Supporting Information on

Multi-heteroatom doped graphene-like carbon nanospheres with 3D inverse opal structure: A promising bisphenol-A remediation material

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There are 7 Pages with 6 Figures and 3 Tables in Supporting Information.

Batch adsorption experiments procedure. The whole batch sorption experiments were performed in 10 mL glass vials. The suspensions of 2 mg NPS-IOC, the BPA stock solution, and the background electrolyte solution (0.01 mol/L $NaNO_3$) were mixed in glass vials together to achieve the setting concentrations. The desired pH values were adjusted by adding negligible volume of 0.01 or 0.1 mol/L HNO_3 and/or NaOH, and the variances of pH were kept below 0.05 before and after adsorption. Then kept glass vials in thermostatic bath with constant agitation (150 rpm). After reaching adsorption equilibrium (24 h), aliquots of 2 ml were taken, following with the filtration by 0.45 μm polyethersulfone membrane before analysis. The concentrations of BPA were measured by using high performance liquid chromatography (HPLC) (Perkin Elmer Flexar) equipped with a Spheri-5 C18 column and UV detector. Water, ethanol with volume ratio of 30:70 was mixed as the mobile phases.

The adsorption percentage was described as (equation 1):

$$R = \frac{(Co - Ce)}{Co} 100\% \qquad (1)$$

Where C_0 was the initial BPA concentration (mg/L) and C_e was the equilibrium BPA concentration (mg/L).

The distribution coefficient (K_d)[1], which was usually applied to understand the adsorption ability of the adsorbent, was defined as (equation 2):

$$K_d = \frac{V}{m} \frac{(C_0 - C_e)}{C_e} \qquad (2)$$

Where m (g) was the mass of adsorbent NPS-IOC added into the glass vials, V (mL) was the volume of the solution, C_0 and C_e represent the initial and equilibrium concentrations.

The sorption capacity Q_e (mg/g) was calculated from the following equations:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (3)$$

Where V was the total volume of the suspension in the test tubes, m was the mass of the adsorbent in the test tube, and C_0 (mg/L) and C_e (mg/L) were the initial and

equilibrium BPA concentrations after reaction, respectively.

The each experimental data was obtained by the average values of triple parallel samples and the data was the averages of detection with the relative errors of 5%.

The **pseudo-first-order kinetic model** is defined as (equation 4):

$$\ln\ (Q_e - Q_t)\ = \ln Q_e - k_1 t \quad (4)$$

The **pseudo-second-order kinetic model** is defined as (equation 5):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e{}^2} + \frac{t}{Q_e} \qquad (5)$$

Where k_1 (min^{-1}) and k_2 (g/mg·min) were the pseudo-first-order and pseudo-second-order rate constant of BPA sorption, and t was adsorption time (min). The Q_e and Q_t were the amounts of BPA adsorbed (mg/g) at equilibrium and at contact time t, respectively.

Langmuir model:

$$Q_e = Q_m \frac{bC_e}{1 + bC_e} \qquad (6)$$

Where C_e denotes the equilibrium concentration of BPA (mg/L), Q_e refers to the amount of BPA adsorbed per unit weight of the adsorbent at equilibrium (mg/g), Q_m (mg/g) is the maximum adsorption capacity.

Freundlich model:

$$Q_e = k_F C_e^n \qquad (7)$$

Where n and k_F ($mg^{1-n}L^n/g$) are Freundlich parameters, n is the level depending on removal equilibrium concentration; k_F is generally related to the adsorption ability of the adsorbent when the value of the adsorbate concentration is equal to 1.[2, 3]

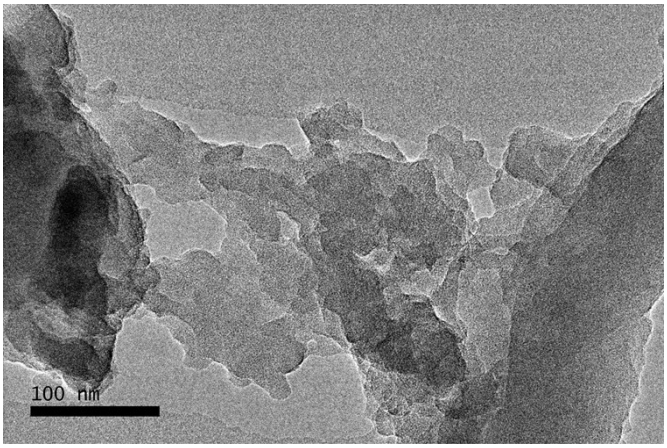

Figure S1. TEM image of NPS-IOC_{20}.

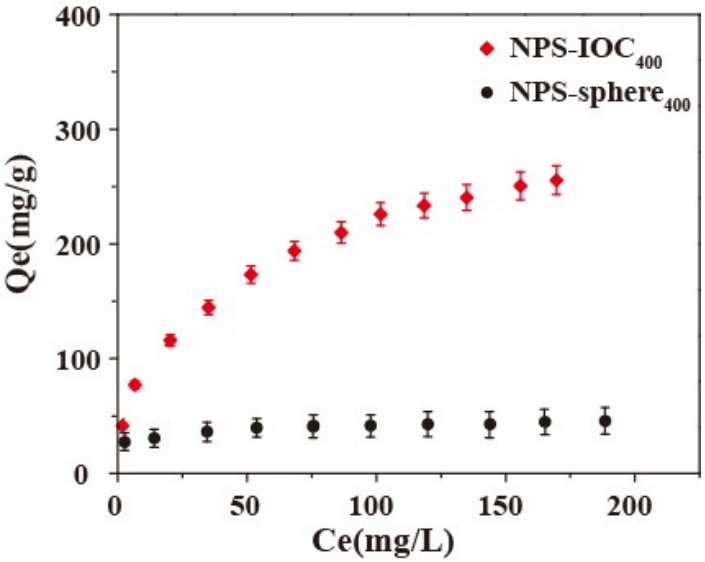

Figure S2. Comparison of NPS-IOC_{400} and NPS-$sphere_{400}$ on the adsorption capacity of BPA. ($C_{[BPA]initial}$ = 10-180 mg/L, T = 298 K, pH = 7.00 ± 0.05, m/V = 0.2 g/L, C_{NaNO_3}=0.01 mol/L, 24h)

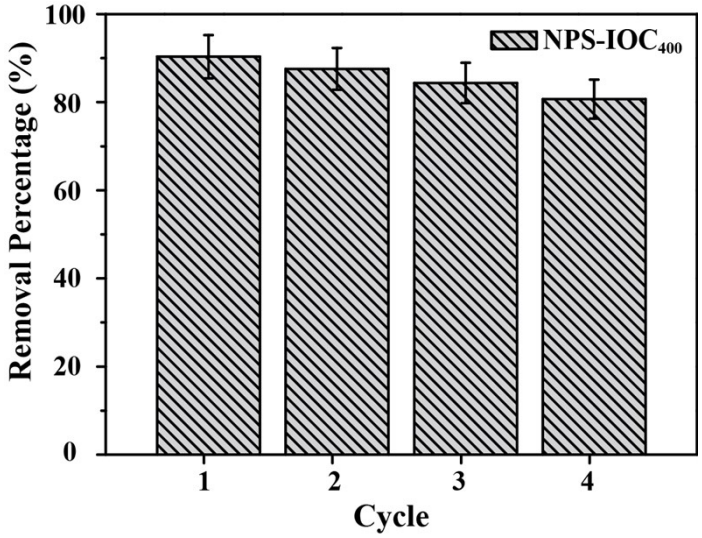

Figure S3. Recycling and stability of NPS-IOC_{400}. ($C_{[BPA]initial}$ = 10 mg/L, T = 298 K,

pH = 7.00 ± 0.05, m/V = 0.2 g/L, C_{NaNO_3}=0.01 mol/L, 24h)

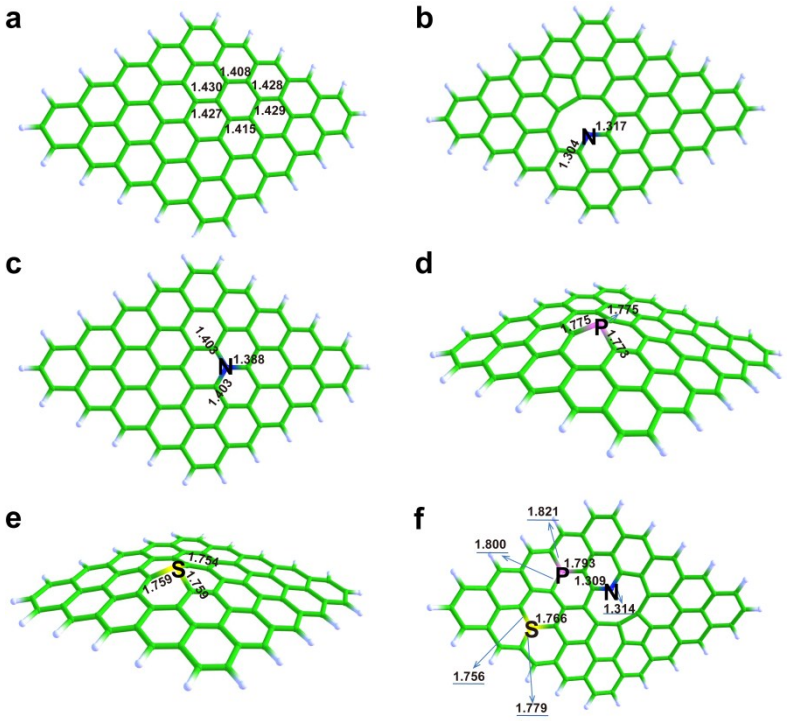

Figure S4. The optimized structures of (a) graphene; (b) phyridinic N-IOC; (c) graphitic N-IOC; (d) P-IOC; (e) S-IOC; (f) NPS-IOC. Bond lengths are in Å.

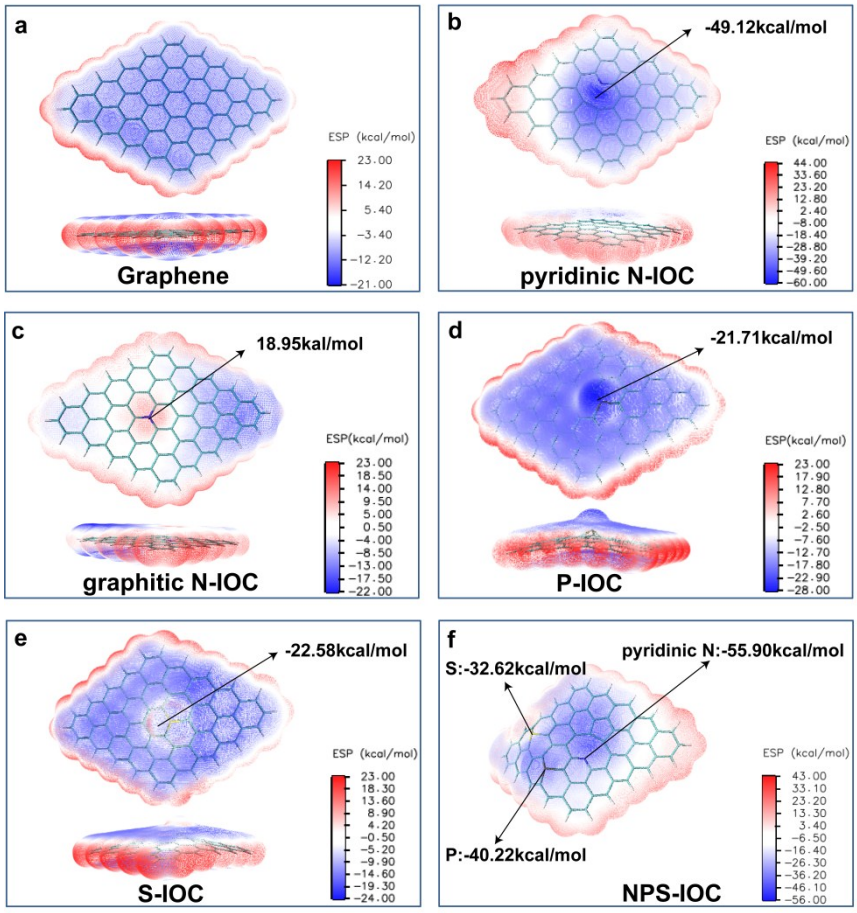

Figure S5. ESP plots of (a) graphene; (b) pyridinic N-IOC; (c) graphitic N-IOC; (d) P-IOC; (e) S-IOC; (f) NPS-IOC. The molecular surface was defined as the 0.001 au (electrons $bohr^{-3}$) contour of the electronic density by Bader.[4] The red and blue regions in the plots were represented the positive and negative potential, respectively.

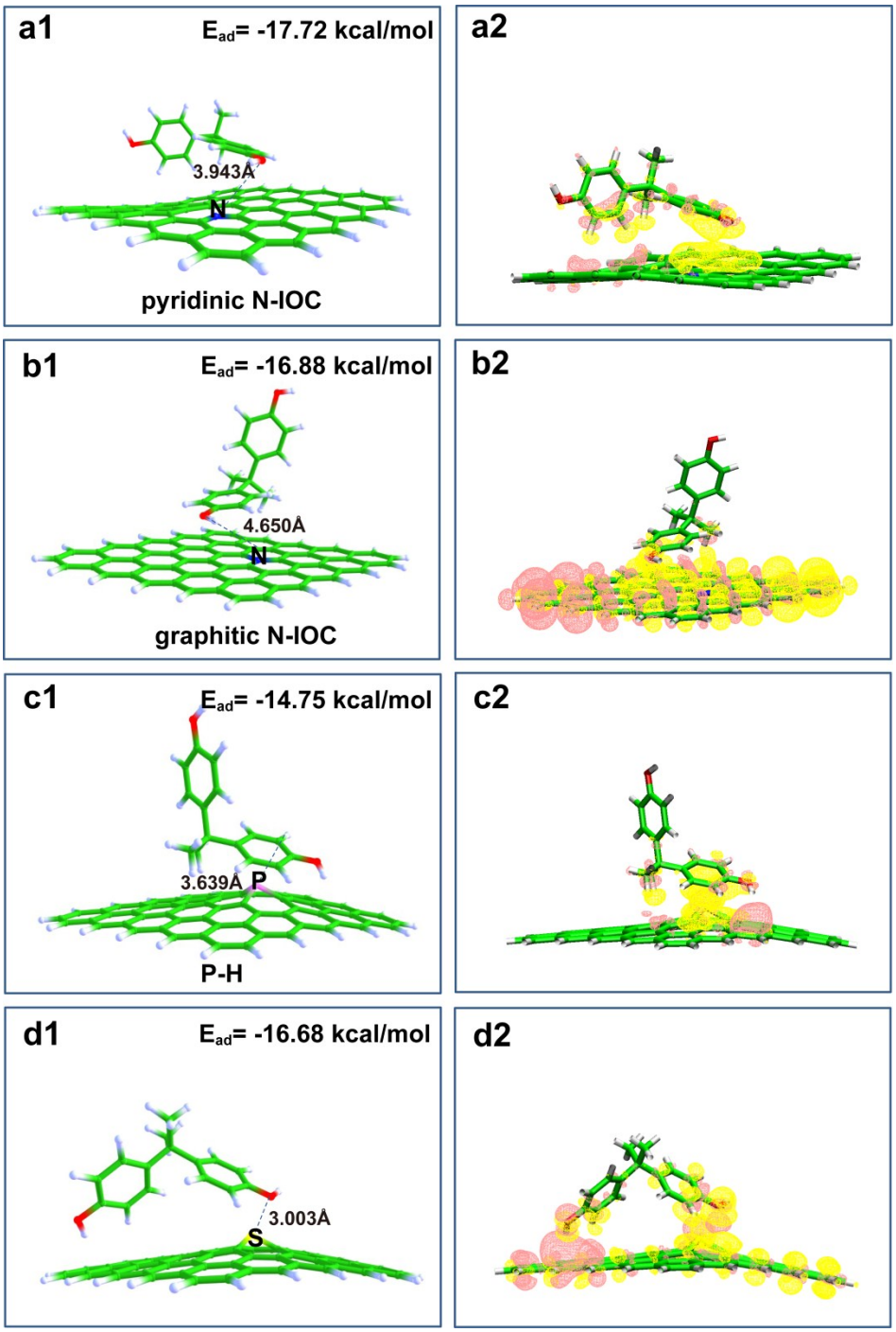

Figure S6. The optimized geometric structures and the charged density difference plots of BPA adsorbed on (a) pyridinic N-IOC; (b) graphitic N-IOC; (c) P-IOC; (d) S-IOC; Bond lengths are in Å.

Table S1. Element contents of NPS-IOC.

Element name	Atomic (%)			
	NPS-IOC_{20}	NPS-IOC_{400}	NPS-IOC_{700}	NPS-IOC_{900}
C	58.65	69.28	78.62	84.92
O	17.55	14.74	10.93	8.06
H	9.31	5.02	2.20	1.15
N	5.59	4.27	3.36	2.39
P	5.30	4.05	3.41	2.52
S	3.60	2.64	1.48	0.96

Table S2. Kinetic parameters of BPA adsorption on NPS-IOC.

Adsorbents	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	$Q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg·min)	$Q_{e,cal}$ (mg/g)	R^2
NPS- IOC_{20}	1.3116	19.64	0.984	0.0493	10.43	0.999
NPS- IOC_{400}	1.1213	92.31	0.998	0.0736	46.73	1.000
NPS- IOC_{700}	0.5908	28.79	0.958	0.0226	15.70	0.999
NPS- IOC_{900}	1.0673	24.34	0.962	0.0326	13.18	0.995

Table S3. The parameters calculated from the Langmuir and Freundlich models.

Adsorbents	Langmuir model			Freundlich model		
	q_{max} (mg/g)	b (L/mg)	R^2	K_F (mg^{1-n} L^n/g)	n	R^2
NPS- IOC_{20}	67.95	0.015	0.962	1.7417	0.703	0.979
NPS- IOC_{400}	255.39	0.030	0.911	28.8366	0.41021	0.989
NPS- IOC_{700}	172.35	0.010	0.968	2.0932	0.8408	0976
NPS- IOC_{900}	146.92	0.004	0.981	3.0289	0.72	0.988

References

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