond to the combined water and C-H stretching vibrations of copolymers respectively. The adsorption bands at 1660 cm^{-1} and 1400 cm^{-1} assigned to the -C=O and C-C stretching vibration in the benzoid ring, respectively. The adsorption bands at 1280 cm^{-1} correspond to the ν (C-N), 1000cm^{-1}-1300 cm^{-1} was -C-F characteristic adsorption band. The adsorption bands at 738 cm^{-1} was assigned to ν (C-F). The adsorption bands at 1100 cm^{-1} correspond to the ν (-Si-O).

The thermal stability of copolymers was studied by the thermal gravimetric

* Address correspondence to Tao Zhu, Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China. E-mail: zhutao@tjut.edu.cn

analysis (TGA) to obtain the range of applicable temperature. The TGA curves of materials are shown in Supporting Information Figure S2. As showed in Figure S2 (b-f), the first stage weight loss of about 10% between 40 and 200°C is attributed to the evaporation of intro and inter-molecular water. The material was possessed of strong hydrophilic groups, which can combine with water molecules by inter-molecular interaction. Then, decarboxylation and dehydration of carboxyl (-COO) are occurred with P-N-F (c) and Si-N-F (f). And weight loss of 80% is occurred 400 °C. This part of weightlessness is the result of the decomposition of the material side chain and backbone. Compared with PS-DVB, the silica had a better thermostability, but thermostability of material which polymerization of the synthesized NVP and DMFA with matrix was worse than without matrix.

3.3.1 Optimization of materials synthesis

The quadratic model of two targets to predict the adsorption efficiency in terms of actual factors is as follows:

$Y_1=3.70+0.39A-0.19B+0.10C+0.025AB+0.55AC+0.20BC-0.088A^2-1.14B^2-0.26C^2$

$Y_2=4.24+0.25A-0.39B+4.638C+0.42AB+0.15AC-0.41BC+0.14A^2-0.72B^2-0.082C^2$

where Y_1 is the adsorption of pyrocatechin, Y_2 is the adsorption of quercetin. A was volume of DMFA, B was the mass of AIBN and C was reaction temperature. The p value was used as a tool to check the significance of each coefficient, and also indicated the interaction strength between each independent variable. The Model F-value of 1.04 and 0.80 for pyrocatechin and quercetin implied that the model were not significant relative to the noise, and there was only a 31% and 28% chance that a

“Model F-Value” that was this large occurred because of noise. The regression coefficients and the corresponding p values were also shown in Table S3. Therefore, volume of DMFA (μL), the mass of AIBN (mg) and reaction temperature (°C) were important factors in the adsorbtion of the pyrocatechin and quercetin.

Figure S3 demonstrate various 3D plots of the response surface model of pyrocatechin and quercetin respectively. In Figure S3 results of adsorption of pyrocatechin and quercetin showed that with increasing initial DMFA volumes from 130.00 to 330.00 μL, since the volume increased from 330 to 530.00 μL the adsorption of material was declined. The data clearly demonstrated 330.00 μL was appropriate volumes of DMFA. The effect of different mass of AIBN (2-20 mg) as cross-linking agent was investigated. It can be seen that an increase mass that exceed 11mg of AIBN decreased total peak area. The reason may be that by increasing the mass of AIBN, the crosslinking between PS-DVB and monomers became too densification to absorb the target.

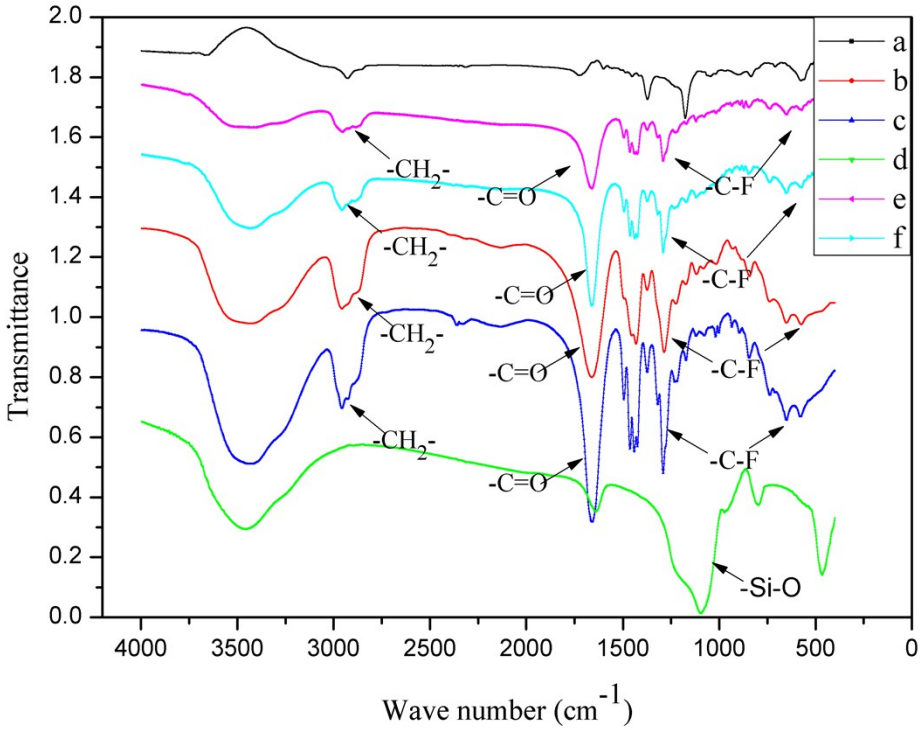

Figure S1. FTIR spectra of PS-DVB (a), P-N (b), P-N-F (c), Si (d), Si-N (e), and Si-N-F (f)

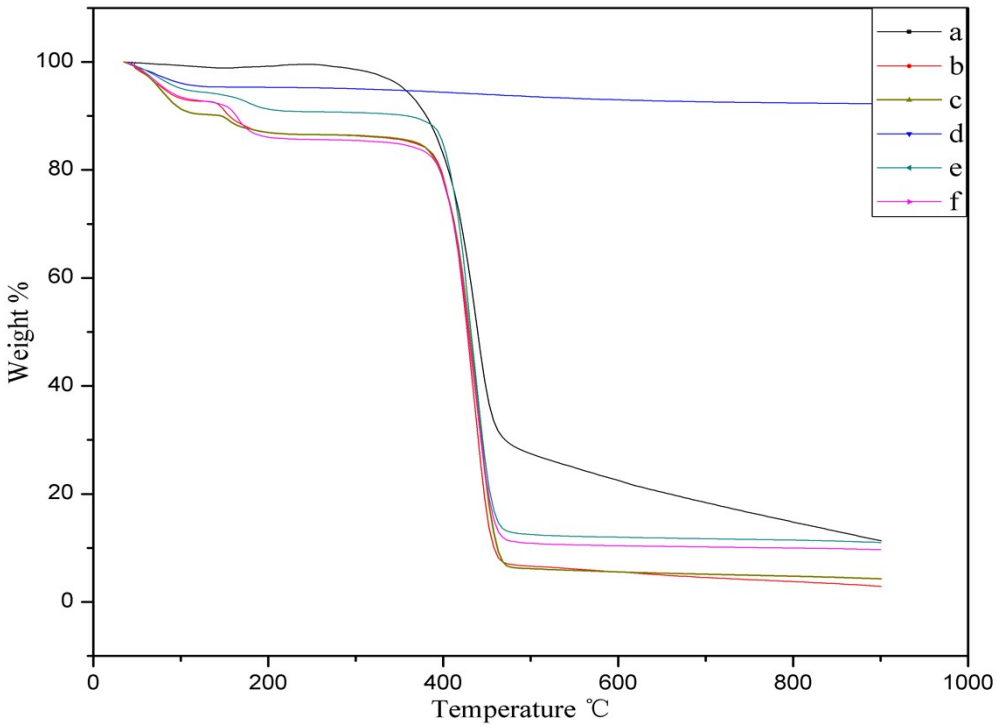

Figure S2. TGA curves of PS-DVB (a), P-N (b), P-N-F (c), Si (d), Si-N (e), and Si-N-F (f) at heating rate 10°C·min^{-1}

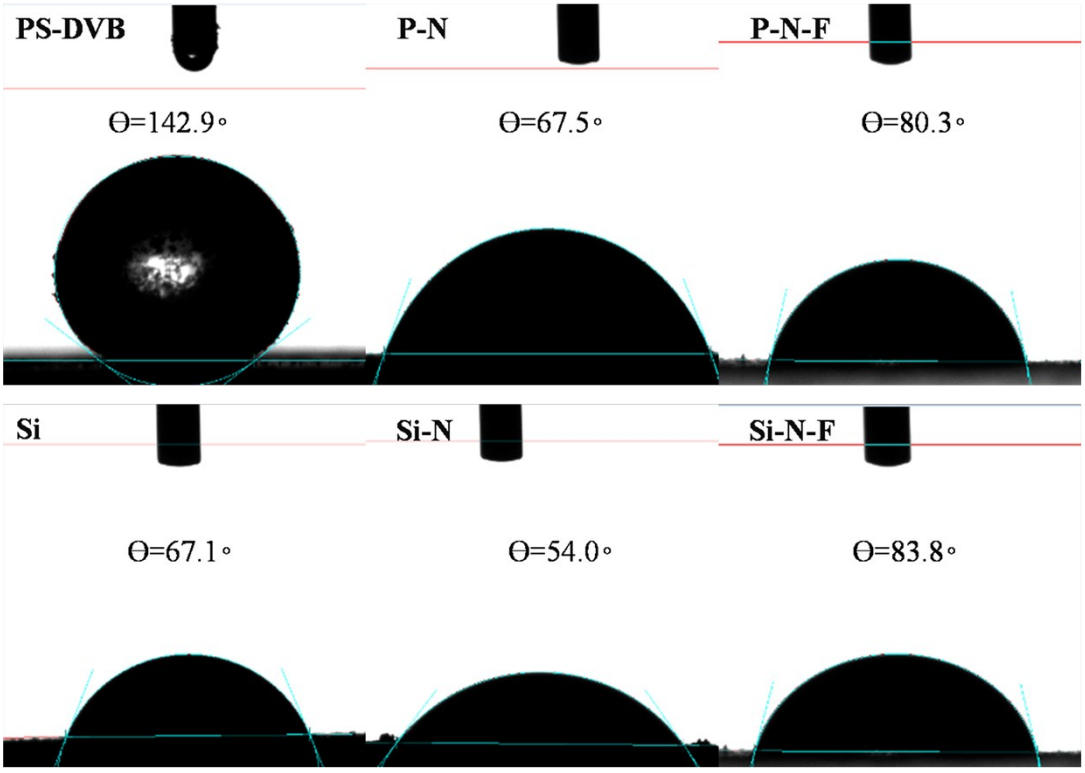

Figure S3. Profiles of a water drop on the films of materials at room temperature.

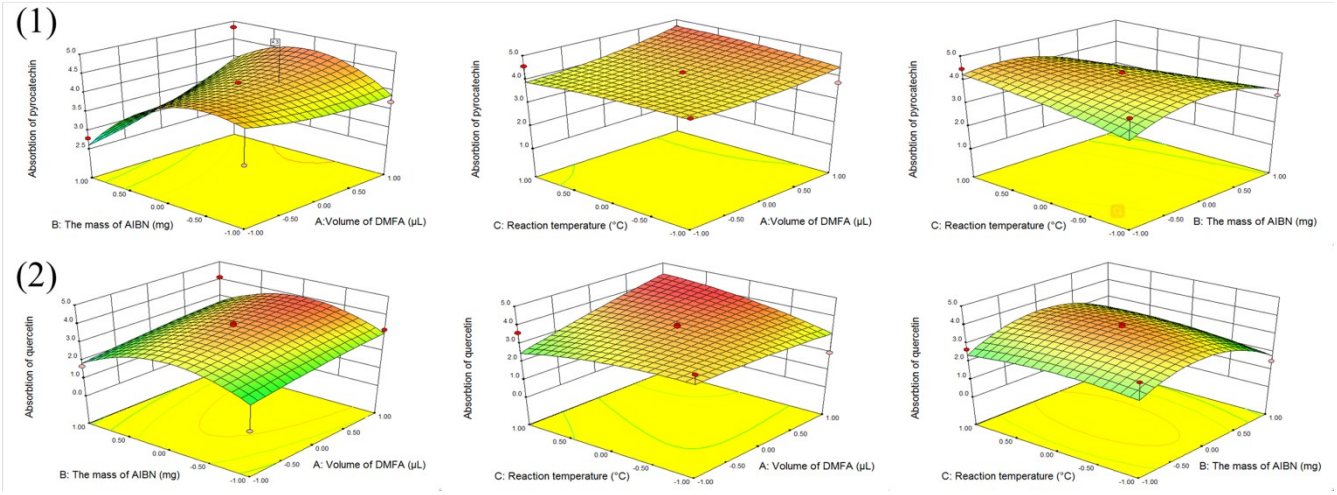

Figure S4. Response surface methodology analysis the significant factors of P-N-F for adsorption with pyrocatechin and quercetin ((1) RSM for absorbtion of pyrocatechin; (2) RSM for absorbtion of quercetin)

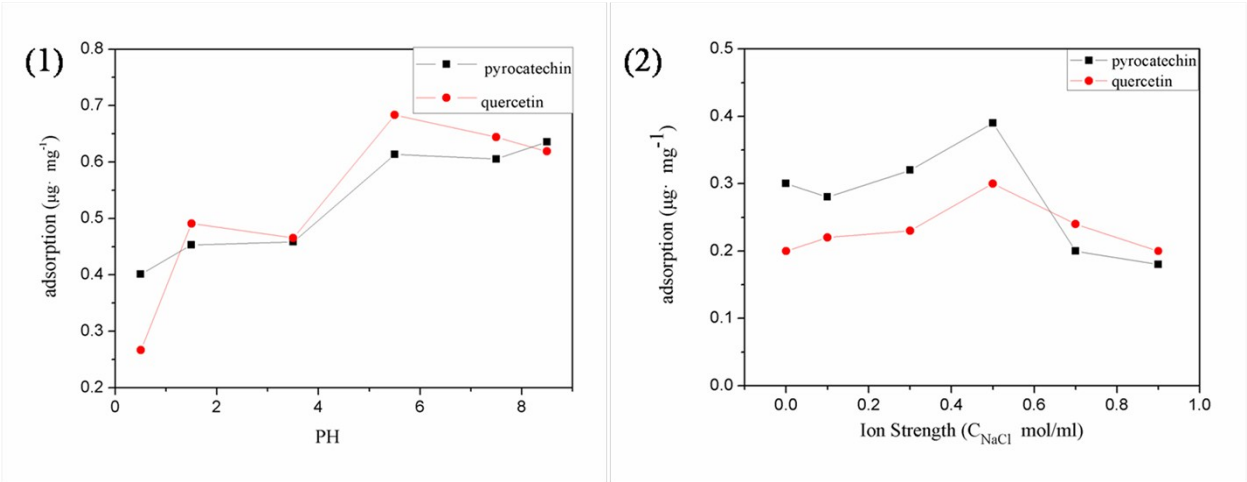

Figure S5. Effect of adsorption (1) pH and (2) ionic strength for pyrocatechin and quercetin

Table S1. Experimental values and levels of variables

	Variables	Level		
		-1	0	1
A	Volume of DMFA (μL)	130	330	530
B	The mass of AIBN (mg)	2	11	20
C	Reaction temperature (°C)	60	80	100

Table S2. Adsorption isotherm parameters of the materials for pyrocatechin and quercetin

Analytes	materials	Adsorption isotherm Equation No.								
		$Q = aC + b$			$Q = aC^{1/c}$			$Q = \frac{aC}{1+bC}$		
		Parameters		r^2	Parameters		r^2	Parameters		r^2
		a	*b*		*a*	*c*		*a*	*b*	
Pyrocatechin	PS-DVB	0.515	5.322	-0.199	0.337	0.099	-0.104	0.523	-7.934	-0.200
	P-N	1.028	0.016	0.846	0.214	0.579	0.924	3.432	-4.761	-0.200
	P-N-F	0.923	0.032	0.925	0.176	0.720	0.961	5.890	-6.233	-0.200
	Si	0.709	0.008	0.899	0.136	0.550	0.888	1.933	-3.412	-0.200
	Si-N	0.577	0.018	0.978	0.063	0.797	0.970	3.327	-3.579	-0.200
	Si-N-F	0.829	0.027	0.977	0.030	0.041	0.993	5.070	-2.523	-0.200
Quercetin	PS-DVB	0.248	1.665	-0.153	0.141	0.148	0.083	0.027	-0.005	-4.173
	P-N	1.084	0.004	0.416	0.418	0.303	0.695	0.364	-0.006	-2.906
	P-N-F	1.170	0.016	0.860	0.250	0.564	0.945	3.703	-1.513	-0.200
	Si	0.646	0.002	0.339	0.267	0.281	0.570	1.403	-0.100	-8.807
	Si-N	0.233	0.011	0.863	0.006	1.106	0.855	0.395	-0.003	0.250
	Si-N-F	0.571	0.014	0.979	0.073	0.738	0.976	2.772	-8.584	-0.200

Table S3. Analysis of Variances (ANOVA) for adsorption of pyrocatechin (a) and

quercetin (b)

Variables	Sum of Squares		*DF*		Mean Square		*F* Value		*p* value Prob.>*F*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Model	5.48	8.94	9	9	0.61	0.99	1.04	0.80	0.31	0.28
A-A	0.51	1.20	1	1	0.51	1.20	0.87	0.97	0.38	0.36
B-B	1.21	0.28	1	1	1.21	0.28	2. 07	0.23	0.19	0.65
C-C	1.721E-004	0.08	1	1	1.721E-004	0.08	2.941E-004	0.06	0.98	0.81
AB	0.70	2.50	1	1	0.70	2.50	1.19	2.01	0.31	0.97
AC	0.090	1.21	1	1	0.090	1.21	0.15	0.97	0.71	0.36
BC	0.66	0.16	1	1	0.66	0.16	1.13	0.13	0.32	0.73
A^2	0.082	0.03	1	1	0.082	0.03	0.14	0.03	0.72	0.88
B^2	2.21	5.45	1	1	2.21	5.45	3.78	4.38	0.09	0.07
C^2	0.029	0.29	1	1	0.029	0.29	0.049	0.23	0.83	0.64
Residual	4.12	8.70	7	7	0.59	1.24				
Lack of fit	0.69	8.68	3	3	0.23	2.89	0.27	0.65	0.25	0.18
Pure Error	3.43	0.02	4	4	0.86	5.00				
Correlation Total	9.57	17.64	16	16						

Table S4. Comparison to previously reported analytical methods

Target	Analytical method	Sample	Linear rage (μmol/L)	LOD ($\mu g \cdot mL^{-1}$)	RSD (%)	Recovery	Reference
pyrocatechin	HPLC	Black mulberry	/	/	0.30	0.10mg/g	[34]
	MIP-DPV	River water	1.85-100	0.08	1.50	98.00%	[35]
	SPE-FLD	urine	0.05-5	0.03	7.60	90.00%	[36]
	MIP-DPV	/	0.5-25	0.06	3.60	94.90%	[37]
	DSPE-HPLC	Apple	3.3-1300	0.05	2.90	83.43%	In this work
quercetin	HPLC	Black mulberry	/	/	2.10	0.10mg/g	[34]
	SWE	onion skin	/	0.01	0.90	17.60mg/g	[38]
	MIP-MSPD	Herba	3.3-1600	/	4.90	102.30%	[39]
	LC-DAD	Habanero chili	3.3-160	0.10	150	80.00%	[40]
	DSPE-HPLC	Apple	3.3-1300	0.08	2.80	83.63%	In this work