Supplementary Information

Integrating biomass and mineral into photocatalyst for efficient photocatalytic N_2 fixation coupled with biomass conversion

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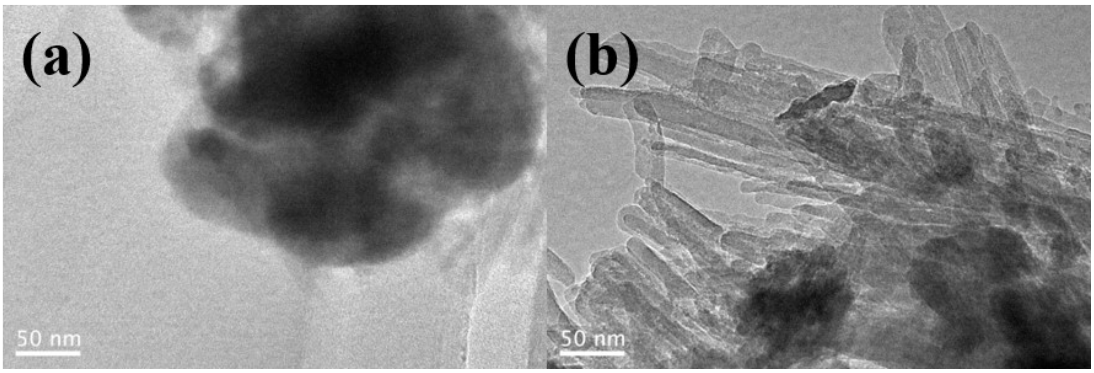
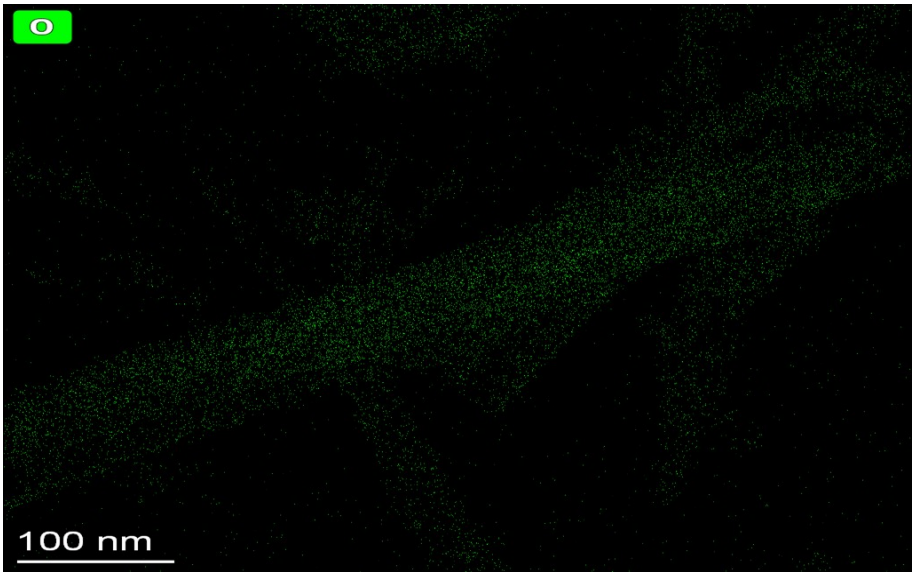
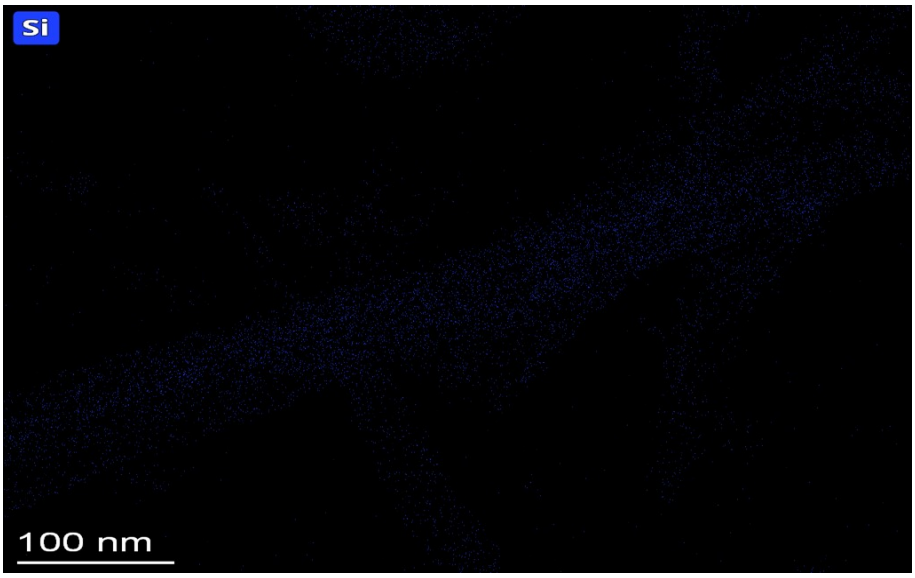


Fig. S1 TEM images of HTCC (a); HTCC/Fe-ATP(b) with chestnut shells as raw material




Mg
100 nm


Si
100 nm

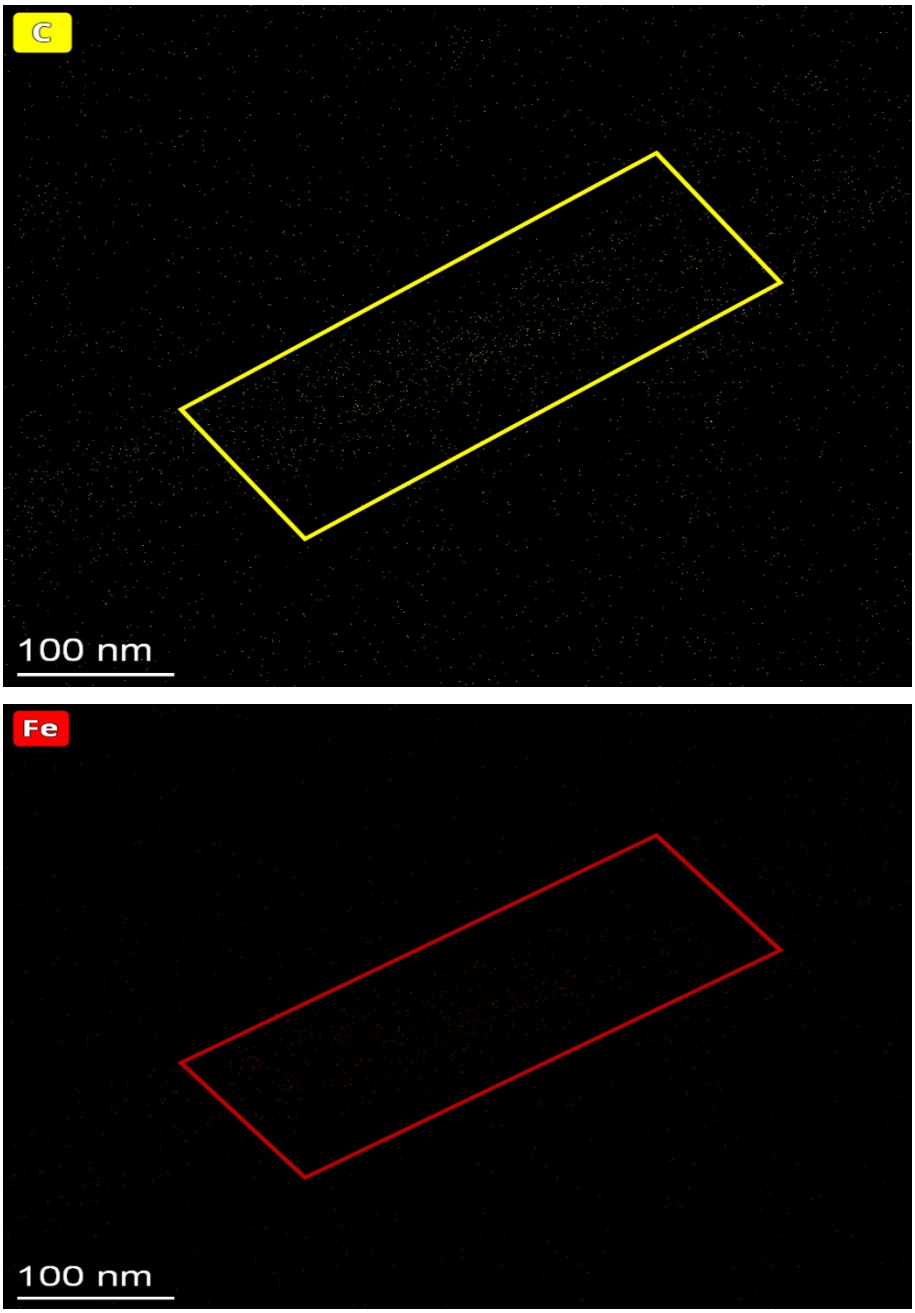
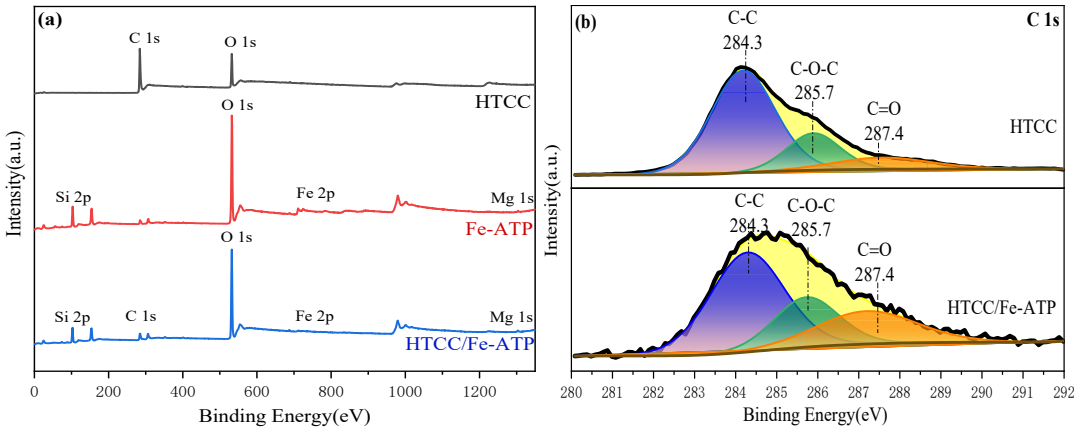


Fig. S2 Different element mappings image of 30% HTCC/Fe-ATP.

XPS analysis

As shown in Fig.S3 (a), the presence of Si, C, O, Fe, Mg in the HTCC/Fe-ATP sample is identified in the survey scan, which is consistent with the results of element mapping. The XPS spectra of C 1s in HTCC and HTCC/Fe-ATP, as shown in Fig.S3 (b), exhibit three characteristic peaks at 284.3 eV, 285.7 eV and 287.4 eV,

corresponding to the existence of C-C, C-O-C and C=O, respectively. For the O 1s spectra in the Fig.S3 (c), two distinct peaks are observed in HTCC at 532.3 eV and 533.2 eV, which can be attributed to C=O and C-O-C. In the O 1s spectrum of Fe-ATP, two peaks are observed at 529.5 eV and 532.1 eV, corresponding to the lattice oxygen (O_L) and surface adsorbed oxygen (O_A), respectively. The O 1s spectrum of the HTCC/Fe-ATP sample displays four typical peaks, representing the C=O and C-O-C bonds of HTCC, as well as the lattice oxygen (O_L) and surface adsorbed oxygen (O_A) of Fe-ATP. Notably, the binding energy of the O_A peak in the HTCC/Fe-ATP composite shifts to lower values, indicating an increase in electron cloud density. This phenomenon can be attributed to the electron transfer process occurring in HTCC/Fe-ATP. In Fig.S3 (d), the Fe 2p spectrum of HTCC/Fe-ATP contains two obvious spin–orbit doublets of Fe $2p_{1/2}$ and Fe $2p_{3/2}$. Among them, four peaks centered at 709.2 eV, 715.2 eV, 723.6 eV and 727.3 eV are assigned to Fe^{2+}, while another three peaks at 711.6 eV, 719.2 eV and 732.6 eV belong to Fe^{3+}. The above results illustrate the coexistence of Fe^{2+} and Fe^{3+} in Fe-ATP structures.



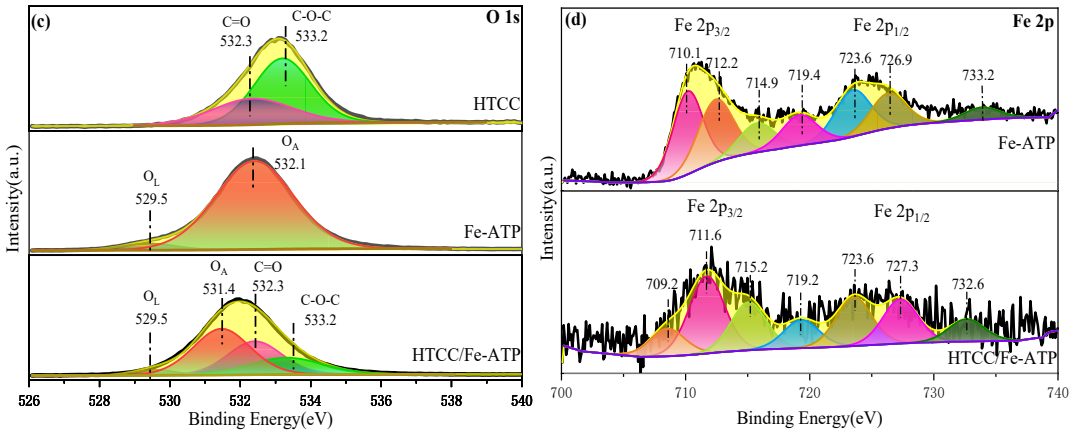


Fig.S3 XPS spectra of the HTCC, Fe-ATP and HTCC/Fe-ATP samples, survey (a); C 1s (b); O 1s (c); Fe 2p (d).

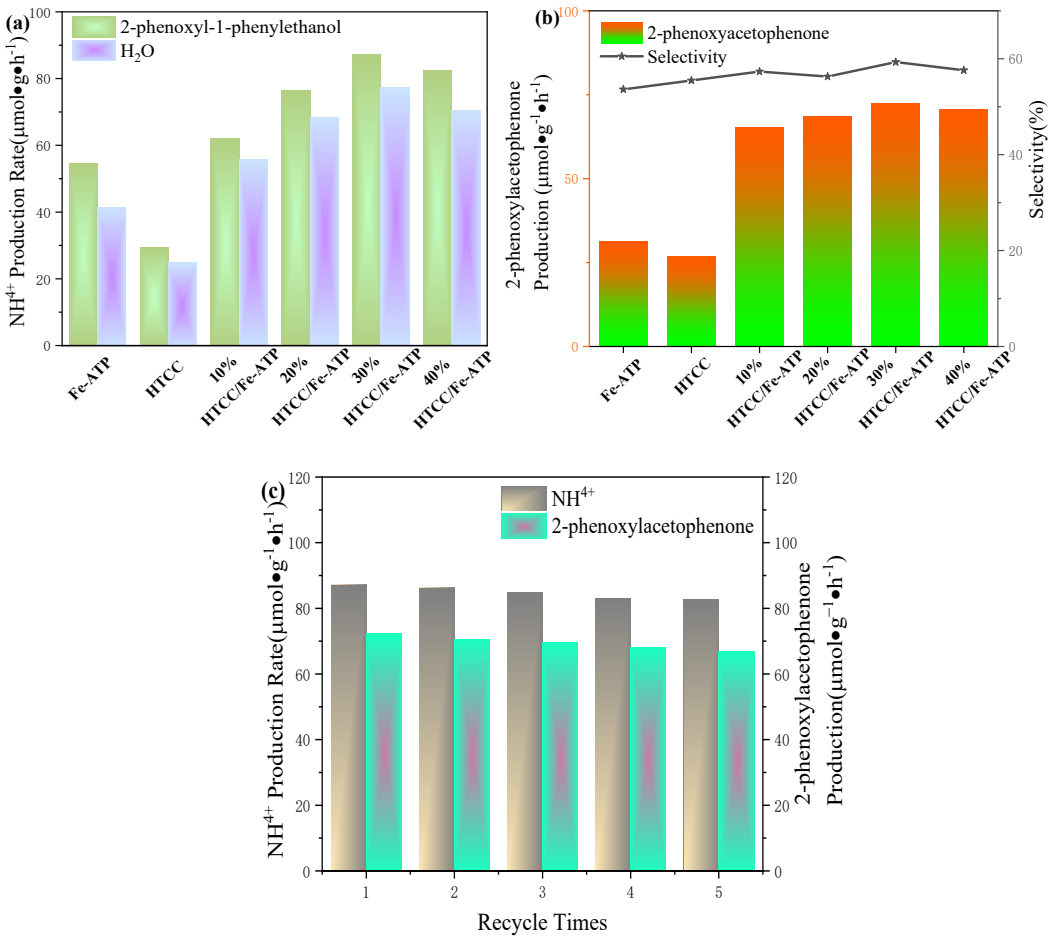


Fig. S4 (a) The photocatalytic nitrogen fixation ability of Fe-ATP, HTCC and 10%~40% HTCC/Fe-ATP in 2-phenoxy-1-phenylethanol solution and aqueous solution; (b) The

photooxidation of 2-phenoxy-1-phenylethanol by Fe-ATP, HTCC and 10%~40% HTCC/Fe-ATP in the coupled system; (c) Photocatalytic 2-phenoxy-1-phenylethanol coupling nitrogen fixation ammonia synthesis 5 cycle diagram by 30% HTCC/Fe-ATP. Typical reaction condition: 40 mg of 2-phenoxy-1-phenylethanol, 100 mg of photocatalysts, 50 mL of solvent (CH_3CN: H_2O =1:9), visible light irradiation, room temperature, 12h. The result was determined by HPLC.

The average lifetime (τ) can be calculated by the following formula:

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

The fitting data are shown in **Table S1**.

Table S1 The fitted PL decay components of as-prepared photocatalysts

Component	A_1(%)	A_2(%)	τ_1(ns)	τ_2(ns)	τ(ns)
HTCC	64.67	35.55	0.3252	2.1793	0.9803
Fe-ATP	58.00	42.00	0.3118	2.0939	1.0603
10% HTCC/Fe-ATP	53.49	46.51	0.4003	2.6489	1.4461
20% HTCC/Fe-ATP	47.85	52.15	0.3184	2.6732	1.5464
30% HTCC/Fe-ATP	28.52	71.48	0.2963	2.4478	1.8343
40% HTCC/Fe-ATP	40.31	59.69	0.3994	2.3384	1.5566

Table S2 Photocatalytic nitrogen fixation with absence of sacrificial agent

Entry	Photocatalysts	Catalyst Dosage	Sacrificial Agent	Light Source	photocatalytic nitrogen fixation rate	Ref
1	Co-Bi_2MoO_6	100 mg	/	visible light	95.5 μmol•g^{-1}•h^{-1}	1

2	In_2O_3/In_2S_3	20 mg	/	300 W Xenon lamp	40.04 μmol•g^{-1}•h^{-1}	2
3	Fe- TiO_2-SiO_2	50 mg	/	300 W Xe lam	32 μmol•g^{-1}•h^{-1}	3
4	N- TiO_2	20 mg	/	300 W Xenon lamp	80.09 μmol•g^{-1}•h^{-1}	4
5	Fe-porous g-C_3N_4	30 mg	/	300 W Xenon lamp	62.42 μmol•g^{-1}•h^{-1}	5
6	HTCC/Fe-ATP	100 mg	benzyl alcohol	300 W Xenon lamp (λ > 420 nm)	102.8 μmol•g^{-1}•h^{-1}	This work

Table S3 Photocatalytic nitrogen fixation coupled with oxidation conversion

Entry	Photocatalysts	Catalyst Dosage	Sacrificial Agent	Oxidation products and yield	Light Source	photocatalytic nitrogen fixation rate	Ref
1	Fe-abtc	20 mg	K_2SO_3	K_2SO_4 N/A	300 W Xe lamp	49.8 μmol•g^{-1}•h^{-1}	6
2	$Ni_{12}P_5/ZnIn_2S_4$	50 mg	benzyl alcohol	benzaldehyde ≈ 90 μmol•g^{-1}	300 W Xe lamp (λ > 400 nm)	47μmol•g^{-1}	7
3	HTCC/Fe-ATP	100 mg	benzyl alcohol	benzaldehyde 155 μmol•g^{-1}•h^{-1}	Xenon lamp (λ > 420 nm)	102.8 μmol•g^{-1}•h^{-1}	This work

Reference

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