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· Supplementary Information

Titanium silicalite-1 zeolite encapsulating Au particles as catalyst for vapor propylene epoxidation with H_2/O_2: a matter of Au-Ti synergic interaction

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Experimental

Characterizations

The ultraviolet-visible spectra (**UV-vis**) were recorded by means of UNICAM UV-300 spectrophotometer (Thermo, USA) from 200 to 800 nm. The diffuse reflectance ultraviolet-visible spectra (**DR UV-vis**) were measured along with Cary-5000 spectrometer using $BaSO_4$ as a reference. The Fourier transform infrared Spectra **(FTIR)** were collected using Nicolet N6700 spectrometer (Thermo, USA) with a resolution of 4 cm^{-1}. The solid nuclear magnetic resonance spectra (**^{29}Si MAS NMR**) were tested along with 500MHz Avance III spectrometer (Bruker, Germany).

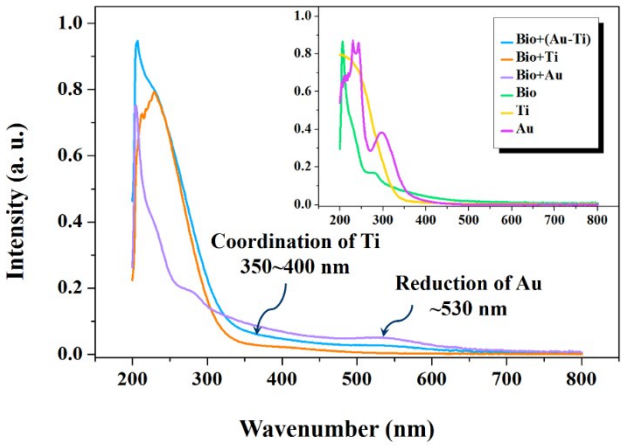

Fig. S1 UV-vis spectra of mixture of bio-extract, Ti-BALDH and $HAuCl_4$, mixture of bio-extract and Ti-BALDH, mixture of bio-extract and $HAuCl_4$, respectively. (inset: UV-vis spectra of bio-extract, Ti-BALDH and $HAuCl_4$, respectively). Bio-extract, Ti-BALDH and $HAuCl_4$ are abbreviated as bio, Ti and Au in the figure legend.

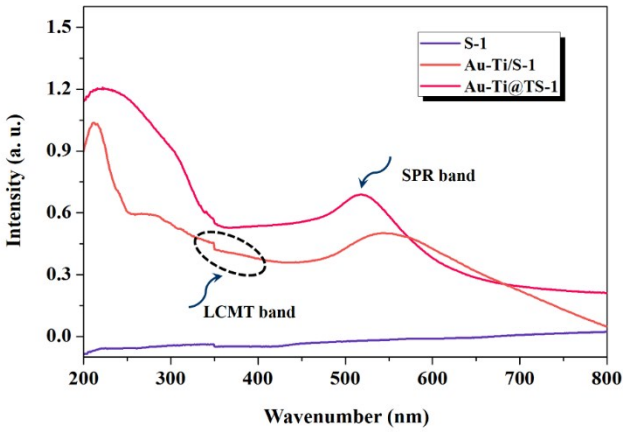

Fig. S2 DR-UV spectra of S-1, Au-Ti/S-1, Au-Ti@MFI, respectively. (Si/Ti=35, Au loading 0.5% for Au-Ti@MFI)

Note: The integration of Au-Ti is explored by UV-vis. As shown in Fig.S1, the bio-extract alone exhibits UV band at ~ 210 nm, attributable to the poly-phenol groups.[1] The mixture of bio-extract and Ti-BALDH shows a LCMT band at 350~400 nm, demonstrating the bio-extract coordination of Ti precursor.[2] Meanwhile, the mixture of bio-extract and $HAuCl_4$ exhibits a SPR band of Au^0 at 530 nm, confirming the bio-extract reduction of Au NPs.[3] The above two characteristic bands arise simultaneously when mixing bio-extract, Ti-BALDH and $HAuCl_4$, implicating the integration of Au

and Ti by bio-extract. Furthermore, similar trend is also found when supporting such Au-Ti integration onto S-1 seed, as shown in Fig. S2 with similar LCMT and SPR bands. These results strongly evidence that Au and Ti could be integrated on the crystal seed by bio-extract prior to solvent-free synthesis.

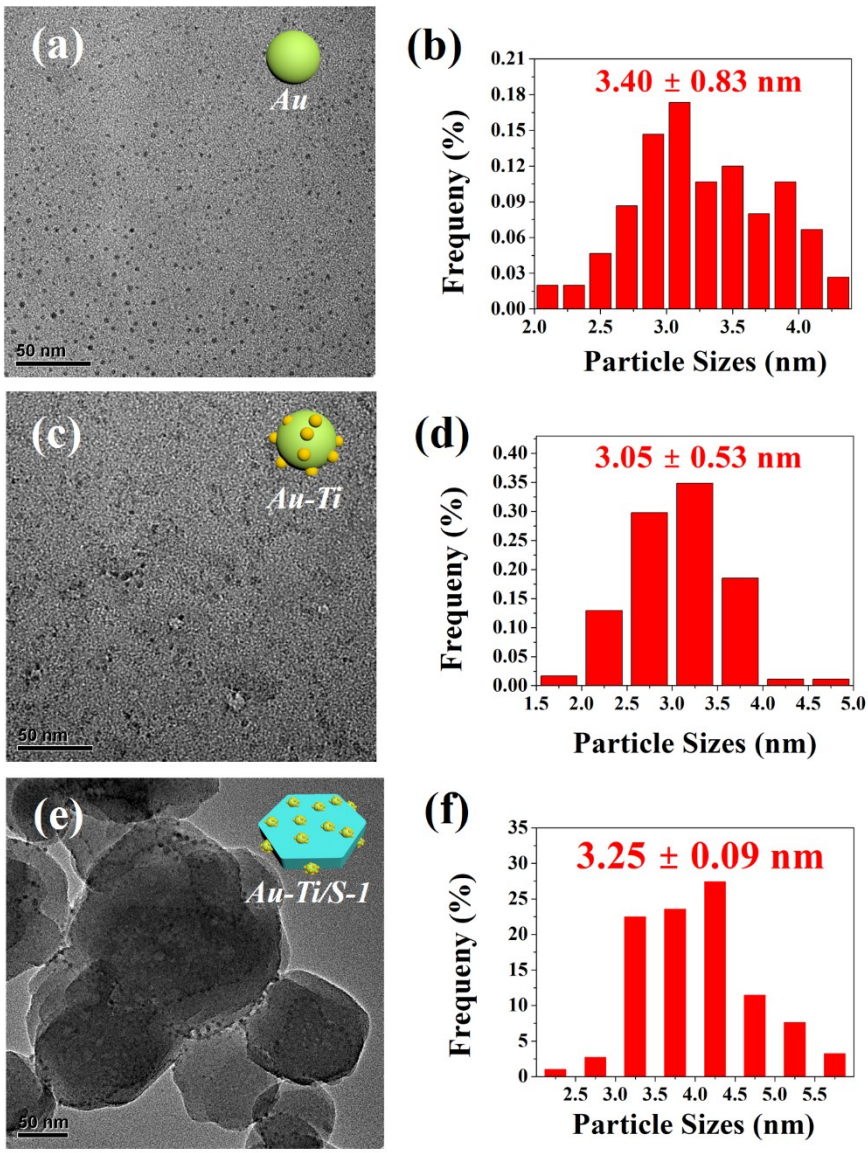

Fig. S3 TEM images and corresponding size-distribution of (a)~(b) bio-reduced Au NPs, (c)~(d) bio-reduced Au NPs integration with Ti, and (e)~(f) Au-Ti/S-1.

Note: After mixing Ti-BALD with the bio-extract reduced Au NPs, a Ti-phenolic complex is generated on the surface of Au NPs with the presence of a low-contrast coating as shown in Fig. S3 (c), indicating the integration of Au and Ti via bio-phenol coordinating.[4-5] The thickness of such Ti-phenolic coating should be thin enough to ensure the uniform mono-dispersion of Au NPs.

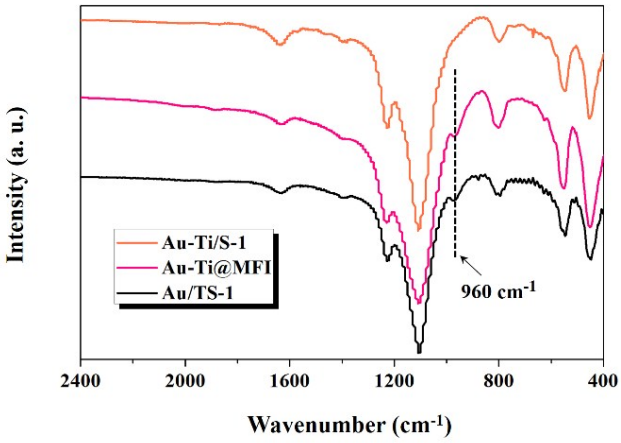

Fig. S4 FTIR spectra of Au-Ti@MFI, Au-Ti/S-1 and Au/TS-1, respectively.

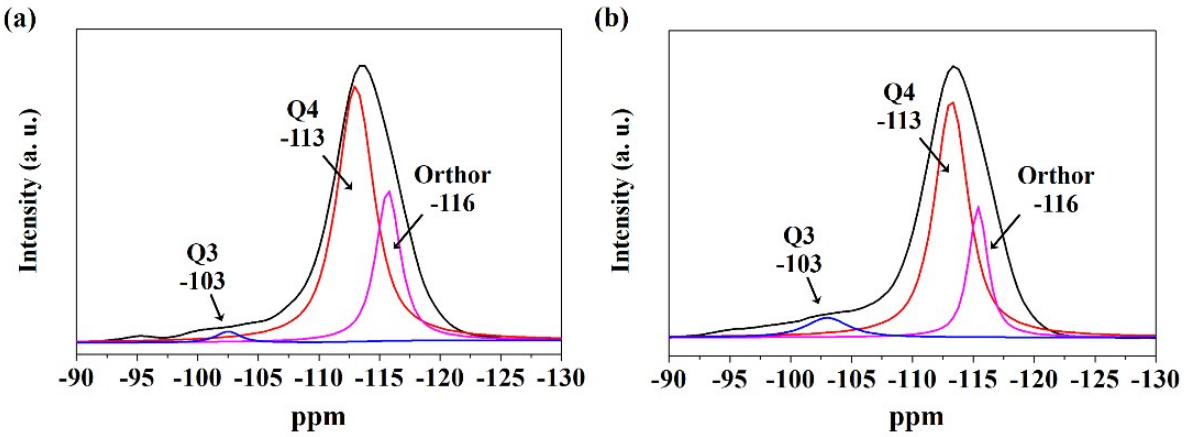

Fig. S5 ^{29}Si MAS NMR spectra of (a) Au-Ti@MFI and (b) Au/TS-1, respectively.

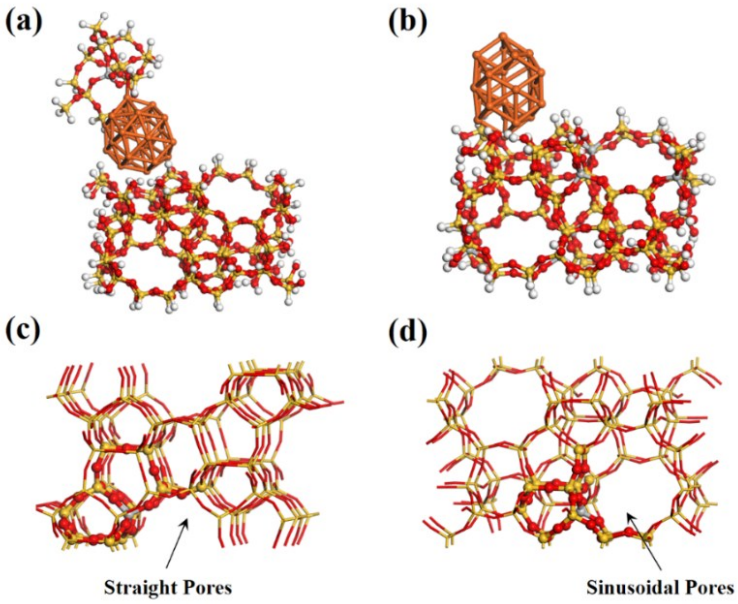

Fig. S6 Optimized structure models of (a) Au-Ti@MFI and (b) Au/TS-1, respectively. The embedded model of TS-1 cluster (T6 substitution) within MFI framework (stick model) from the view of (c) straight pores and (d) sinusoidal pores. Colour codes: Au, orange sphere, Ti, grey sphere; O, red sphere; Si, yellow sphere; H, white sphere.

Note: The Ti atom is located at T6 site (seen from Fig. S6 (c)~(d)) in the MFI framework, due to the adequate reaction space for reactant adsorption in the intersection of the straight and sinusoidal channels.

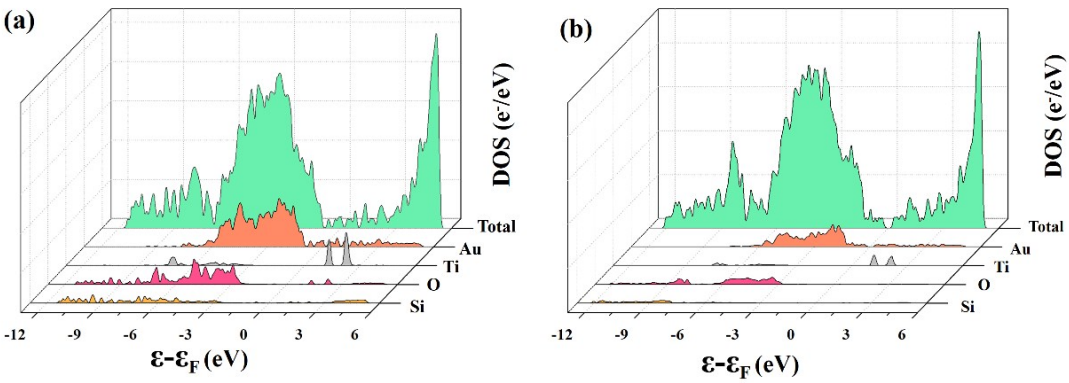

Fig. S7 Projected DOS of Au-Ti interface in (a) Au-Ti@MFI and (b) Au/TS-1, respectively.

Note: When the states of Au and Ti overlap below the Fermi level, an electronic interaction would occur between them.[6] Therefore, density of state (DOS) was used to study the states of Au and Ti as shown in in Fig. S7. In the case of Au-Ti@MFI, Au state coincides with Ti state

below the Fermi level, indicating great possibility of charge transfer between Au and Ti. As a comparison for Au/TS-1, scarce overlaps of Au-Ti states can be observed, implicating scarce possibility of charge transfer. Thus, when Au NPs are encapsulated adjacent to Ti, the states of Au and Ti overlap more, leading to an enhanced Au-Ti electronic interaction consequently.

Tab. S1 Performance of Au-Ti@MFI for propylene epoxidation with different Si/Ti ratios.

	Conversion of C_3H_6 % [c]	**Efficiency of H_2 %** [d]	**Selectively of PO %** [e]	**PO Space-time yield g_{PO}/kg_{cat} h** [f]
100[b]	10.3	13.2	84.1	143.4
50	13.4	17.3	86.7	191.5
35	14.8	23.0	83.9	205.0

[a] Reaction conditions: Catalyst, 0.15 g; temperature, 300 °C; Feed gas, $C_3H_6/O_2/H_2/N_2$=1:1:1:7 (vol%); space velocity, 7000 $ml \cdot g^{-1} \cdot h^{-1}$; **Au loading, 0.5 wt%**.
[b] Referred to the Si/Ti ratio of outer TS-1 encapsulation
[c~f] Calculated from the equations described in Experimental Section.

Tab. S2 Performance of Au-Ti@MFI for propylene epoxidation with different Au loadings

	Conversion of C_3H_6 % [c]	**Efficiency of H_2 %** [d]	**Selectively of PO %** [e]	**PO Space-time yield g_{PO}/kg_{cat} h** [f]
0.25 wt% [b]	9.7	14.1	85.5	136.0
0.50 wt%	14.8	23.0	83.9	205.0
1.0 wt%	13.2	16.5	84.8	184.8

[a] Reaction conditions: Catalyst, 0.15 g; temperature, 300 °C; Feed gas, $C_3H_6/O_2/H_2/N_2$=1:1:1:7 (vol%); space velocity, 7000 $ml \cdot g^{-1} \cdot h^{-1}$, **Si/Ti ratio, 35**.
[b] Referred to the overall Au loading of catalyst.
[c~f] Calculated from the equations described in Experimental Section.

Tab. S3 Performance of Au/TS-1 for propylene epoxidation with different Si/Ti ratios.

	Conversion of C_3H_6 % [c]	**Efficiency of H_2 %** [d]	**Selectively of PO %** [e]	**PO Space-time yield g_{PO}/kg_{cat} h** [f]
100[b]	5.2	13.9	74.9	63.7
50	7.2	13.8	77.0	91.1
35	8.7	19.7	76.6	110.5

[a] Reaction conditions: Catalyst, 0.15 g; temperature, 300 °C; Feed gas, $C_3H_6/O_2/H_2/N_2$=1:1:1:7 (vol%); space velocity, 7000 $ml \cdot g^{-1} \cdot h^{-1}$; **Au loading, 0.5 wt%**.
[b] Referred to the Si/Ti ratio of TS-1 support.
[c~f] Calculated from the equations described in Experimental Section.

Tab. S4 Performance of Au/TS-1 for propylene epoxidation with different Au loadings.

	Conversion of C_3H_6 % [c]	**Efficiency of H_2 %** [d]	**Selectively of PO %** [e]	**PO Space-time yield g_{PO}/kg_{cat} h** [f]
0.25 wt% [b]	6.5	14.7	74.4	80.1
0.50 wt%	8.7	19.7	76.6	110.5
1.0 wt%	10.9	17.2	77.0	138.1

[a] Reaction conditions: Catalyst, 0.15 g; temperature, 300 °C; Feed gas, $C_3H_6/O_2/H_2/N_2$=1:1:1:7 (vol%); space velocity, 7000 $ml \cdot g^{-1} \cdot h^{-1}$, **Si/Ti ratio, 35**.
[b] Referred to the overall Au loading of catalyst.
[c~f] Calculated from the equations described in Experimental Section.

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