

Supporting Information

**N, P co-doped microporous carbon as metal-free catalyst for
selective oxidation of alcohols with air in water**

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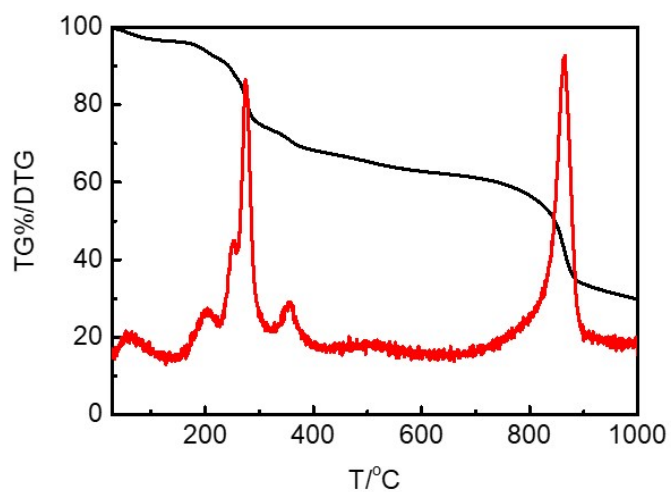


Figure S1. TG/DTA curves of pPDA-PA aerogel.

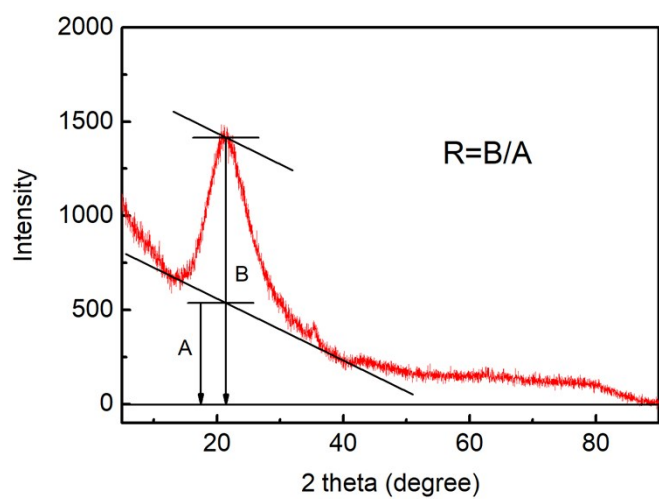


Figure S2. A sketch map for the calculation of the R values.

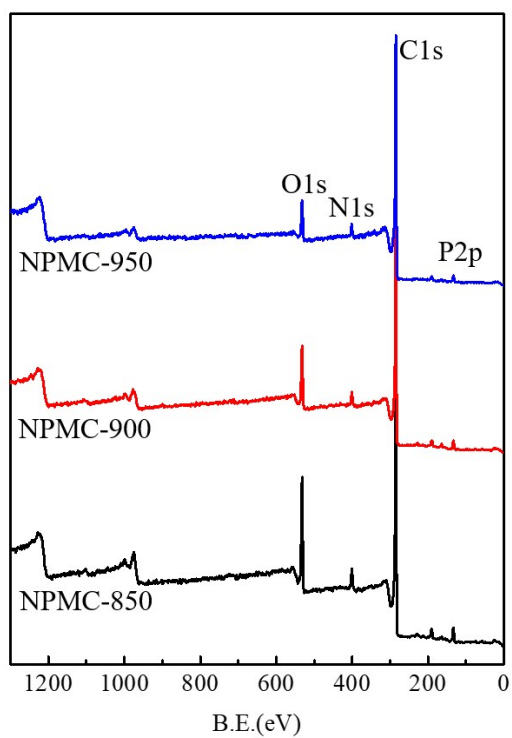


Figure S3. XPS survey spectra of the NPMCs.

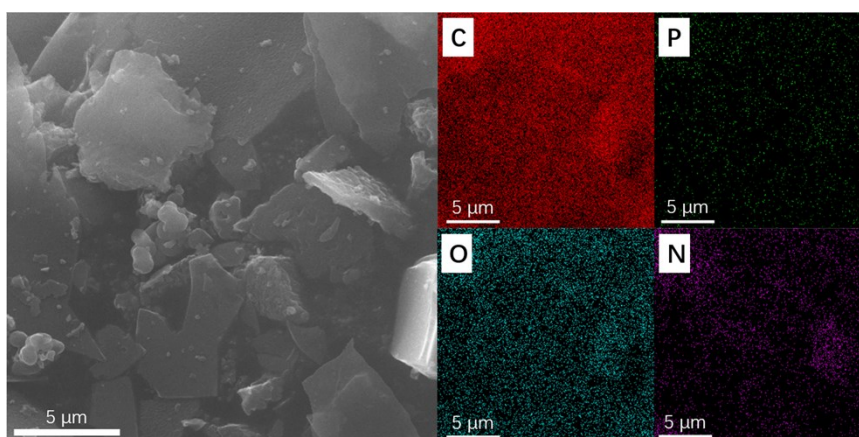


Figure S4. Energy-dispersive spectroscopy (EDS) elemental mapping images of NPMC-900.

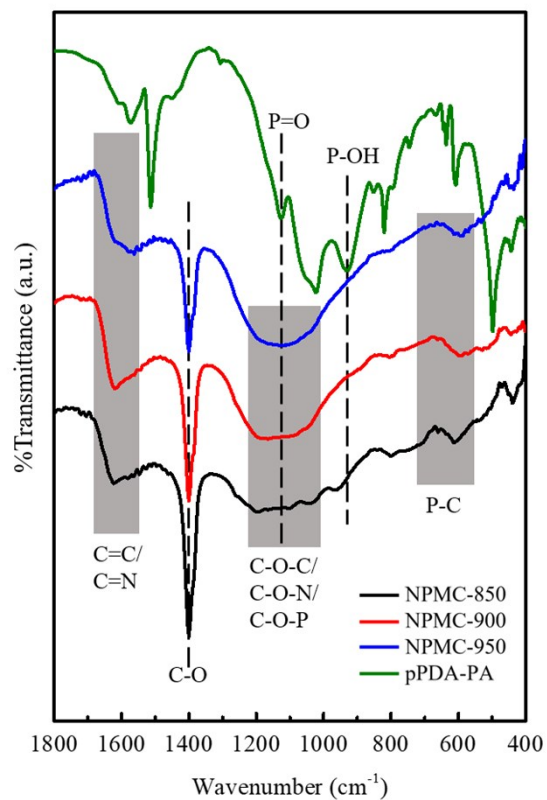


Figure S5. FT-IR spectra of NPMCs

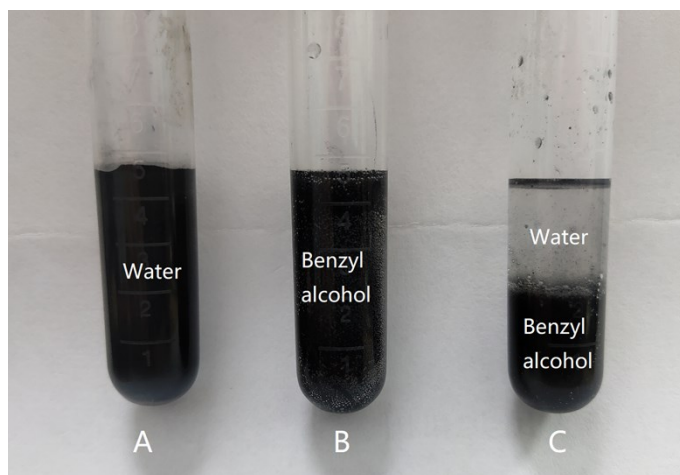


Figure S6. Photographs of NPMC-900 dispersed in water (A), Benzyl alcohol (B) and Water/Benzyl alcohol mixture (C).

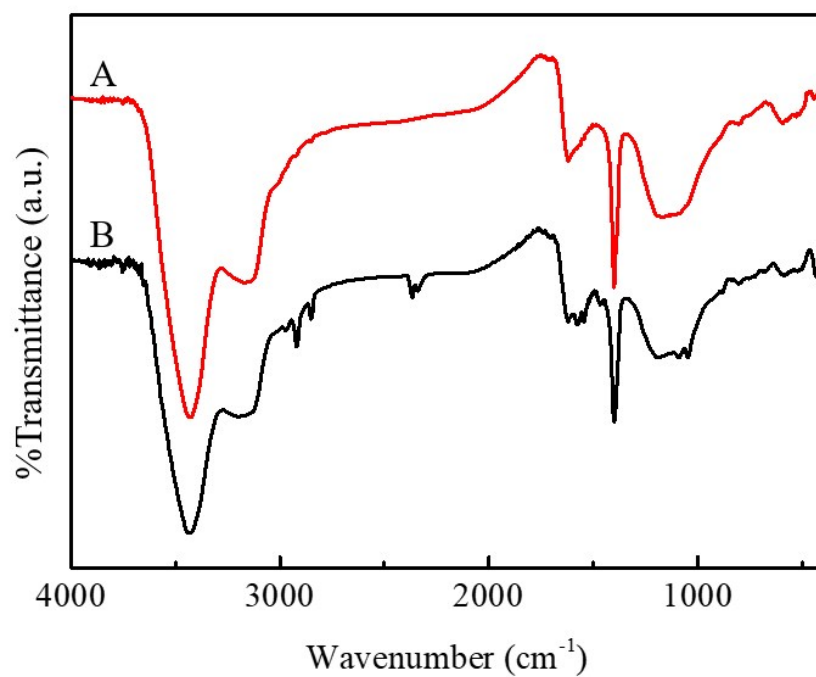


Figure S7. FT-IR spectra of NPMC-900 (A) and recovered NPMC-900 (B)

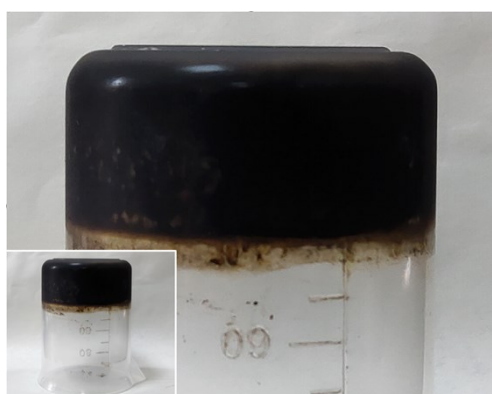


Figure S8. Photos of pPDA-PA hydrogel

Table S1. Carbon yields and porous structure of NPMCs

| Catalyst | Yield/% | $S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$ | $S_{\text{micro}}/\text{m}^2 \text{g}^{-1}$ | $V_{\text{tot}}/\text{m}^3 \text{g}^{-1}$ | $V_{\text{micro}}/\text{m}^3 \text{g}^{-1}$ |
|----------|---------|---|---|---|---|
| NPMC-850 | 24.07 | 621 | 581 | 0.351 | 0.292 |
| NPMC-900 | 20.85 | 676 | 613 | 0.439 | 0.346 |
| NPMC-950 | 18.19 | 731 | 674 | 0.443 | 0.351 |
| NPC-900 | 22.36 | 227 | 214 | 0.134 | 0.113 |

Table S2. Raman spectra data of NPMCs

| Catalyst | G/cm ⁻¹ | D/cm ⁻¹ | $I_{\text{G}}/I_{\text{D}}$ |
|----------|--------------------|--------------------|-----------------------------|
| NPMC-850 | 1590 | 1354 | 1.01 |
| NPMC-900 | 1594 | 1353 | 1.01 |
| NPMC-950 | 1596 | 1354 | 1.00 |

Table S3. Calculated atomic % of C, P, N and O for NPMCs

| Catalyst | P at% | C at% | N at% | O at% | Total |
|----------|-------|-------|-------|-------|-------|
| NPMC-850 | 3.09 | 76.08 | 5.27 | 15.56 | 100 |
| NPMC-900 | 2.72 | 81.00 | 4.14 | 12.14 | 100 |
| NPMC-950 | 2.04 | 86.86 | 3.63 | 7.47 | 100 |

Table S4. Calculated % of P-C and P-O present in NPMCs

| Catalyst | Absolute % | | | Relative % | | |
|----------|------------|-------|-------|------------|-------|-------|
| | % P-C | % P-O | Total | % P-C | % P-O | Total |
| NPMC-850 | 1.05 | 2.04 | 3.09 | 34.05 | 65.95 | 100 |
| NPMC-900 | 0.73 | 1.99 | 2.72 | 27.16 | 72.84 | 100 |
| NPMC-950 | 0.64 | 1.40 | 2.04 | 31.31 | 68.69 | 100 |

Table S5. Calculated % of different type of oxygen present in NPMCs

| Catalyst | Absolute % | | | Relative % | | |
|----------|---------------|-------------------------|-------|---------------|-------------------------|-------|
| | % C=O/ P=O | % C-O/ P-O-C/ P-O | Total | % C=O/ P=O | % C-O/ P-O-C/ P-O | Total |
| NPMC-850 | 4.01 | 11.56 | 15.57 | 25.75 | 74.25 | 100 |
| NPMC-900 | 3.57 | 8.56 | 12.13 | 29.42 | 70.58 | 100 |
| NPMC-950 | 2.54 | 4.93 | 7.47 | 34.03 | 65.97 | 100 |

Table S6. Calculated % of different type of nitrogen present in NPMCs

| Catalyst | Absolute % | | | | |
|----------|-------------|------------|-------------|------------|-------|
| | pyridinic N | pyrrolic N | graphitic N | oxidized N | Total |
| NPMC-850 | 1.04 | 1.54 | 2.28 | 0.41 | 5.27 |
| NPMC-900 | 0.69 | 0.83 | 1.99 | 0.63 | 4.14 |
| NPMC-950 | 0.37 | 0.56 | 2.18 | 0.52 | 3.63 |
| | Relative % | | | | |
| | pyridinic N | pyrrolic N | graphitic N | oxidized N | Total |
| NPMC-850 | 19.74 | 29.15 | 43.28 | 7.83 | 100 |
| NPMC-900 | 16.61 | 20.01 | 48.04 | 15.34 | 100 |
| NPMC-950 | 10.22 | 15.29 | 60.20 | 14.29 | 100 |

Table S7. Results of the selective oxidation of benzyl alcohols in water over different catalysts

| Entry | Catalyst | Conv. ^b /% | Sel. ^b /% |
|-------|------------|-----------------------|----------------------|
| 1 | NPMC- 800 | 85 | >99 |
| 2 | NPMC- 1000 | 50 | >99 |

^a Reaction conditions: benzyl alcohol (0.5 mmol), catalyst (50 mg), water (1 mL), 1-atm air initially filled in the pressure bottle, 120 °C, 5 h; ^b determined by GC.

Table S8. Performance of reported metal-free catalysts for selective oxidation of benzyl alcohol

| Entry | Ref. | Cat. | m(cat.) | Benzyl alcohol | solvent | T /°C | T /h | oxidant | Conv . % | Sel. % |
|-------|-----------|--------------------------------|---------|----------------|-------------|-------|------|--------------------------------|----------|--------|
| 1 | This work | NPMC-900 | 50mg | 0.5mmol | water | 120 | 5 | air | 99 | >99 |
| 2 | [8] | PGc | 50mg | 100mg | water | 100 | 24 | O ₂ | 90 | 96 |
| 3 | [15] | H ₂ SO ₄ | 1mmol | 1mmol | DMSO | 150 | 1 | H ₂ SO ₄ | 99 | 94 |
| 4 | [16] | AC | 100mg | 1.1mmol | ethanol | 120 | 5 | air | 23 | >99 |
| 5 | [18] | NG-900 | 30mg | 0.1mmol | water | 70 | 10 | O ₂ | 13 | >99 |
| 6 | [19] | GO | 100mg | 50 mg | - | 150 | 24 | air | 99 | 85 |
| 7 | [42] | NSC | 10mg | 1mmol | 1,4-dioxane | 90 | 5 | HNO ₃ | 96 | 92 |
| 8 | [43] | PS-Gc | 50mg | 0.1 mL | water | 80 | 48 | O ₂ | 54 | 88 |
| 9 | [44] | Au/NPC | 20mg | 0.5mmol | Toluene | 25 | 1 | O ₂ | 99 | >99 |
| 10 | [45] | Pd _{NPs} @PANI/HNS | 20mg | 1mmol | Toluene | 80 | 5 | O ₂ | 95 | 95 |

Table S9. Porous structure of NPMC-900 and recovered NPMC-900

| Catalyst | S _{BET} | S _{micro} /m ² g ⁻¹ | V _{tot} /m ³ g ⁻¹ | V _{micro} /m ³ g ⁻¹ |
|-----------------|------------------|--|--|--|
| NPMC-900 | 676 | 613 | 0.439 | 0.346 |
| Reused NPMC-900 | 681 | 614 | 0.445 | 0.348 |

