Supporting Information

How to tailor porous boron nitride properties for applications in interfacial processes

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Table S1. Summary of studies relating to doping of porous boron nitride (BN) presented in Table 1.

Dopant	BN structure	Dopant content	Dopant chemical environment	Dopant role in the study	Nature of the study	Ref.
C	Porous BN	5 - 20 wt% C	Within basal planes	Reduction of bandgap	Experimental	[1]
C	Porous BN	10 -12 wt% C	Within basal planes	Addition of sorption sites	Experimental	[2]
C	BN nanosheets	8 - 15 wt% C	Within basal planes	Addition of sorption sites Reduction of bandgap	Experimental	[3]
C	BN nanosheets	Approx. 6 - 9 at% C	Within basal planes	Addition of active catalytic sites Reduction of bandgap	Experimental	[4]
C	BN nanosheets	14 - 23 at% C	Within basal planes	Addition of sorption sites	Computational + Experimental	[5]
O	BN nanosheets	5 - 20 at% O	Within basal planes On edges	Reduction of bandgap Tuning of magnetic properties	Computational+ Experimental	[6]
O	Porous BN	-	Within basal planes	Tuning of magnetic properties	Computational + Experimental	[7]
O	Porous BN	Only at% of B and N atoms included	Within basal planes	Reduction of bandgap	Experimental	[8]
C, O	Porous BN	8 at% C 6 at% O	Within basal planes	Increase in specific surface area and adsorption capacity	Experimental	[9]
Si	BN nanotubes	-	Within basal planes	New synthesis technique	Experimental	[10]
Si	BN nanotubes	0.08 at% Si experimental, 5 at% Si computational	Within basal planes	Reduction of bandgap	Computational+ Experimental	[11]
P	Porous BN	1 - 5 wt% P	Within basal planes	Addition of sorption sites	Experimental	[12]
S	h-BN	-	Within basal planes	Reduction of bandgap	Computational	[13]
S	h-BN	-	Within basal planes	Reduction in electrical resistivity	Experimental	[14]
F, C, O	Porous BN	-	Within basal planes	Reduction of bandgap	Computational	[15]

				Addition of sorption and catalytic sites		
P, S, O, F, Cl	h-BN monolayer	-	Within basal planes	Different reduction of bandgap depending on dopant	Computational	[16]
Cu	BN nanobelts	1 - 4 wt% Cu	Within basal planes	Creation of electric field within material Electron transfer between reactant and Cu sites	Experimental	[17]
Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, Ag	h-BN monolayer	-	On monolayer surface	Reduction of reaction limiting potential	Computational	[18]
Pt, Pd, Au, Ag	BN monolayer	-	Within and on monolayer surface	Reduction of bandgap Tuning of magnetic properties	Computational	[19]
Au	Porous BN	-	Composite form	Introduction of plasmonic heating	Experimental	[20]

Table S2. Summary of bottom-up methods to produce shaped porous BN along with the material properties.

Materials	**Precursors**	**Reaction conditions**	**S_{BET} [m^2 g^{-1}]**	**ρ[a] [mg cm^{-3}]**	**Ref.**
BN aerogel	Graphene, boron oxide	1600-1800 °C (N_2)	440	60	[21,22]
BN aerogel	Graphene/carbon nanotube, borazine	900 °C (Ar/H_2); etching 600 °C	180-1450	0.6-4.6	[23]
BN aerogel	Graphene aerogel, borazine	1500 °C (Ar); etching 600 °C	1080	0.1	[24]
BN aerogel	Graphene oxide/carbon nanotube, boron oxide	1600 °C (N_2)	720	N/A	[25]
BN aerogel	N-doped graphite, boron oxide	1700 °C (N_2)	170	30.4	[26]
BN aerogel	Polymeric aerogel, boric acid	1000-1200 °C (NH_3)	1150-1410	180	[27]
BN aerogel	M·2B aerogel	1100 °C (NH_3)	780	15	[28]
BN aerogel	M·2B aerogel	1200 °C (NH_3)	920	15.5	[29]
BN aerogel	M·2B aerogel	1400 °C (Ar)	990	86.4	[30]
BN aerogel	M·2B pellet	900-1350 °C (N_2)	720-1030	154	[31]
BN aerogel	BNNS, 1,4-butanediol diglycidyl ether	RT aqueous reaction (24 h)	N/A	10.4-30	[32]
BN aerogel	BNNS, urea	RT aqueous reaction (1 week)	280	1.4-20	[33]
Structured BN	Porous BN powder	Spark plasma sintering	430	786	[34]
Structured BN	Boric acid-cured melamine resin	1000 °C (NH_3)	1530	310	[35]

[a] ρ = bulk density of shaped BN

Table S3. Summary of separation studies using porous BN as adsorbent, showing the type of separations (split into liquid/vapor and gas phase), example of species involved, adsorption conditions (initial concentration of pollutant (C_0)), quantity adsorbed (maximum adsorbed amount (q_{max})), and sorption mechanisms suggested (related to Table 3).

Separation in liquid/vapor phase	**Example species**	**C_0 range studied (mg L^{-1})**	**q_{max} range (mg g^{-1})**	**Sorption mechanisms suggested**	**Ref.**
Trace metal removal from water	Cu^{2+}	200 - 1870	200 - 819	Mainly ion-exchange interactions dominated by electrostatic and surface complexation. Hydrogen bonding and physisorption also reported. Increased adsorption in the presence of defects and higher SSA	36,37
	Pb^{2+}	6 - 200	204 - 845		
	Cr^{3+}	52 - 100	120 - 387		
	Ce^{3+}	52	282		
	Ni^{2+}	52 - 700	95 - 235		
	Co^{2+}	52	215		
	Cd^{2+}	200 - 600	107- 561		
	As^{5+}	1 - 50	5 - 32		
Removal of dyes from water	Methylene blue	10 - 350	107 - 13973	Mainly π-π stacking interactions. Electrostatic interactions, physisorption	36–38
	Methyl Orange	40	298 - 395		
	Rhodamine B	3 - 100	76 - 992		
	Basic Yellow	90	424		
	Congo Red	50 - 130	307 - 782		
PFAS from water	PFOS	200	~57	Electrostatic interactions	39
	PFDA	50	~90		
Oils and organic solvents	Engine oil	--	18000 - 56800	Capillarity effect, pore filling, SSA	40–42
	Ethanol	--	14000 - 25000		
	Acetone	--	25000		
	Toluene	--	16000 - 32000		
	Toluene/n-heptane/methanol	--	~600		
	Cyclohexane	--	5000		
Removal of bio waste from water	Tetracyclines	20 - 300	118 - 1100	π-π stacking interactions, electrostatic interactions, van der Waals forces	36–38
	Levofloxacin	20 - 300	318		
	Sulfamethazine	20 - 300	19		
Desulfurization of oil	Dibenzothiophene (DBT) in n-octane	500 - 800	35 - 65 mgS g^{-1}	Lewis acid-base interactions	43,44
Iodine removal	Iodine vapor	--	2120	Physisorption, Lewis acid-base interactions	45
	Iodine/ n-hexane	50	61		
Separation in gas phase	**Species involved**	**Conditions**		**q_{max} range (mmol g^{-1})**	**Sorption mechanisms suggested**	**Ref.**
		T (°C)	**P (bar)**			
Pre-combustion carbon capture	CO_2/H_2	25	20	CO_2: ~8	Physisorption. Pore characteristics and electrostatic interactions key at low pressure. At high pressure volume and SSA play key role	2,46
		25	40	CO_2: ~19		
Post-combustion carbon capture	CO_2/N_2	25	1	CO_2: 1.6 – 4.6 N_2: 0.2 – 0.3		

Natural gas sweetening	CO_2/CH_4	25 25	1 70	CO_2: 1.6 – 3.9 CH_4: 0.6 – 0.7 CH_4: ~9.0	Physisorption. Electrostatic interactions affect less CH_4	[2,46,47]
Formaldehyde from air	HCHO	25	1	0.63 (20 ppm C_0)	Physisorption, hydrogen bonding, π-π conjugation	[48]
Light hydrocarbons separation	N_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8	25	1	N_2: 0.1 CH_4: 0.5 C_2H_4: 2.1 C_2H_6: 3.0 C_3H_6: 4.5 C_3H_8: 5.5	Pure physisorption (dispersion forces)	[49]
Ammonia	NH_3	25	1	NH_3: 5.3 CO_2: 0.9	Physisorption, Lewis acid-base interactions and H-bonding	[50]

Table S4. Summary of gas storage studies using porous BN as adsorbent, showing the surface area of the material, and the performance metrics at given conditions (related to Table 4).

Gas stored	SSA_{BET} ($m^2 g^{-1}$)	T (°C)	P (MPa)	Gas uptake (wt%)	Desorption level (%)[a]	Ref
H_2	150	RT[b]	10	1.8	30	51,52
	210	RT	10	2.6	30	51,52
	260	RT	10	2.9	20	52
	790	RT	10	4.2	50	53
	1560	-196	0.1	1.07	N/A	54
	215	25	10	4.07	N/A	55
	1150	-196	1	2.3	100	56
	1690	25	3	5.6	84	57
	1040-1070	-196	0.1	1.41-1.6	N/A	58
			1	1.9-2.14	N/A	
	1900	-196	1	2.6	100	59
	540	RT	5	5.7	89	60
	400-1290	-196	0.1	0.98-1.35	N/A	61
			1	1.65-2.33	100	
CH_4	440-720	0	0.1	0-3	N/A	62
	1050	0	0.1	1.1	N/A	47
	1500	25	7	13.6	N/A	35

[a] Percentage of gas released when the pressure is reduced to ambient condition; [b] RT stands for room temperature.

Table S5. Summary of catalysis studies using porous BN as a catalyst, showing the type of catalysis (i.e., heterogenous catalysis, photocatalysis or electrocatalysis), the targeted reaction and some of the key performance indicators (related to Table 5).

Heterogeneous catalysis						
Reaction studied	**Reaction conditions**	**Feed ratio/reactant mixture**	**Conversion rate**	**Selectivity rate**	**Catalyst stability**	**Ref.**
Oxidative dehydrogenation of propane	T = 490 °C	2:1:3.67 propane:O_2:N_2	14.0% propane	79% propylene	Min 32 h	63
Oxidative dehydrogenation of n-butane, isobutane	T = 460 °C	1:1:8 alkane:O_2:N_2	7.2% n-butane	76.2% butene	-	64
			6.2% isobutane	75.4% butene	-	
Methane oxidation	T = 690 °C	2:1:4 methane:O_2:N_2	20.5% methane	76% CO	Min 20 h	65
	T = 720 °C		37.0% methane	81.4% CO	-	
Styrene epoxidation	T = 80 °C	26.5 mmol TBHP 25 mL acetonitrile 10 mmol styrene	17.7-23.9% styrene	76.2-88.0% styrene oxide	Min 9 h	66
Aerobic oxidative desulfurization	T = 150 °C ambient pressure	40 mL oil (500 ppm DBT)	-	84.8-98.8% DBT removal	Min 10 recycling cycles	67
Acetylene hydrochlorination	T = 200 °C	1:1 HCl:acetylene	72% acetylene	> 96% vinyl chloride	-	68
Acetylene hydrochlorination	T = 280 °C	1:2 HCl:acetylene	>99% acetylene	> 99% vinyl chloride	Min 1000 h	
Photocatalysis						
Reaction	**Reaction phase**	**Irradiation range**	**Light source**	**Sacrificial agent**	**Production rate**	**Ref.**
H_2 generation	Liquid	200-2500 nm	300 W Xe arc lamp	TEOA	47.1 μmol H_2 $g^{-1}.h^{-1}$	69
H_2 generation	Liquid	Specified as UV-Vis (300-800 nm)	300 W Xe lamp	TEA	~45.0 μmol H_2 h^{-1}	1
		> 420 nm		TEA	3.6 μmol H_2 h^{-1}	
CO_2 photoreduction	Gas	> 420 nm		H_2O	4.7 μmol CO h^{-1} 1.5 μmol H_2 h^{-1}	
CO_2 photoreduction	Gas	> 325 nm	300 W Xe arc lamp	H_2	1.2 μmol CO g^{-1} h^{-1}	70
		> 400 nm			0.2 μmol CO g^{-1} h^{-1}	
CO_2 photoreduction	Gas	Specified as UV-vis	300 W Xe lamp	H_2O	12.5 μmol CO g^{-1} h^{-1} 3.3 μmol H_2 g^{-1} h^{-1}	71
Electrocatalysis						
Reaction	**Catalyst**	**Formation rate**	**Solution**	**Faradic efficiency/ Electron transfer number**	**Time/ Durability**	**Ref.**

N_2 fixation to NH_3	h-BNNS	22.4 μg NH_3 h^{-1} mg_{cat}^{-1}	0.1 M HCl	4.7% @-0.75V vs RHE	2 h	[72]
N_2 fixation to NH_3	Porous BN	18.2 μg NH_3 h^{-1} mg_{cat}^{-1}	0.1 M Na_2SO_4	5.5% @-0.70V vs RHE	2 h	[73]
Oxygen reduction reaction	Pt/porous BN	< 0.6% H_2O_2	0.1 M $HClO_4$	>3.99 electrons	10^4 cycles	[74]
Oxygen reduction reaction	BNNT BNNS sputter-deposited BN	-	0.5 M H_2SO_2	-	-	[75]

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