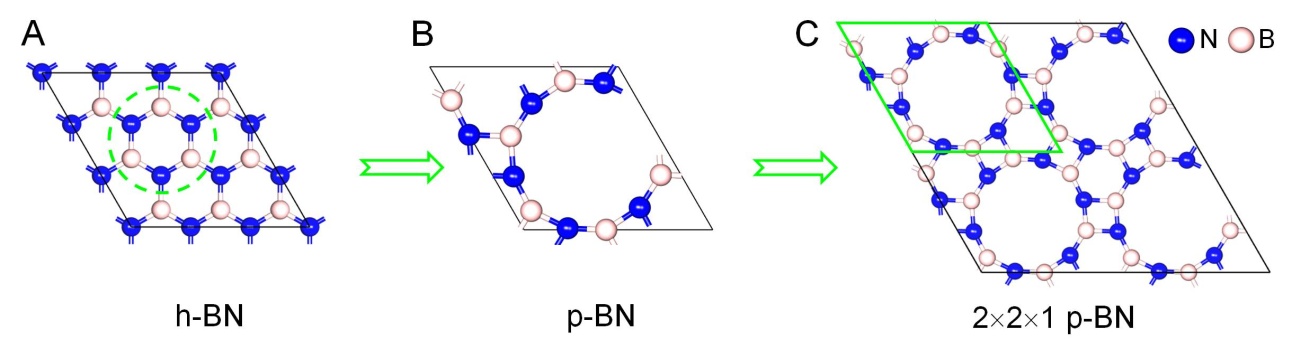
Supplementary Material

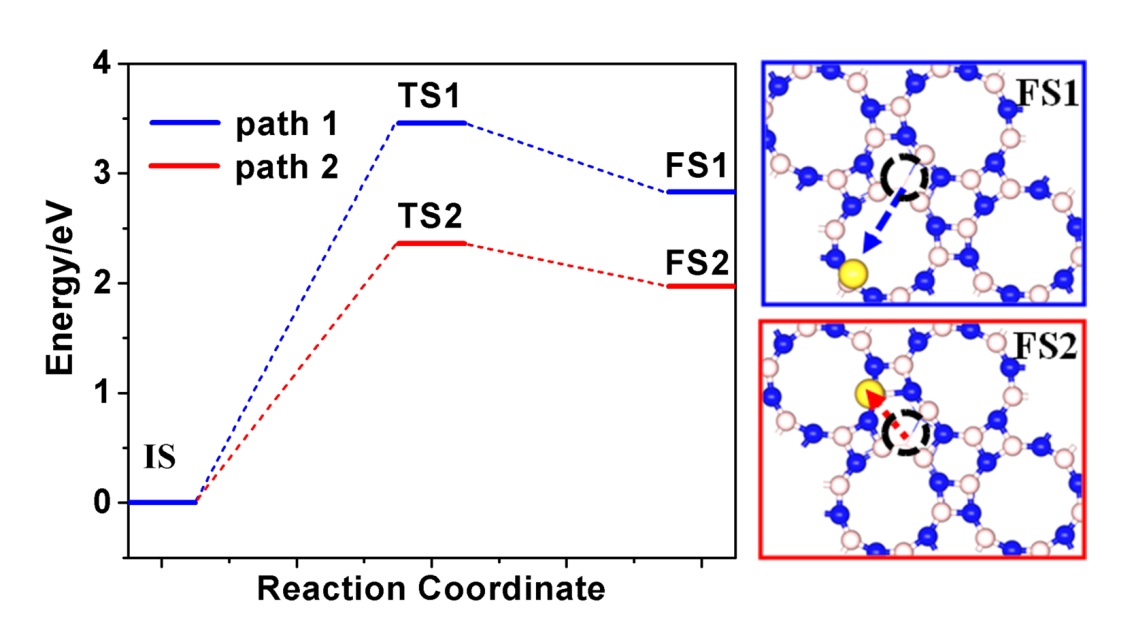
**1 Supplementary Figures**



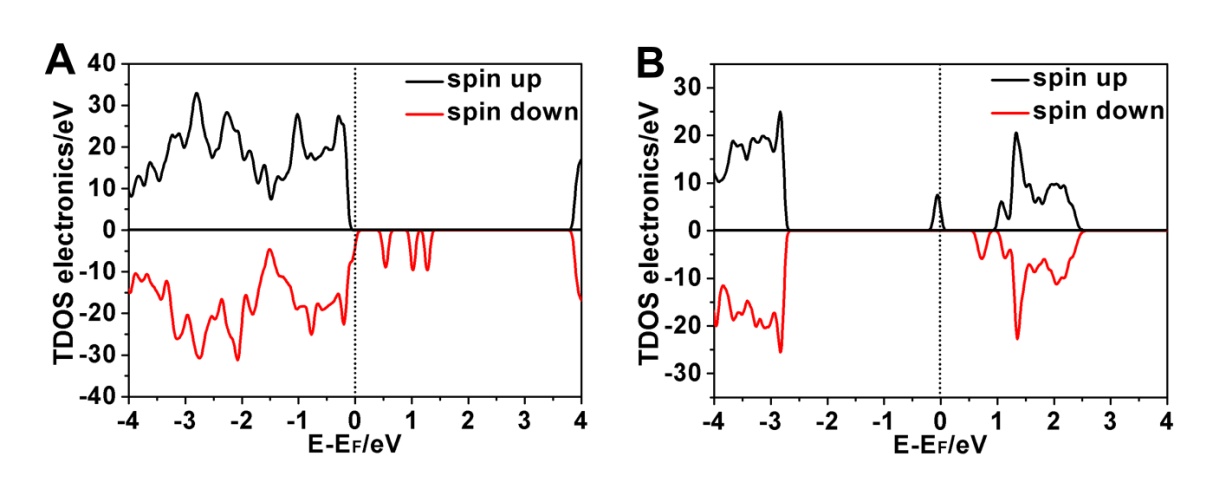
**FIGURE S1**│The geometries of original h-BN **(A)**, optimized primitive cell porous BN (p-BN) **(B)**, and supercell 2×2×1 p-BN **(C)**, respectively.

C:\Users\Administrator\Desktop\VN.tif

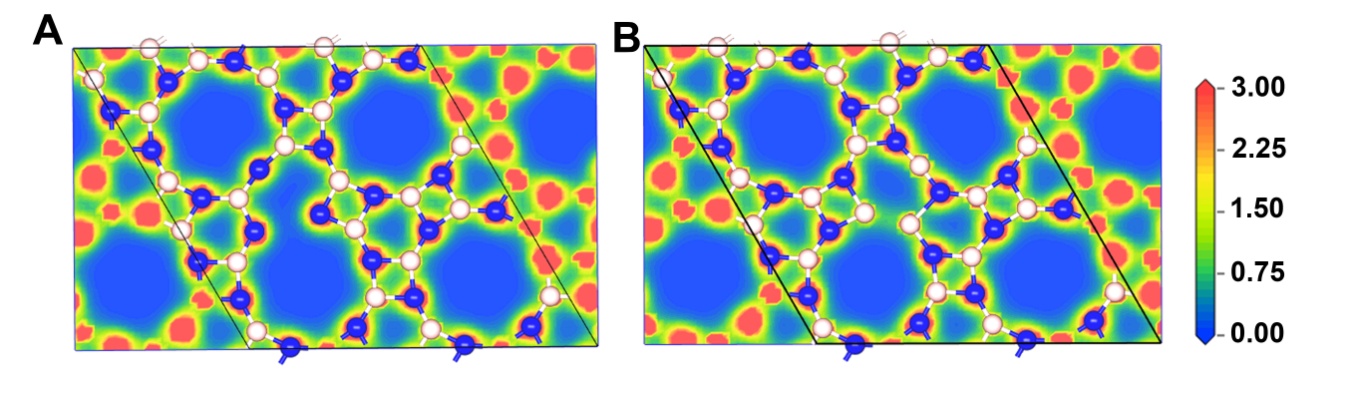
**FIGURE S2│**Thecohesive energies of isolated Aun cluster, Aun/p-BN-VN (n=2~13) and Au bulk.



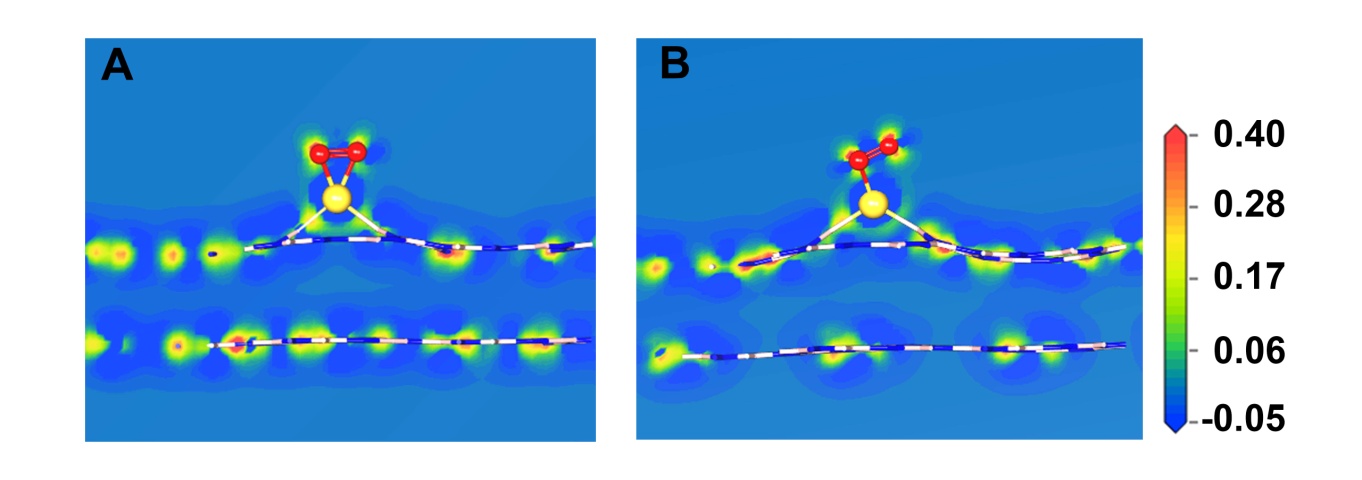
**FIGURE S3│**Potential energy diagrams for the migration of a single Au atom on VN vacancy.



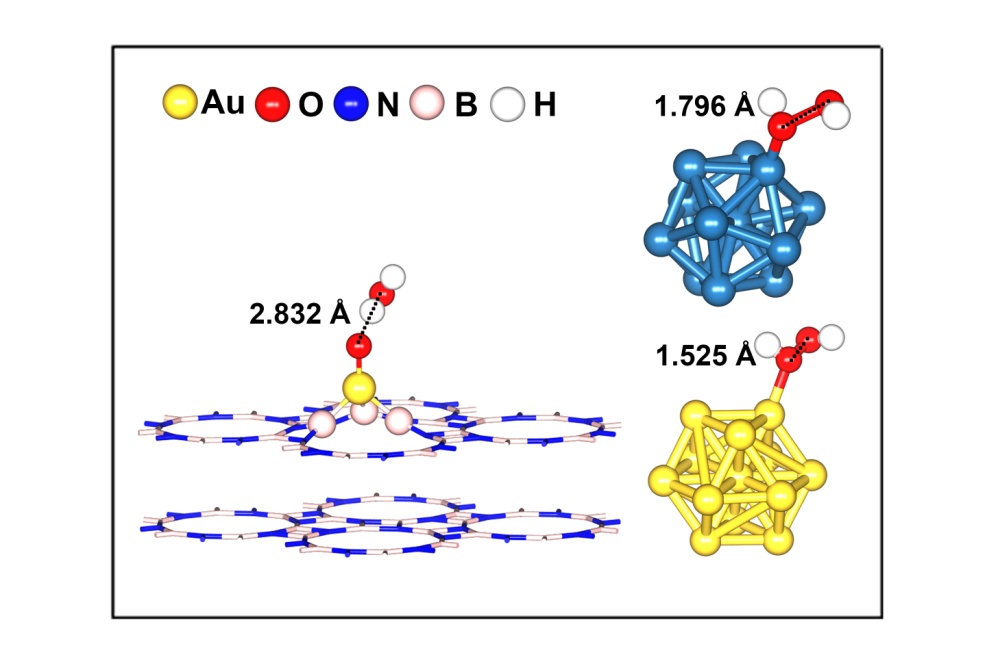
**FIGURE S4│**Total density of states (TDOS) for p-BN with VB defect (A) and p-BN with VN defect (B).

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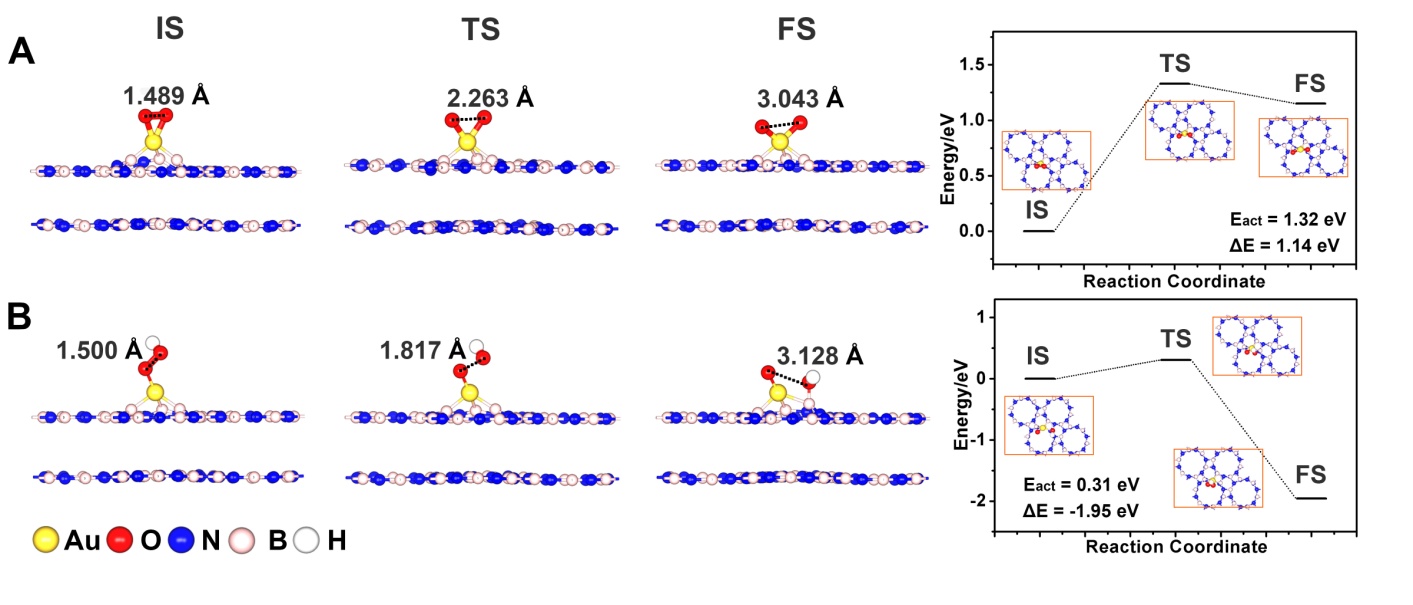
**FIGURE S5│**The total charge density of p-BN with VB defect (A) and p-BN with VN defect (B).



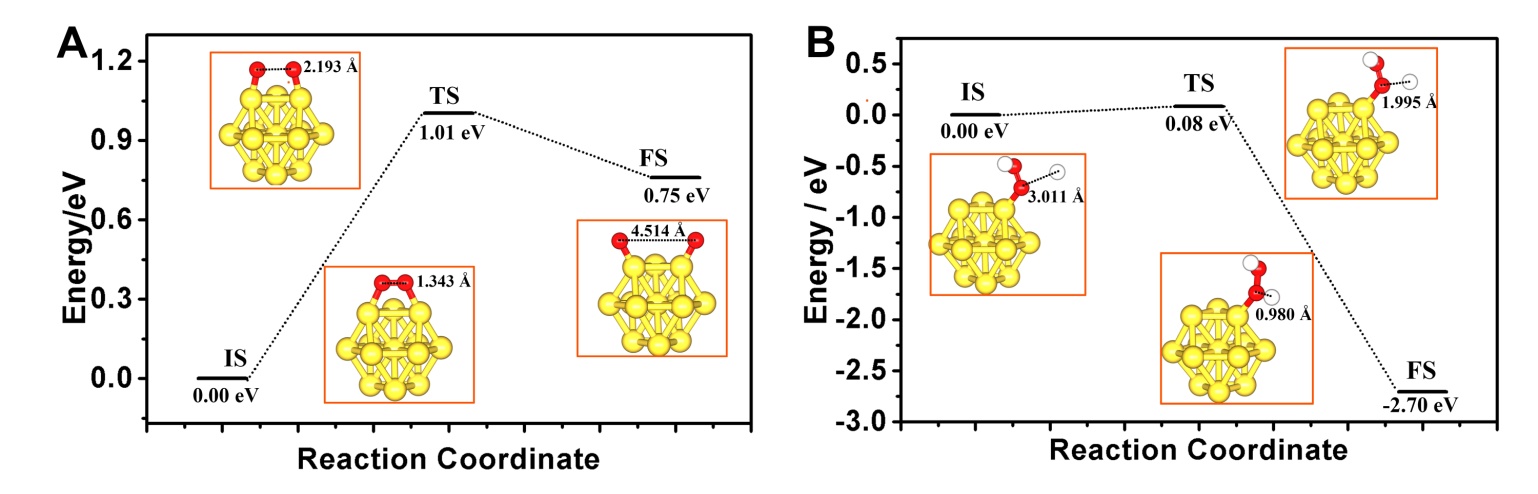
**FIGURE S6│** The charge-density difference plots of O2 adsorbed on Au/p-BN-VN: **(A)** \*O2-Bridge, **(B)** \*O2-Pauling.



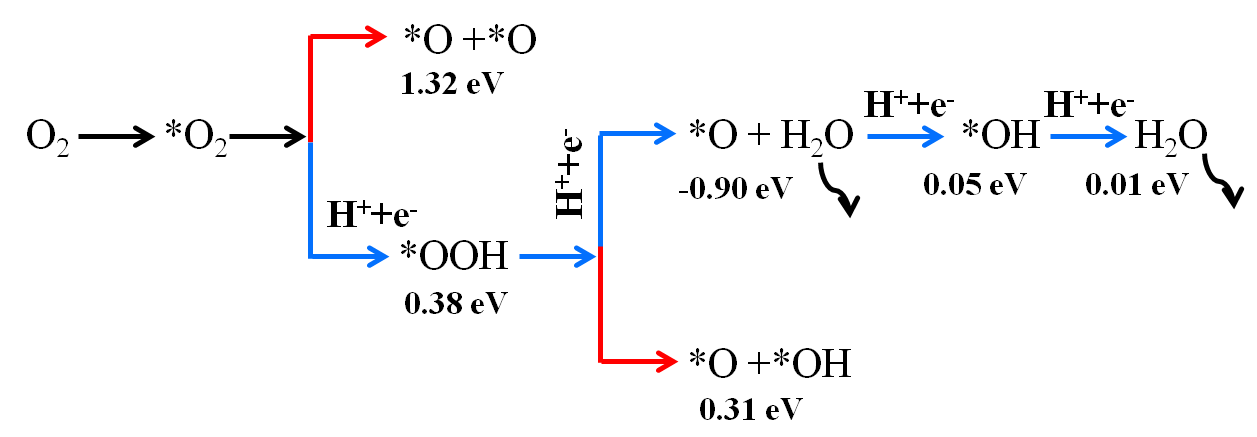
**FIGURE S7**│The geometry structures of H2O2 adsorption on Au/p-BN-VN, Pt13 and Au13 cluster.



**FIGURE S8**│The structures for initial state (IS), transition state (TS), final state (FS) and potential energy profile for **(A)** \*O2→ \*O + \*O, **(B)** \*OOH → \*OH + \*O on a Au atom supported p-BN with VN.



**FIGURE S9**│The structures for initial state (IS), transition state (TS), final state (FS) and potential energy profile for **(A)** \*O2→ \*O + \*O, **(B)** \*OOH + H+ + e- → H2O2\* on Au13 cluster.



**FIGURE S10**│The possible reaction pathways for ORR on Au/p-BN-VN surface. The \* denotes the adsorption site on the Au/p-BN-VN surface. The values (in units of eV) represent the activation energy. The paths with the blue sign is the most favorable due to their lower activation energies.

**2 Supplementary Tables**

**Table S1**│ The adsorption energies (*E*ads, eV), O-O lengths, and charges transfer amount from catalysts to O2 obtained by the Hirshfeld Charge analysis of the adsorbed \*O2-Bridge on metal (Pt, Pd, and Au)/p-BN with B and N vacancy defect.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalysts | *E*ads O2 (eV) | *d*O-O (Å) | *d*M-O (Å) | Charge (e) |
| Pt/p-BN-VB | 1.043 | 1.312 | 2.016 | 0.202 |
| Pt/p-BN-VN | 2.213 | 1.347 | 2.141 | 0.230 |
| Pd/p-BN-VB | 0.611 | 1.302 | 2.070 | 0.205 |
| Pd/p-BN-VN | 1.976 | 1.336 | 2.070 | 0.343 |
| Au/p-BN-VB | 0.522 | 1.280 | 2.008 | 0.128 |
| Au/p-BN-VN | 1.658 | 1.489 | 1.979 | 0.513 |

**Table. S2**│ The calculated adsorption energies (*E*ads/eV) of \*O2, \*OOH, \*O, \*OH and H2O on Au/p-BN-VN, which obtained in a H2O solvent environment by COSMO.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | O2 (Bridge) | O2(Pauling) | OOH | OH | O | H2O |
| Eads/eV | 1.658 | 0.717 | 1.925 | 3.282 | 5.413 | 0.488 |
| Eads/eV(COSOM) | 2.031 | 1.150 | 1.911 | 3.274 | 5.752 | 0.509 |