Electronic supplementary information

Polar atom-pair catalysts for electrochemical C–N coupling

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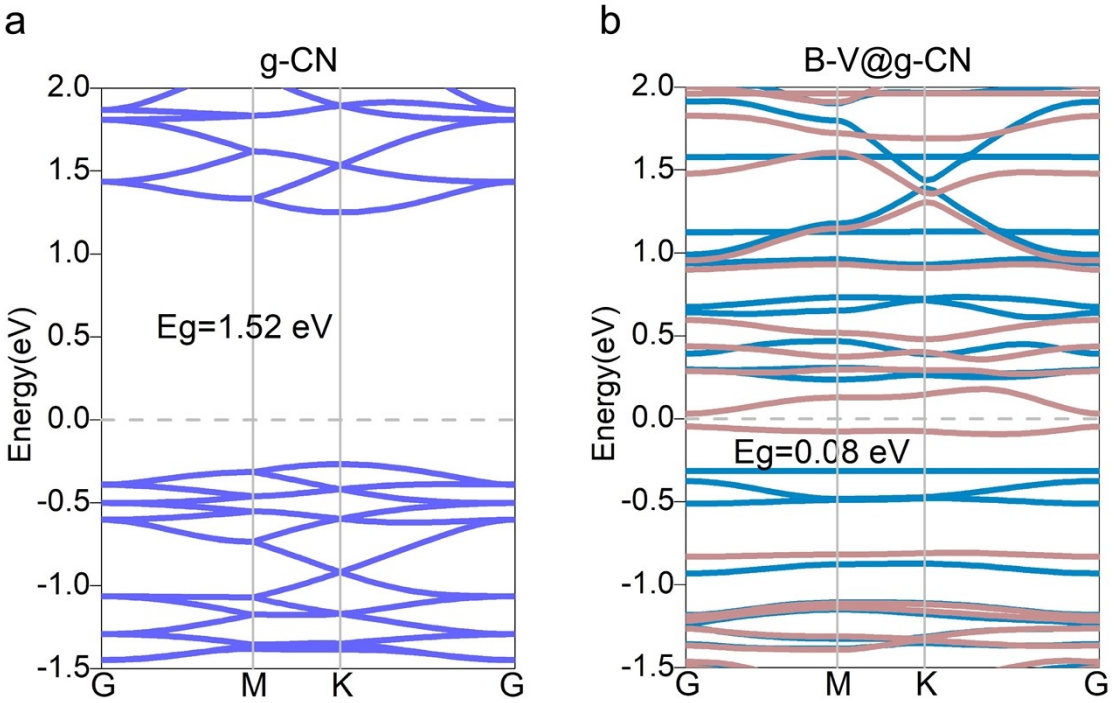

Figure S1 Band structures of (a) g-CN and (b) B-V@g-CN APC at the PBE functional level. The blue and brown lines indicate spin up and spin down bands.

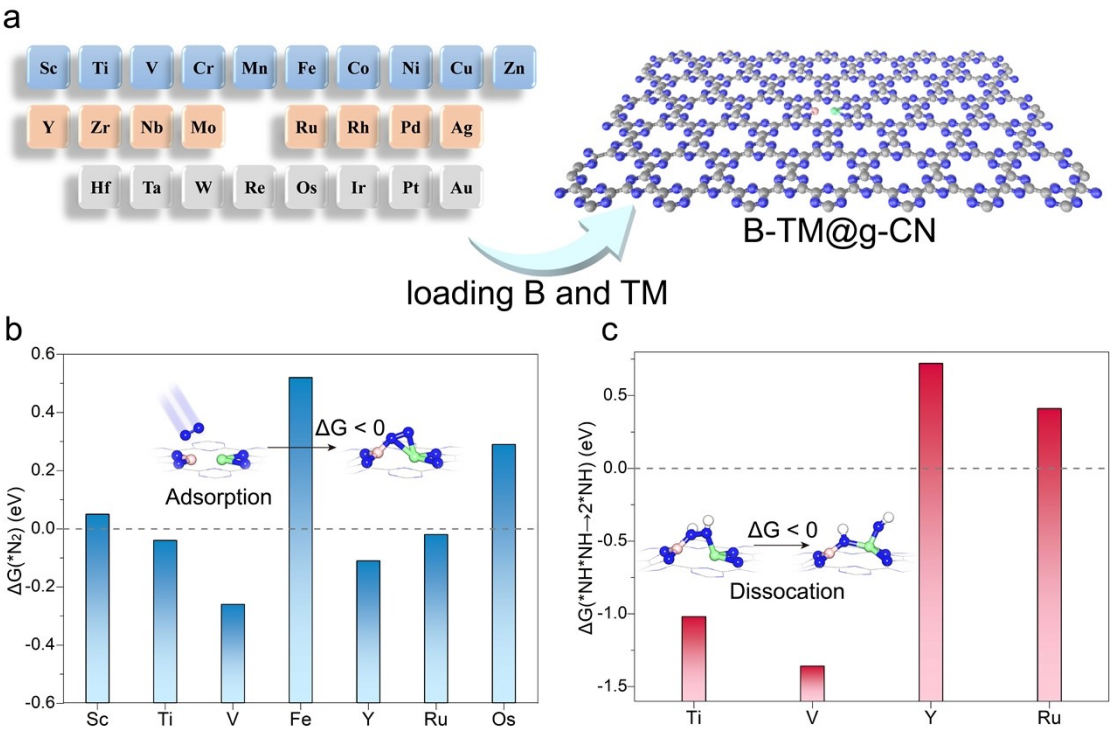

Figure S2 Design and screening of B-TM@g-CN APCs. (a) B-TM@g-CN APCs was constructed by anchoring B and 26 TM SAs into sub-nanocavity of g-CN. (b) N_2 adsorption free energies on B-TM@g-CN APCs. (c) The ΔG of *NH*NH dissociation on B-TM@g-CN APCs.

The lattice constant of g-CN is a=b= 7.11 Å, which is consistent with the previous theoretical calculation result[1]. We established a 2×2×1 g-CN supercell model as the support for loading B and TM SAs, with corresponding cell size of 14.22×14.22×20 $Å^3$. B and 26 TM SAs are anchored to the sub-nanopore of g-CN to form B-TM@g-CN APCs (**Figure S2(a)**). The detailed geometric structures of B-TM@g-CN APCs are displayed in **Figure S3**. To achieve the full activation of N_2, the cooperative adsorption and activation of N_2 on APC is necessary, allowing N_2 to bind to B and TM in a cooperative side-on configuration (**Figure S4**) with $\Delta G(*N_2)$ less than 0. Other adsorption configurations of N_2, such as side-on, end-on and physical adsorption were also considered. As shown in **Figure S2(b)**, seven catalysts satisfy the cooperative side-on adsorption configuration, and only B-Ti, B-V, B-Y, and B-Ru@g-CN APCs meet the spontaneous N_2 adsorption requirement. Exothermic *NH*NH dissociation process is favorable for C-N coupling reaction. The atomic structures of *NH*NH and 2*NH species on B-Ti, B-V, B-Y, and B-Ru@g-CN APCs are shown in **Figure S5**. Proton-assisted N≡N bond breaking results in two *NH species, one *NH adsorbing between

the B and TM sites, and the other *NH coordinating only with TM. **Figure S2(c)** indicates that only B-Ti and B-V@g-CN APCs satisfy ΔG(*NH*NH→2*NH) < 0.

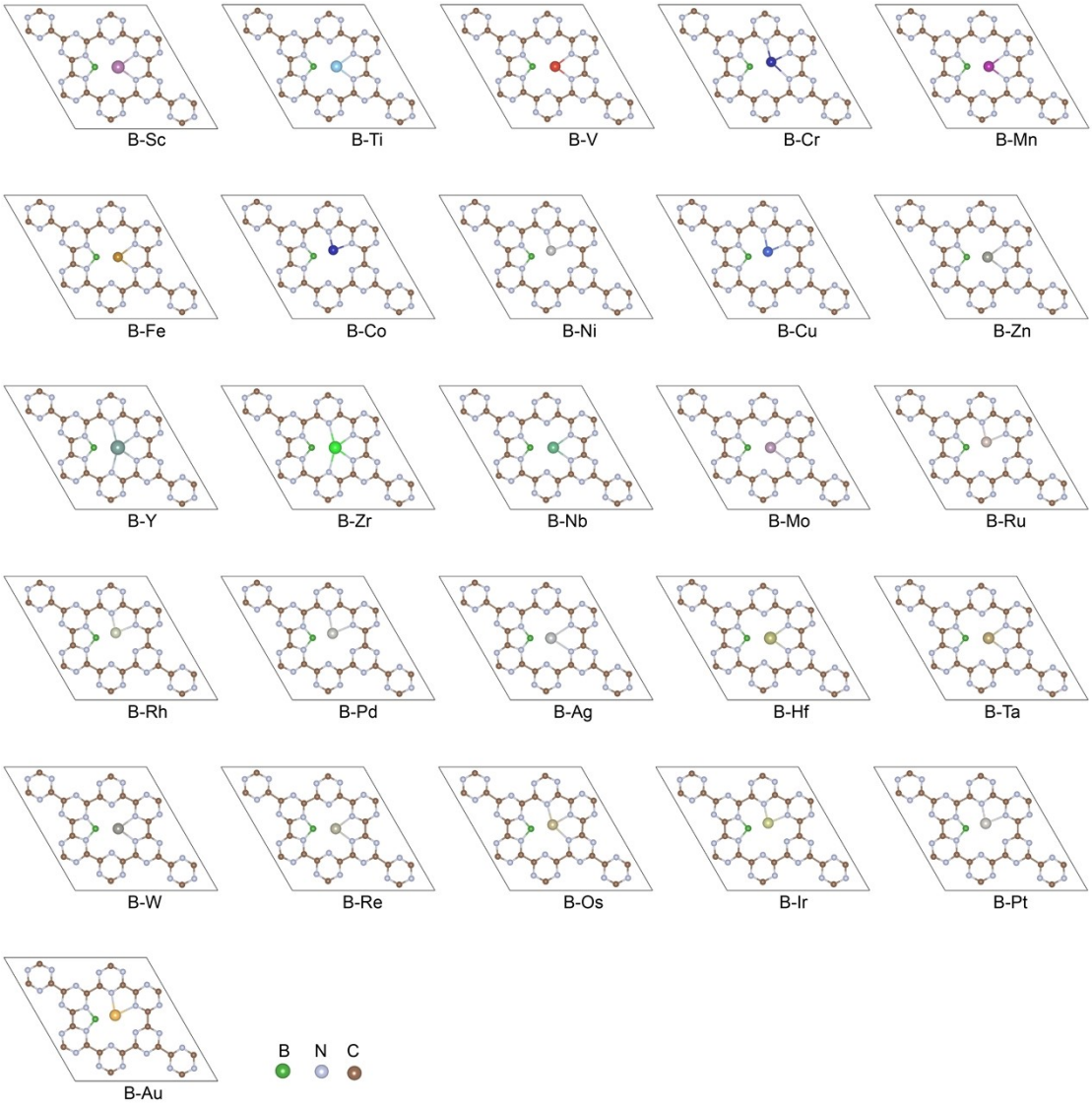

Figure S3 Atomic structures of B-TM@g-CN APCs.

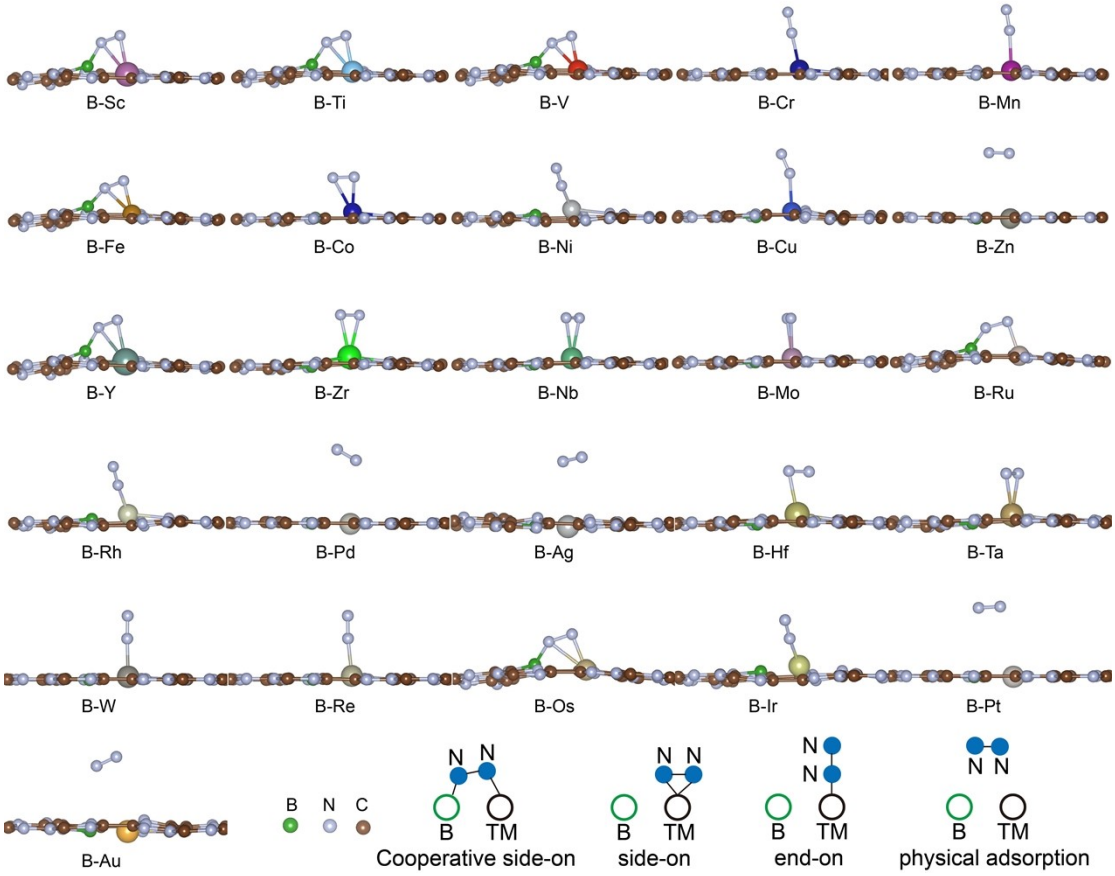

Figure S4 Atomic structures of N_2 adsorption on B-TM@g-CN APCs.

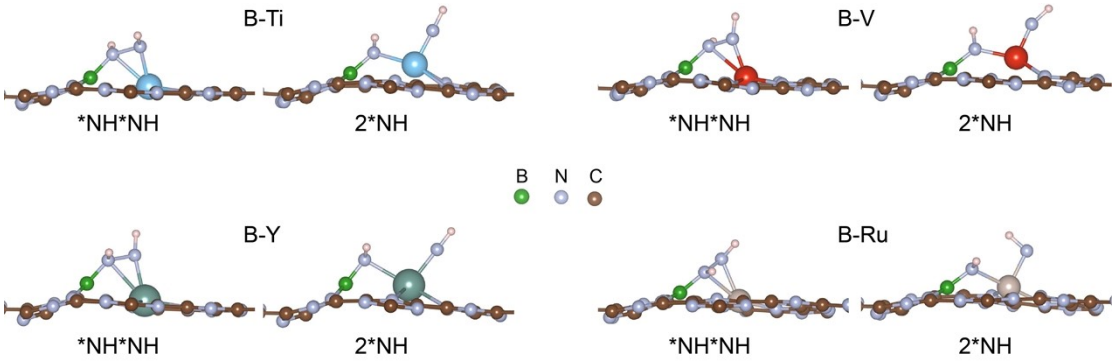

Figure S5 Atomic structures of *NH*NH and 2*NH adsorption on B-TM@g-CN APCs.

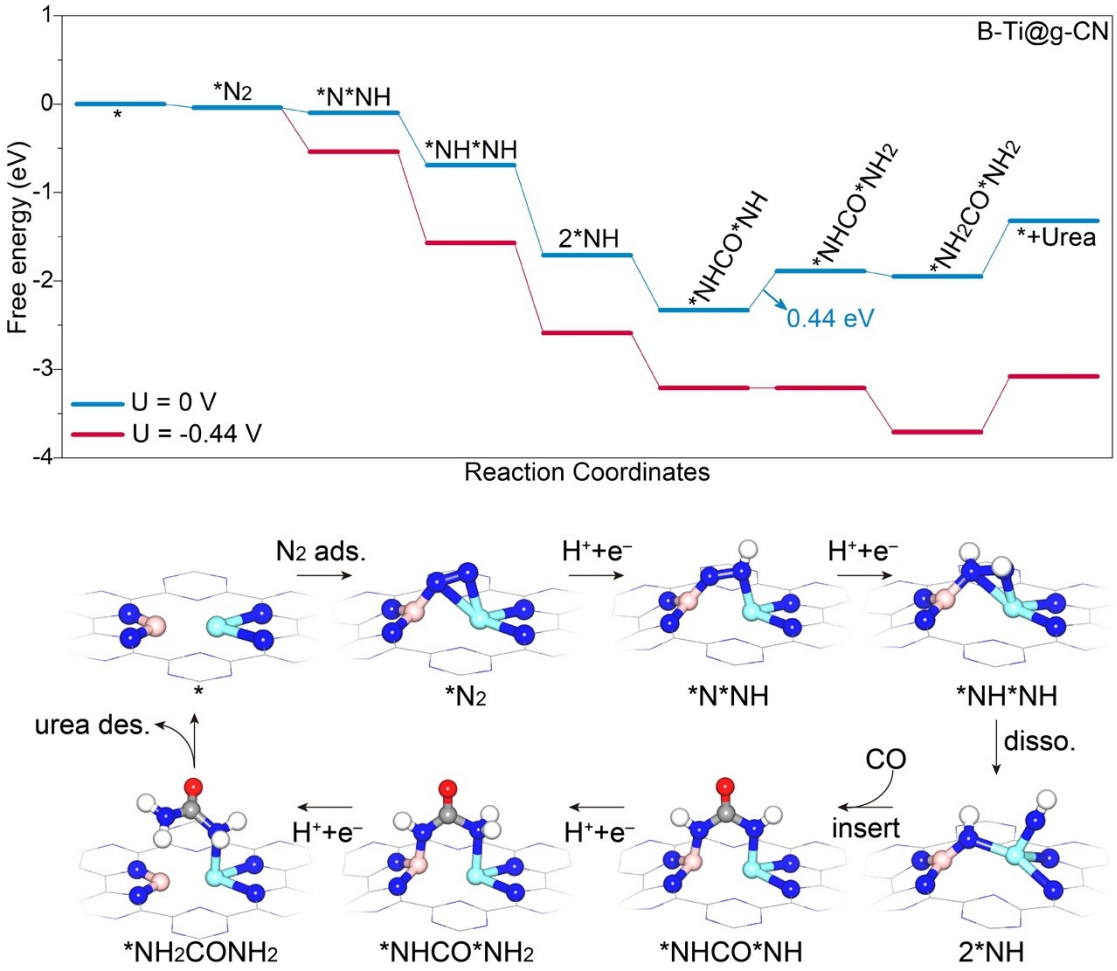

Figure S6. Free energy diagram and optimized reaction intermediates for the electrochemical urea synthesis reaction at B-Ti@g-CN APC. Color labels: N (blue), H (white), O (red), B (pink) and Ti (cyan).

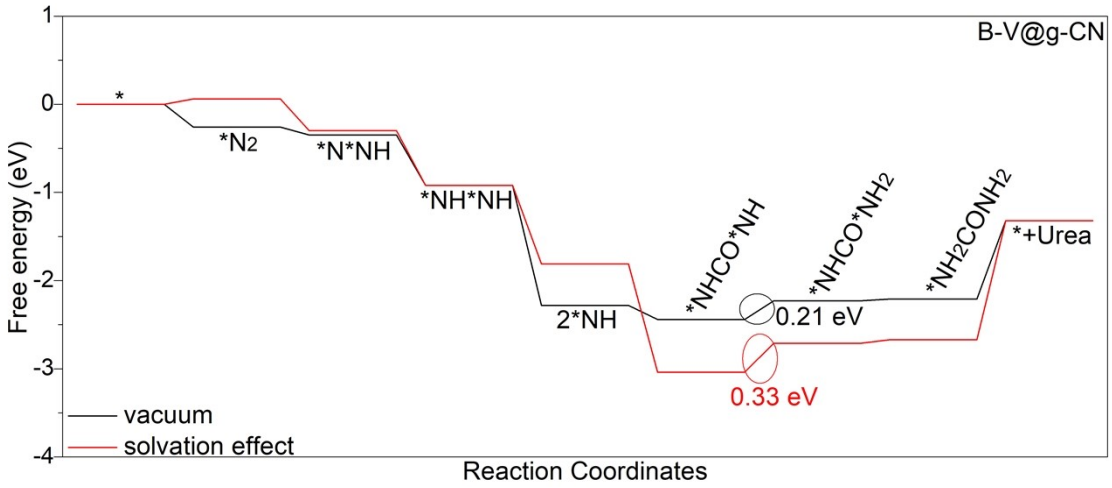

Figure S7 Influence of solvation effect on the free energy of electrochemical urea synthesis reaction.

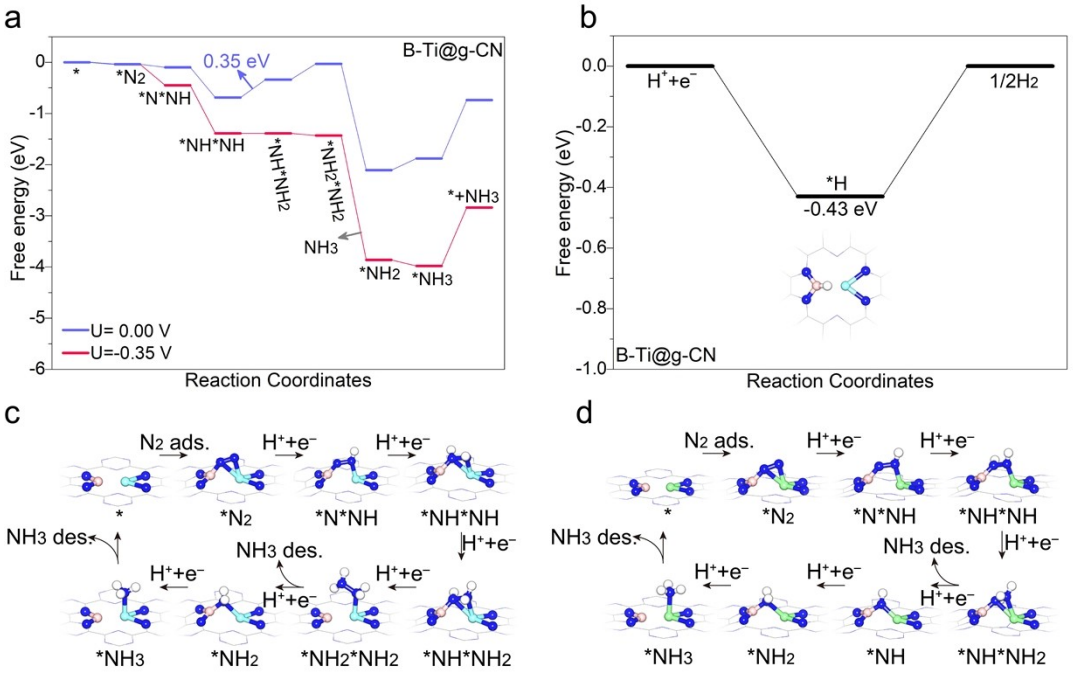

Figure S8. Free energy diagram and optimized reaction intermediates for (a) eNRR and (b) HER at B-Ti@g-CN APC. The reaction intermediates of eNRR on (c) B-Ti and (d) B-V@g-CN APCs are shown in this figure. Color labels: N (blue), H (white), B (pink), Ti (cyan) and V (green).

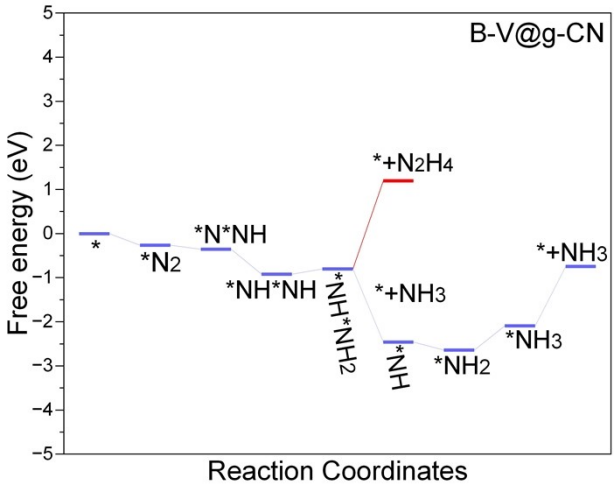

Figure S9. Free energy landscape of reaction for electrocatalytic reduction of N_2 to hydrazine (N_2H_4) and NH_3 on B-V@g-CN APC.

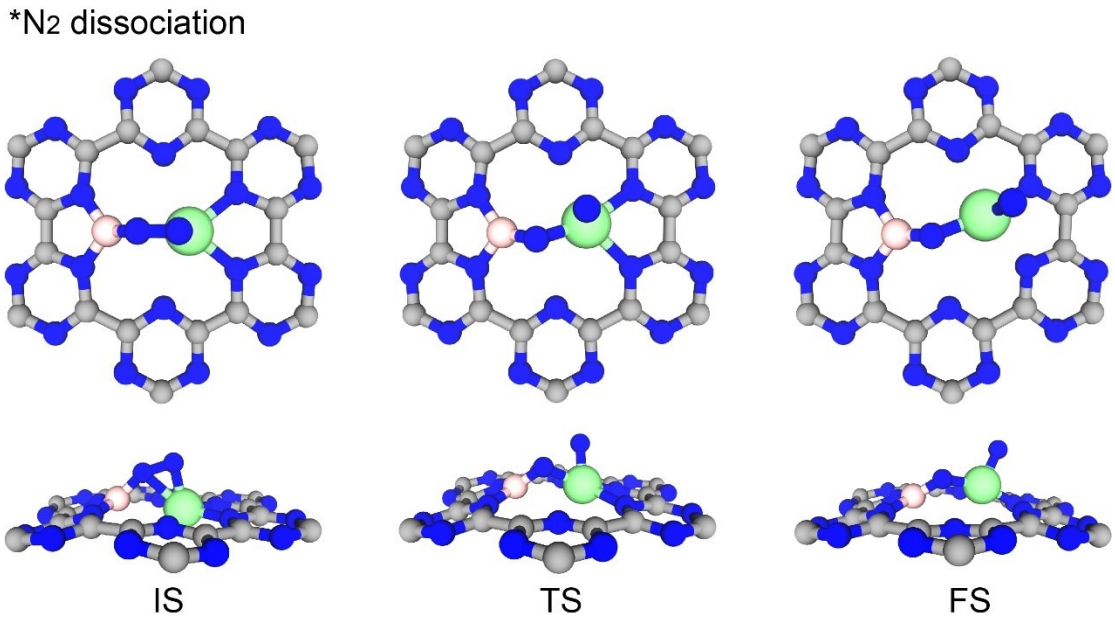

Figure S10. Geometrical structures of the initial state (IS), transition state (TS) and final state (FS) of $*N_2$ dissociation on B-V@g-CN APC. Color labels: C (grey), N (blue), B (pink) and V (green).

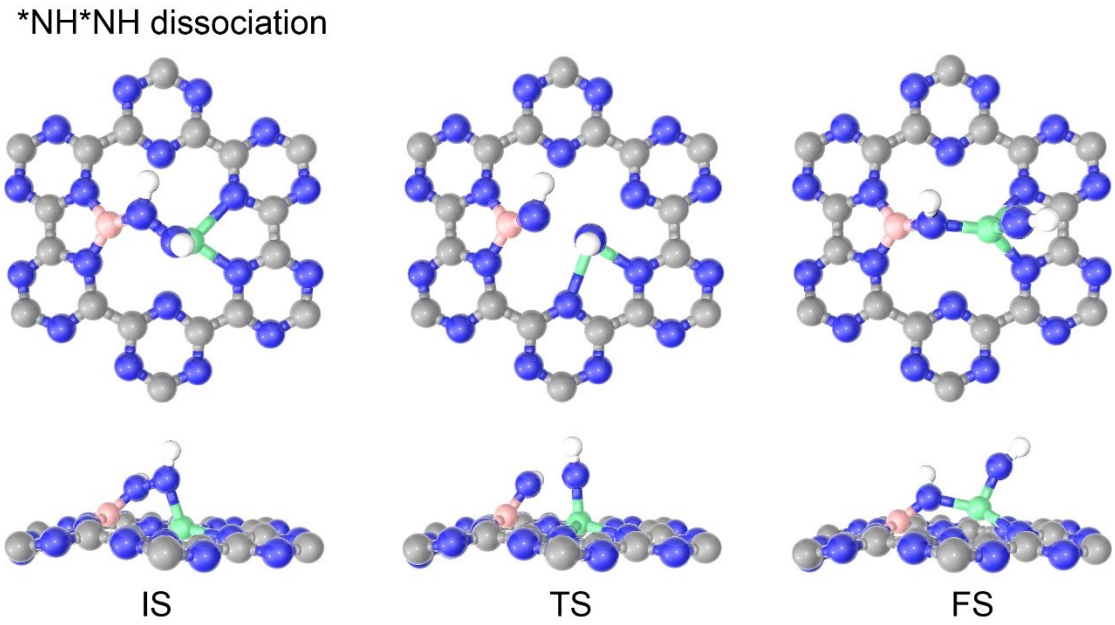

Figure S11. Geometrical structures of the initial state (IS), transition state (TS) and final state (FS) of *NH*NH dissociation on B-V@g-CN APC. Color labels: C (grey), N (blue), H (white), B (pink) and V (green).

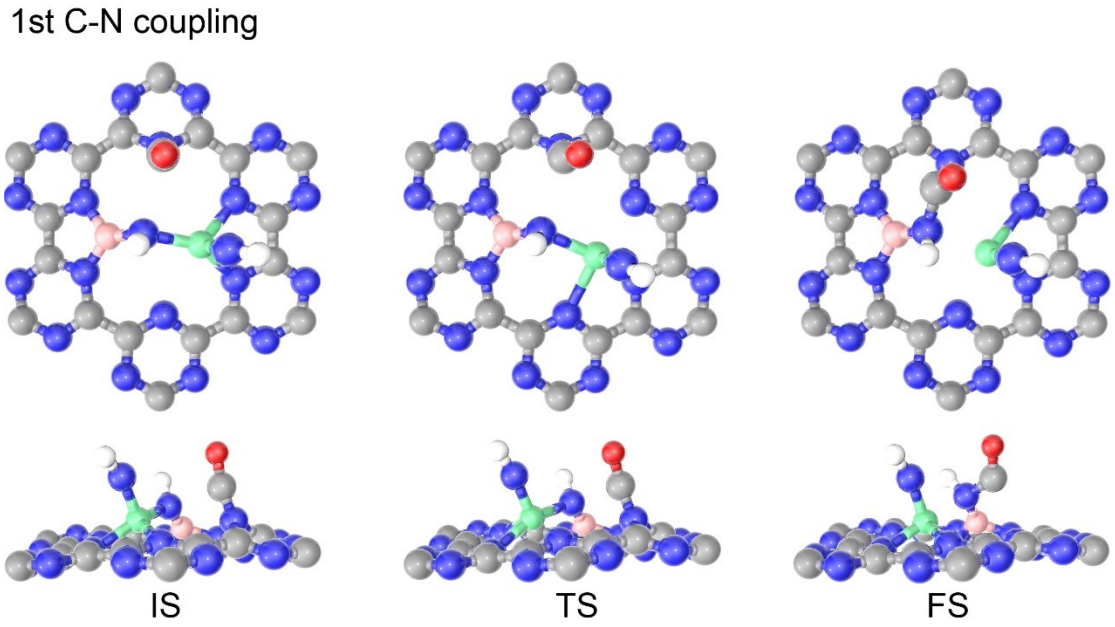

Figure S12. Geometrical structures of the initial state (IS), transition state (TS) and final state (FS) of the first C-N coupling on B-V@g-CN APC. Color labels: C (grey), N (blue), H (white), O (red), B (pink) and V (green).

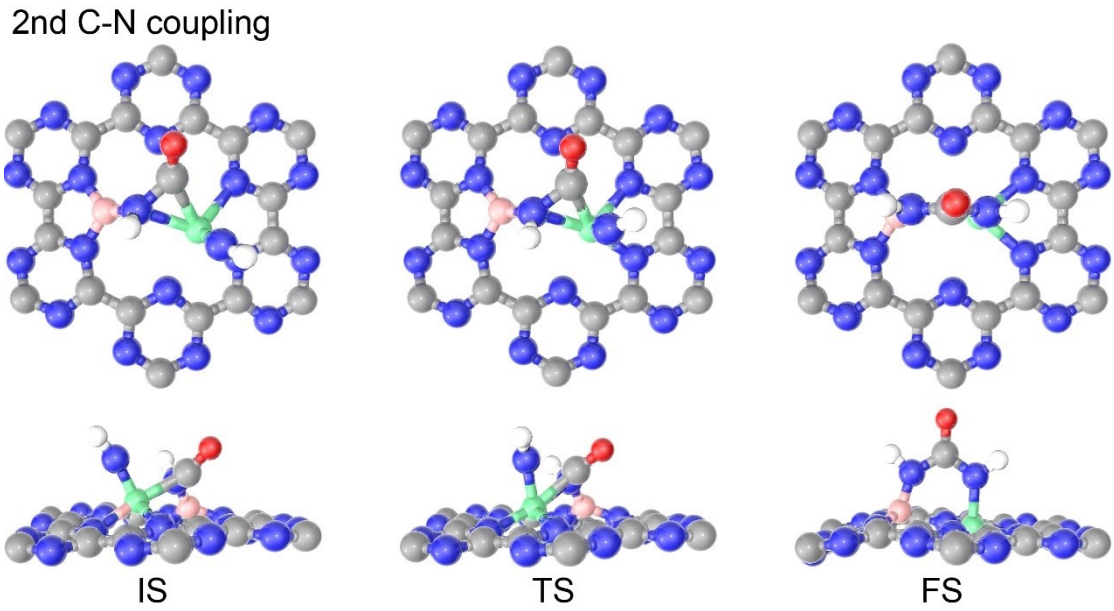

Figure S13. Geometrical structures of the initial state (IS), transition state (TS) and final state (FS) of the second C-N coupling on B-V@g-CN APC. Color labels: C (grey), N (blue), H (white), O (red), B (pink) and V (green).

Table S1 Comparison of the activity of different catalysts for electrochemical urea synthesis.

	U_L (V)	PDS
Pd_1Cu_1/TiO_2[2]	–0.64	*NCO*NH→*NCO*NH_2
Mott-Schottky Bi-$BiVO_4$[3]	–0.48	*NCO*NH→*NHCO*NH
InOOH nanoparticles[4]	–0.67	*NCO*N→*NCO*NH
$Ni_3(BO_3)_2$ nanocrystals[5]	–0.76	*NCO*N→*NCO*NH
$Ga_{79}Cu_{11}Mo_{10}$@C[6]	–0.60	*NHCO*NH→*NHCO*NH_2
MBenes[7]	–0.49 ~ –0.65	*NHCO*NH→*NHCO*NH_2
$Co_2@N_6G$[8]	–0.61	*NHCO*NH_2→*NH_2CO*NH_2
Dual-Si-doped g-C_6N_6[9]	–0.79	*NCO*NH→*NCO*NH_2
B_2@g-C_2N[10]	–1.11	*NHCO*NH_2→*NH_2CO*NH_2
B_2@g-C_6N_6[10]	–1.18	*NHCO*NH_2→*NH_2CO*NH_2
This work	**–0.21**	***NHCO*NH→*NHCO*NH_2**

Table S2 The zero-point energy (ZPE) and entropy (S) of the adsorbed species during urea or ammonia electrosynthesis on B-V@g-CN APC. (T = 298.15 K)

B-V@g-CN APC	ZPE	TS
***N_2**	0.18	0.08
***N*NH**	0.51	0.07
***NH*NH**	0.84	0.12
2*NH	0.76	0.12
***NHCO*NH**	1.11	0.18
***NHCO*NH_2**	1.46	0.18
***NH_2CONH_2**	1.74	0.34
***NH*NH_2**	1.18	0.10
***NH**	0.40	0.05
***NH_2**	0.75	0.05
***NH_3**	1.03	0.17

Table S3 The zero-point energy (ZPE) and entropy (S) of the adsorbed species during urea or ammonia electrosynthesis on B-Ti@g-CN APC. (T = 298.15 K)

B-Ti@g-CN APC	ZPE	TS
***N_2**	0.20	0.09
***N*NH**	0.51	0.07
***NH*NH**	0.85	0.10
2*NH	0.76	0.13
***NHCO*NH**	1.12	0.22
***NHCO*NH_2**	1.45	0.19
***NH_2CONH_2**	1.74	0.29
***NH*NH_2**	1.20	0.12
***NH_2*NH_2**	1.47	0.22
***NH_2**	0.76	0.05
***NH_3**	1.02	0.16

The zero-point energy (ZPE) and entropy (S_v) are calculated as follows[11,12]:

$$\mathrm{ZPE} = \sum_i \frac{1}{2} h\nu_i$$

$$S_v = \sum_i R\left\{\frac{h\nu_i}{k_B T}\left[\exp\left(\frac{h\nu_i}{k_B T}\right) - 1\right]^{-1} - \ln\left[1 - \exp\left(-\frac{h\nu_i}{k_B T}\right)\right]\right\}$$

where i is the frequency number, and ν_i is the frequency (cm^{-1}). $k_B = 1.38 \times 10^{-23}$ J/K, $h = 6.63 \times 10^{-34}$ J s, and $R = 8.314$ J mol^{-1} K^{-1}. For the standard hydrogen electrode reaction $H^+ + e^- \rightarrow 1/2H_2$, the free energy of $H^+ + e^-$ is equal to the free energy of $1/2H_2$, that is, $G(H^+ + e^-) = 1/2G(H_2)$[13].

Table S4 Free energy change (eV) of urea or ammonia electrosynthesis on B-V@g-CN APC. (T = 298.15 K)

Elementary steps	Free energy change (eV)
$* + N_2 \rightarrow *N_2$	–0.26
$*N_2 + H^+ + e^- \rightarrow *N*NH$	–0.09
$*N*NH + H^+ + e^- \rightarrow *NH*NH$	–0.57
$*NH*NH \rightarrow 2*NH$	–1.36
$2*NH + CO \rightarrow *NHCO*NH$	–0.16
$*NHCO*NH + H^+ + e^- \rightarrow *NHCO*NH_2$	0.21
$*NHCO*NH_2 + H^+ + e^- \rightarrow *NH_2CONH_2$	0.02
$*NH_2CONH_2 \rightarrow * + Urea$	0.89
$*NH*NH + H^+ + e^- \rightarrow *NH*NH_2$	0.12
$*NH*NH_2 + H^+ + e^- \rightarrow *NH + NH_3$	–1.66
$*NH + H^+ + e^- \rightarrow *NH_2$	–0.18
$*NH_2 + H^+ + e^- \rightarrow *NH_3$	0.55
$*NH_3 \rightarrow * + NH_3$	1.35

Table S5 Free energy change (eV) of urea or ammonia electrosynthesis on B-Ti@g-CN APC. (T = 298.15 K)

Elementary steps	Free energy change (eV)
$* + N_2 \rightarrow *N_2$	–0.04
$*N_2 + H^+ + e^- \rightarrow *N*NH$	–0.06
$*N*NH + H^+ + e^- \rightarrow *NH*NH$	–0.59
$*NH*NH \rightarrow 2*NH$	–1.02
$2*NH + CO \rightarrow *NHCO*NH$	–0.62
$*NHCO*NH + H^+ + e^- \rightarrow *NHCO*NH_2$	0.44
$*NHCO*NH_2 + H^+ + e^- \rightarrow *NH_2CONH_2$	–0.06
$*NH_2CONH_2 \rightarrow * + Urea$	0.63
$*NH*NH + H^+ + e^- \rightarrow *NH*NH_2$	0.35
$*NH*NH_2 + H^+ + e^- \rightarrow *NH + NH_3$	0.31
$*NH + H^+ + e^- \rightarrow *NH_2$	–2.08
$*NH_2 + H^+ + e^- \rightarrow *NH_3$	0.23
$*NH_3 \rightarrow * + NH_3$	1.14

Table S6 The number of electrons (n_e) involved in the dissolution of the pure transition metals, standard dissolution potentials (U_{diss}^0). Data references are from published literature[14,15].

Transition metals	n_e	U_{diss}^0 (V)
Sc	3	–2.08
Ti	2	–1.63
V	2	–1.18
Cr	2	–0.91
Mn	2	–1.19
Fe	2	–0.45
Co	2	–0.28
Ni	2	–0.26
Cu	2	0.34
Zn	2	–0.76
Y	3	–2.37
Zr	4	–1.45
Nb	3	–1.10
Mo	3	–0.20
Ru	2	0.46
Rh	2	0.60
Pd	2	0.95
Ag	1	0.80
Hf	4	–1.55
Ta	3	–0.60
W	3	0.10
Re	3	0.30
Os	8	0.84
Ir	3	1.16
Pt	2	1.18
Au	3	1.50

The atomic coordinates of the initial state (IS), transition state (TS) and final state (FS) during the C-N coupling reaction over B-V@g-CN APC.

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0.0000000000000000 0.0000000000000000 20.0000000000000000

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0.0000000000000000 0.0000000000000000 20.0000000000000000

C N B V H O

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Direct

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0.2781842511050844	0.0765045762236615	0.1637436775856660
0.4443338439372754	0.2284108607170120	0.1590871185847264
0.2925060818195853	0.2450500271587659	0.1740513872363647
0.7288506740092309	0.4381064786191370	0.1487979465575453
0.5616612444500774	0.2776379940031150	0.1500068062655420
0.7188567834213238	0.2741399515145700	0.1409920924093677
0.7743626615280433	0.0518038058658739	0.1553004128372654
0.9348531920977948	0.2093951647605233	0.1480311970790438
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0.2712368693887585	0.7305521113133132	0.1458314881598246
0.7089104485328989	0.9290535881505371	0.1617687501540387
0.5457932350666578	0.7728598726219349	0.1655002975433436
0.7021571906514125	0.7663975016307996	0.1682733969472295
0.7825305611296287	0.5563450995602497	0.1564588274224249
0.9323386179445677	0.7240994325373878	0.1579521848459453
0.7639783461736448	0.7072581481947506	0.1683203490618901
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C N B V H O
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0.2779596874882070 0.0788953081926910 0.1655190935580465
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0.4235555726384638	0.7202320404651259	0.1646687547524299
0.2698383591216179	0.7325519870369391	0.1465653792066705
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0.7824922834257306	0.5576485063719591	0.1587121217648859
0.9314222819893244	0.7257626255027659	0.1612652186864305
0.7618529170801956	0.7068454878528093	0.1705122674658046
0.5509494751662494	0.5866912634978931	0.2609517183497185
0.4056328589236266	0.3025833539259546	0.1751245961954353
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0.3857267164815259	0.1237149985239384	0.1574708613461855
0.1207179438076175	0.2386119565203708	0.1620730139499881
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0.8836007228589973	0.2686149875383715	0.1401265742372808
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0.8832690817977022	0.1014296460086411	0.1538333667600712
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0.7809372859922395	0.3857985812997328	0.1419270194007730
0.6188889746911936	0.3910927824338480	0.1603587157852824
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0.1048417181876245	0.7381817539908748	0.1531568466309554
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C N B V H O

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0.2773230885172247	0.0783050009072274	0.1641369947285777
0.4438975909894023	0.2297275391659849	0.1614720134041343
0.2915498636523795	0.2467977922001027	0.1713765798063103
0.7292991310872813	0.4388046135701037	0.1526611637668250
0.5617051603582766	0.2790442870602918	0.1559342460968909
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0.7734389889059545	0.0522248086983552	0.1554840266734425
0.9336278468565127	0.2098187256141314	0.1470908744569160
0.7748218815756817	0.2112039749759661	0.1444544334910896
0.2112531417043757	0.9549591000892115	0.1613972179873850
0.0523665203639208	0.7943757863339760	0.1578967188014226
0.2130386120732923	0.7967665222311788	0.1522053614247198
0.2520413265942333	0.5655002901501015	0.1425695302068977
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0.5439283575230520	0.7737718932810491	0.1653672997238898
0.6985770210596076	0.7655409368679053	0.1643189244200093
0.7817604147069060	0.5565624298367174	0.1572338506754394
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0.0941689326298366	0.3840520169246846	0.1304468870269124
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2nd_coupling_FS
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14.2170000075999994 0.0000000000000000 0.0000000000000000
-7.1085000037999997 12.3122831722000008 0.0000000000000000
0.0000000000000000 0.0000000000000000 20.0000000000000000
C N B V H O
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Direct
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0.2898821524999683 0.2370429377061597 0.1682078784766427
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0.2269536753999994 0.7928152624813013 0.1488714655545673

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0.5527072178465329	0.7629087229941306	0.1677777910040038
0.7148605002051897	0.7682356074646877	0.1607505808441038
0.7927412762817354	0.5588341832496753	0.1519324680955055
0.9452627215091552	0.7248011782031631	0.1535570747473278
0.7802584589037626	0.7146547276784502	0.1571443168097653
0.4906949696700843	0.5009656881229204	0.3011742792471317
0.4007736842492339	0.2963665867919079	0.1653140204109441
0.2306649681056679	0.1280161401938692	0.1675457523730266
0.3939586331249145	0.1235664789704001	0.1583205222526912
0.1187039104958332	0.2291020909357010	0.1592168842790220
0.2713968687647499	0.4056998063145224	0.1702282025940108
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0.8844938263817448	0.2661800316601279	0.1486184287818116
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0.6110250605063144	0.2238882403005555	0.1565854011018947
0.7839477451195509	0.3842731470200379	0.1511976214130181
0.6212979396984976	0.3973894887655425	0.1544956733787304
0.3895135022040435	0.7710453769245901	0.1583001847918260
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0.3656349344267164	0.5945673096200866	0.1696654187794321
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0.8870486366035879	0.7760543407226606	0.1567018881812063
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