Electronic Supplementary Information for

New etching process of zinc oxide with controllable etching rate and crystal plane: experiment, calculation, and membrane application

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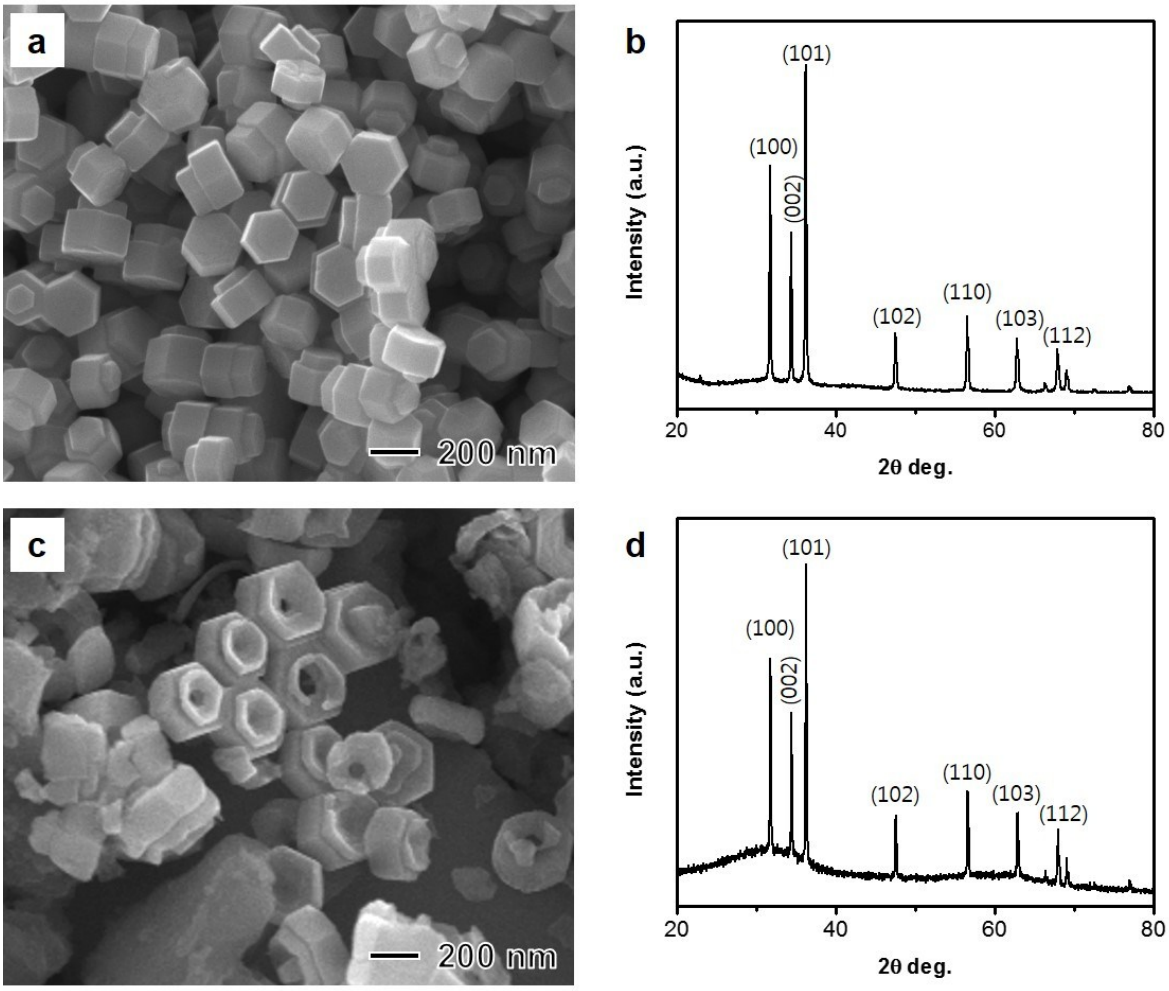

Fig. S1 Comparative analysis of before and after reactions.

(a) SEM image and (b) XRD patterns of ZnO nanobolts synthesized by heating an aqueous solution containing $Zn(NO_3)_2 \cdot 6H_2O$ and octylamine at 60 °C and for 1 h. (c) SEM image and (d) XRD patterns of ZnO nanonuts synthesized by heating an aqueous solution containing ZnO nanobolts and titanium(IV) butoxide at 60 °C for 1 h.

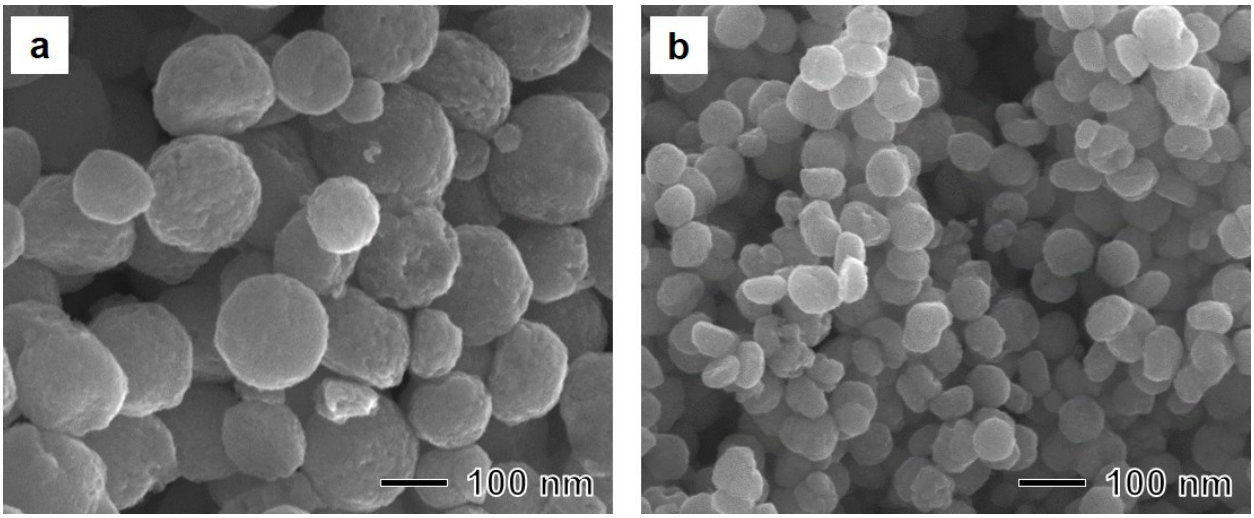

Fig. S2 Etching spherical ZnO particles using titanium(IV) butoxide.

SEM images of spherical ZnO particles (a) before and (b) after addition of titanium(IV) butoxide .

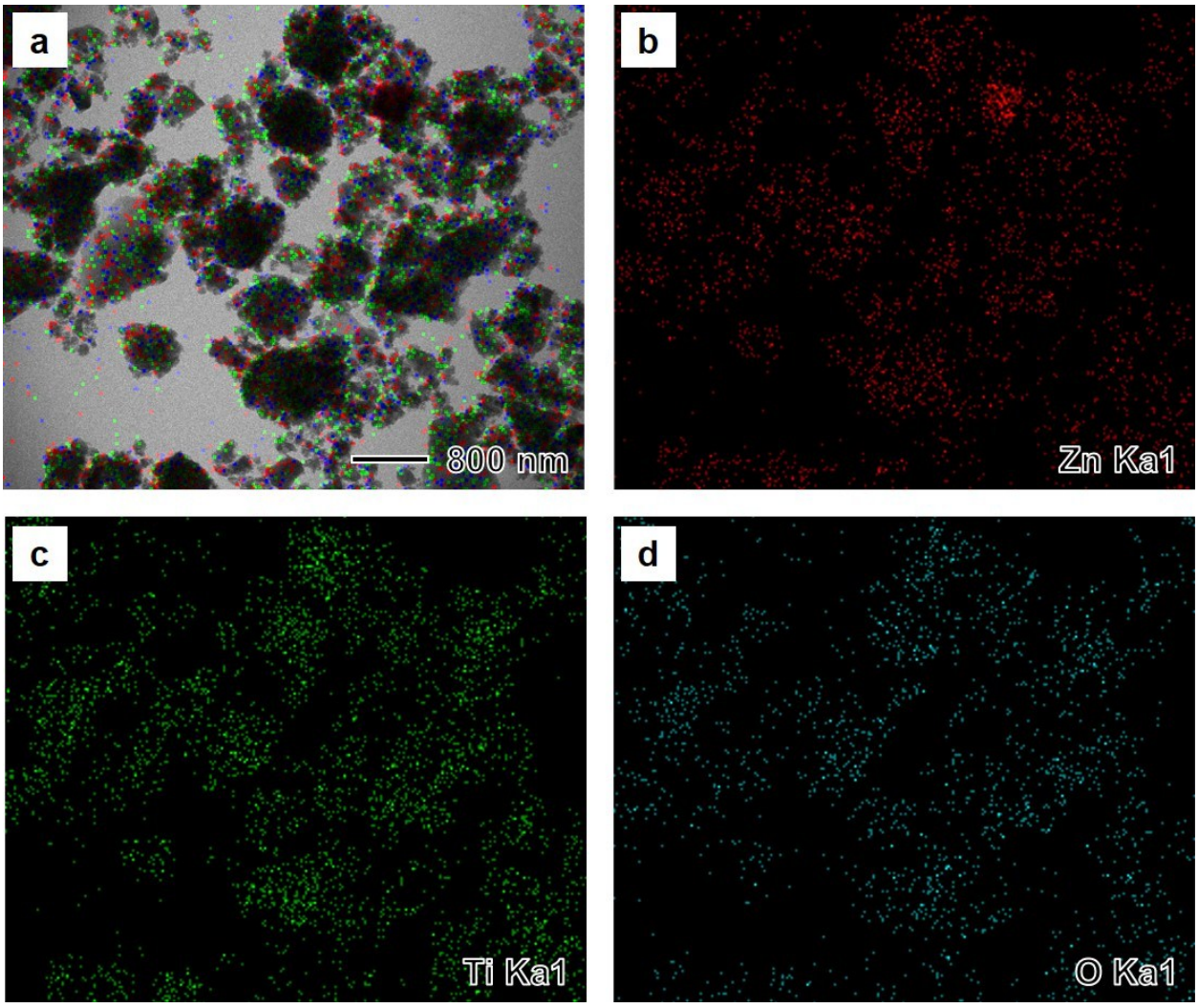

Fig. S3 Elemental mapping of irregular particles made by 24 h reaction.

TEM image and elemental mapping of the sample prepared by heating an aqueous solution containing ZnO nanobolts and titanium(IV) butoxide at 60 °C for 24 h.

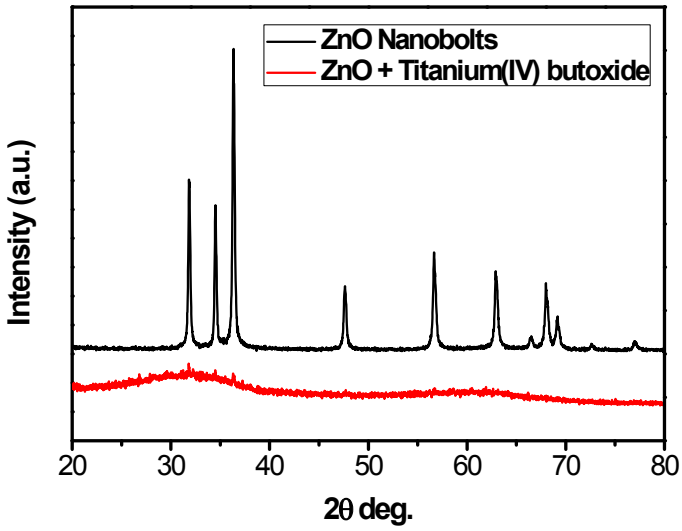

Fig. S4 XRD patterns of samples before and after 24h reaction.

XRD patterns of the sample prepared by heating an aqueous solution containing ZnO nanobolts and titanium(IV) butoxide at 60 °C for 24 h.

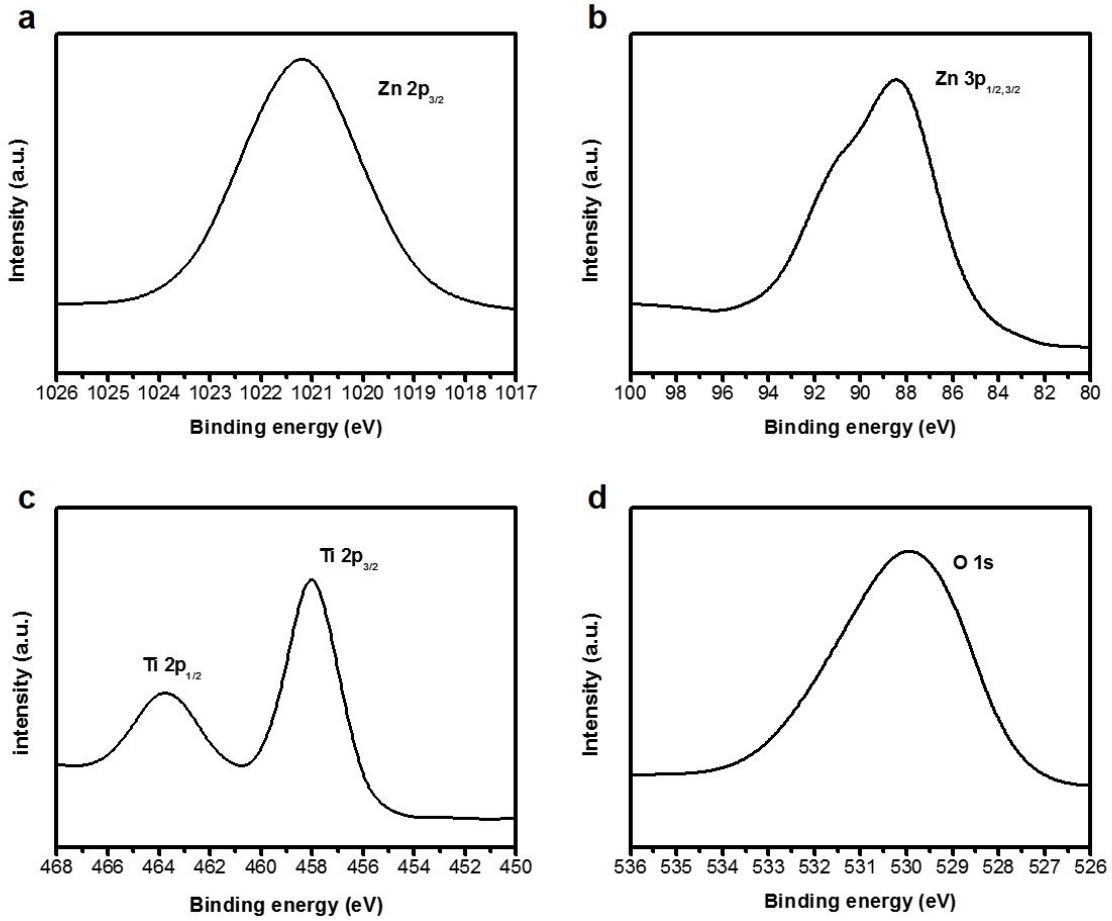

Fig. S5 XPS spectra of sample after 24h reaction.

XPS spectra of the sample prepared by heating an aqueous solution containing ZnO nanobolts and titanium(IV) butoxide at 60 °C for 24 h.

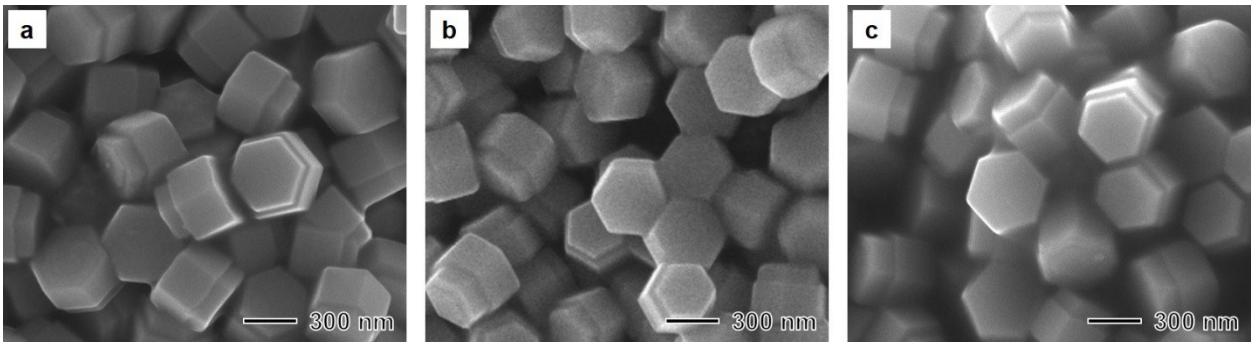

Fig. S6 SEM images of different pH treated ZnO nanobolts.

SEM images of samples prepared by heating aqueous solution containing ZnO nanobolts at 60 °C for 1 h under different pH values. pH values of solution were (a) pH 3.7, (b) pH 7.3, and (c) pH 12, respectively.

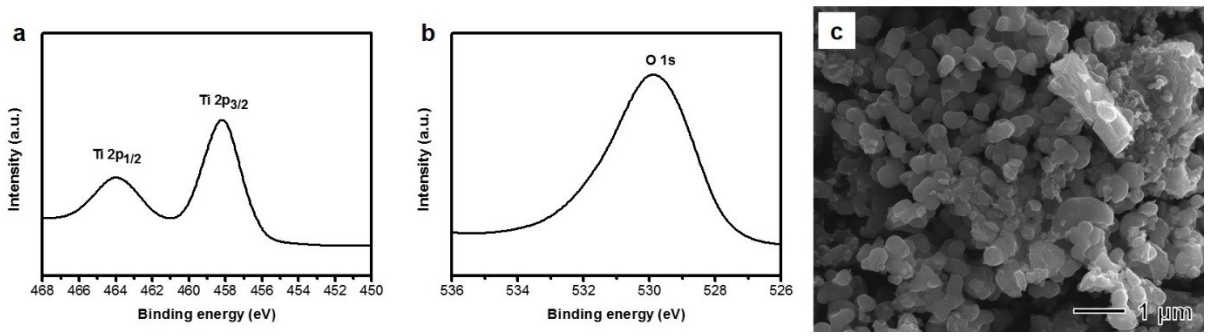

Fig. S7 XPS spectra and SEM images of synthesized amorphous TiO_2.

(a and b) XPS spectra and (c) SEM image of amorphous TiO_2 which were synthesized by heating an aqueous solution containing only titanium butoxide at 60 °C for 1 h.

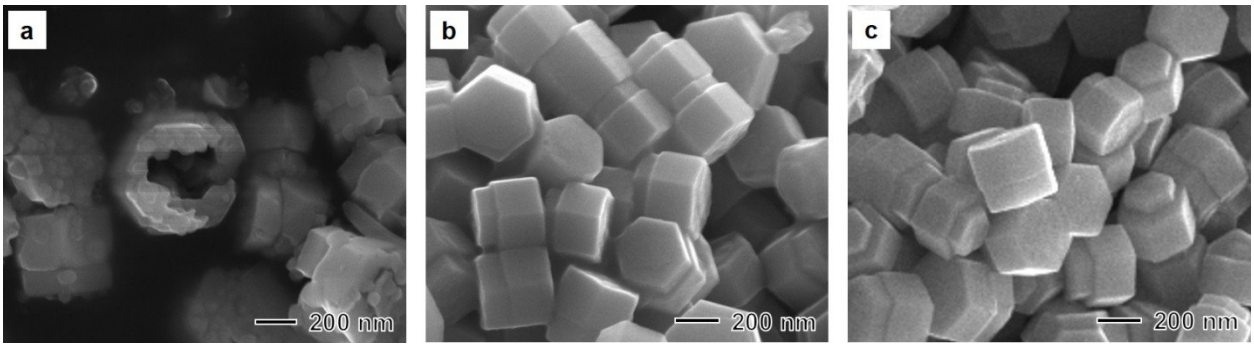

Fig. S8 Effect of kinds of transition metal cations.

SEM images of sample prepared by heating aqueous solution containing ZnO nanobolts and different kinds of transition metal precursor at 60 °C for 1 h. Kinds of metal precursor were (a) $MnCl_2$, (b) KCl, and (c) $CaCl_2$, respectively.

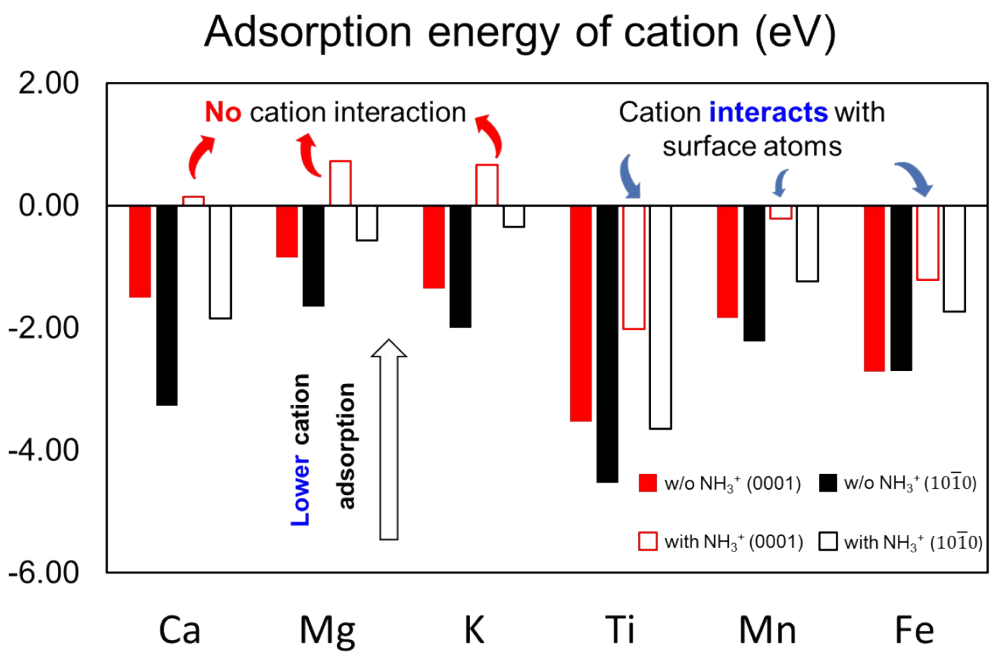

Fig. S9 Effect of kinds of transition metal cations.

Adsorption energies (eV) of Ca, Mg, K, Ti, Mn, and Fe cations on ZnO(0001) and ($10\bar{1}0$) with and without -NH_3^+

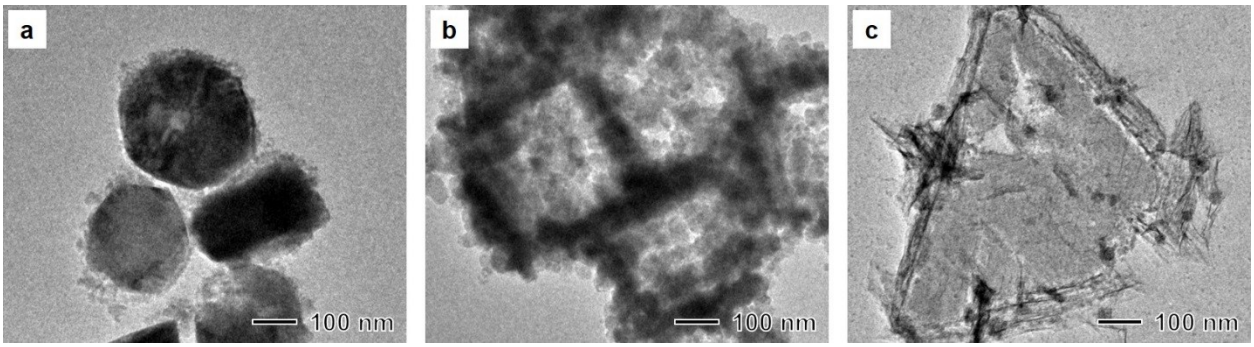

Fig. S10 Morphology change by increasing additional amount of $FeCl_2$.

TEM images of sample prepared by heating aqueous solution containing 1 mmol ZnO nanobolts and various amount of $FeCl_2$ at 60 °C for 1 h. Amount of $FeCl_2$ were (A) 0.2 mmol, (B) 1 mmol, and (C) 1.5 mmol, respectively.

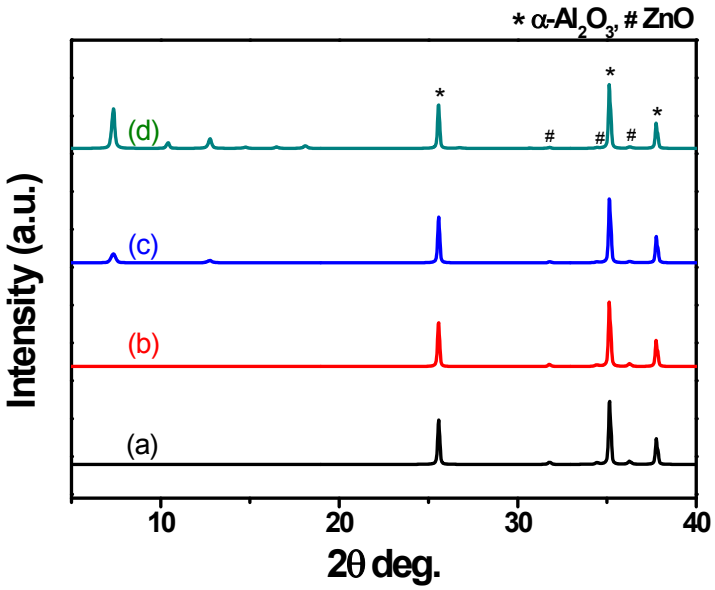

Fig. S11 XRD analyses of sample during fabrication of ZIF-8 membrane.

XRD patterns of (a) ZnO layers prepared via 5 times dip-coating, (b) ZnO layer after the etching process, (c) ZIF-8 seed layer, and (d) ZIF-8 membrane after secondary growth.

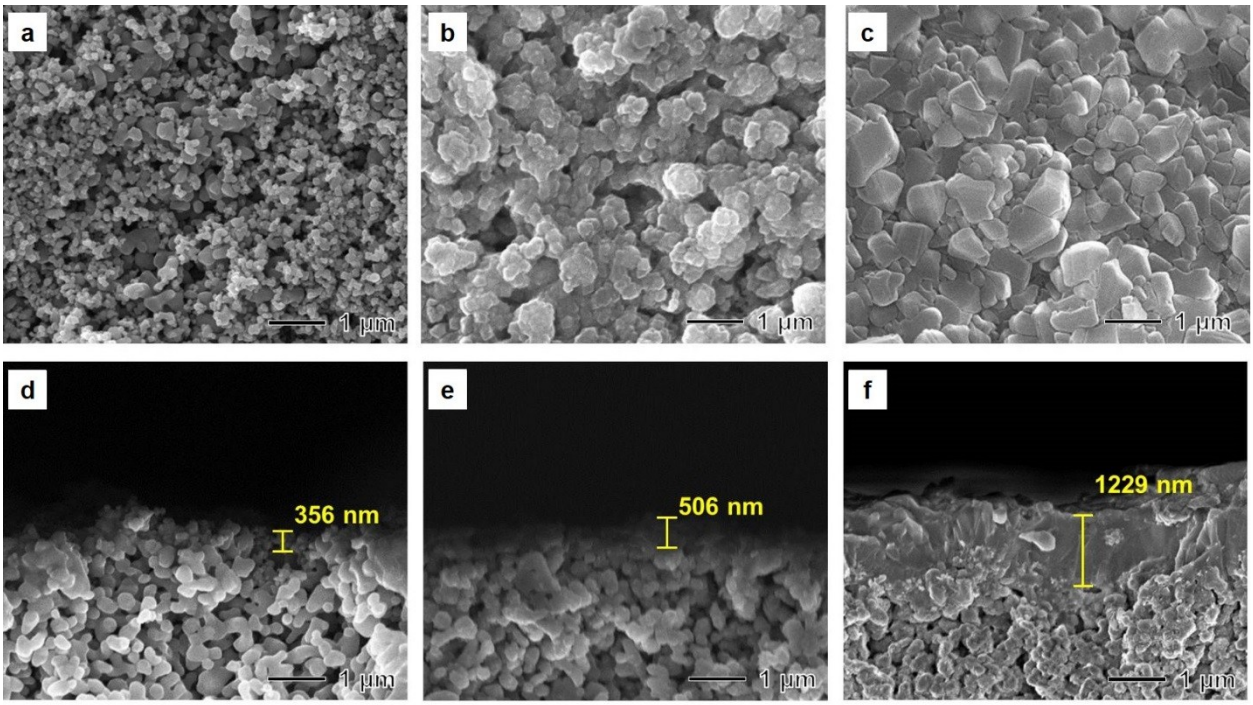

Fig. S12 Fabrication of ZIF-8 membrane using the 2 times dip-coating.

SEM images of (a and d) ZnO layer prepared via 2 times dip-coating, (b and e) ZIF-8 seed layer, and (c and f) ZIF-8 membrane after secondary growth.

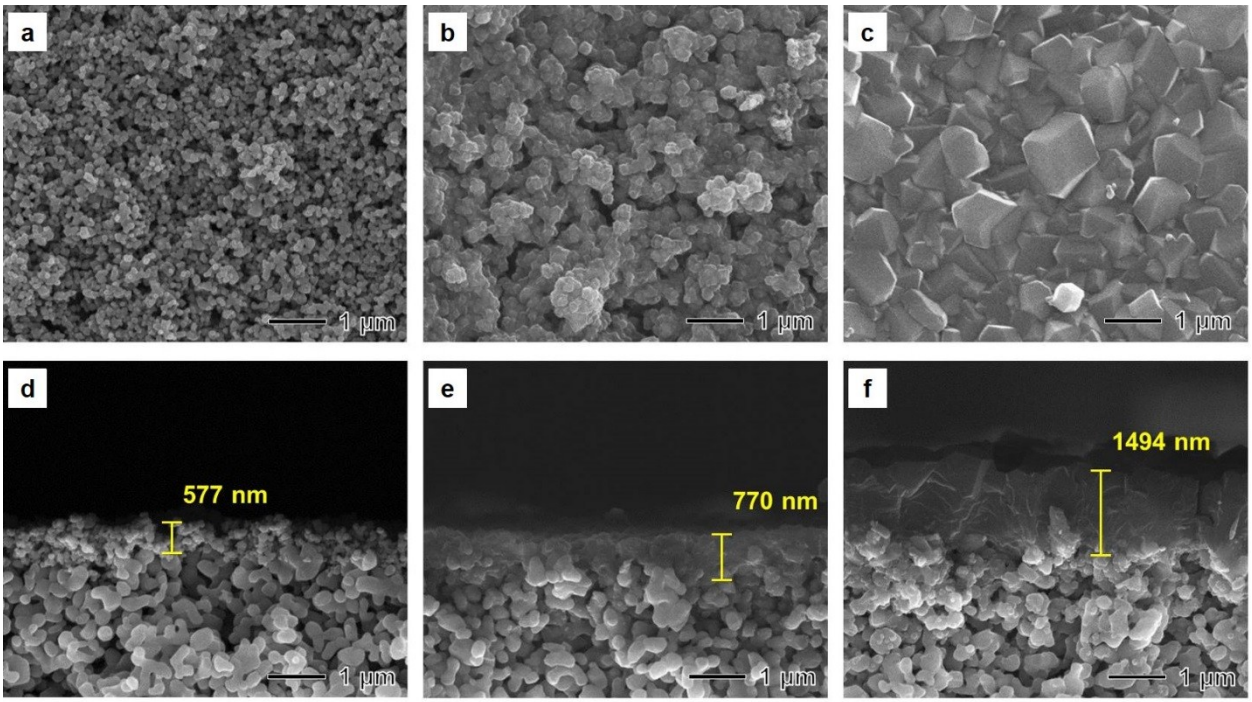

Fig. S13 Fabrication of ZIF-8 membrane using the 3 times dip-coating.

SEM images of (a and d) ZnO layer prepared via 3 times dip-coating, (b and e) ZIF-8 seed layer, and (c and f) ZIF-8 membrane after secondary growth.

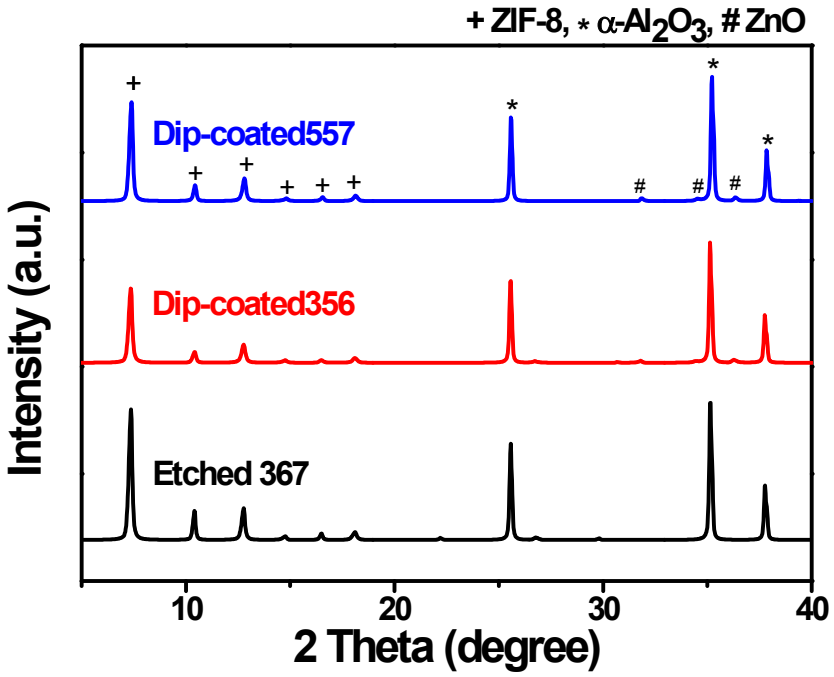

Fig. S14 XRD analyses of ZIF-8 membranes synthesized using different methods.

XRD patterns of ZIF-8 membranes synthesized using etched ZnO layer (etched367), 2 times dip-coating ZnO layer (dip-coated356), and 3 times dip-coating layer (dip-coated577).

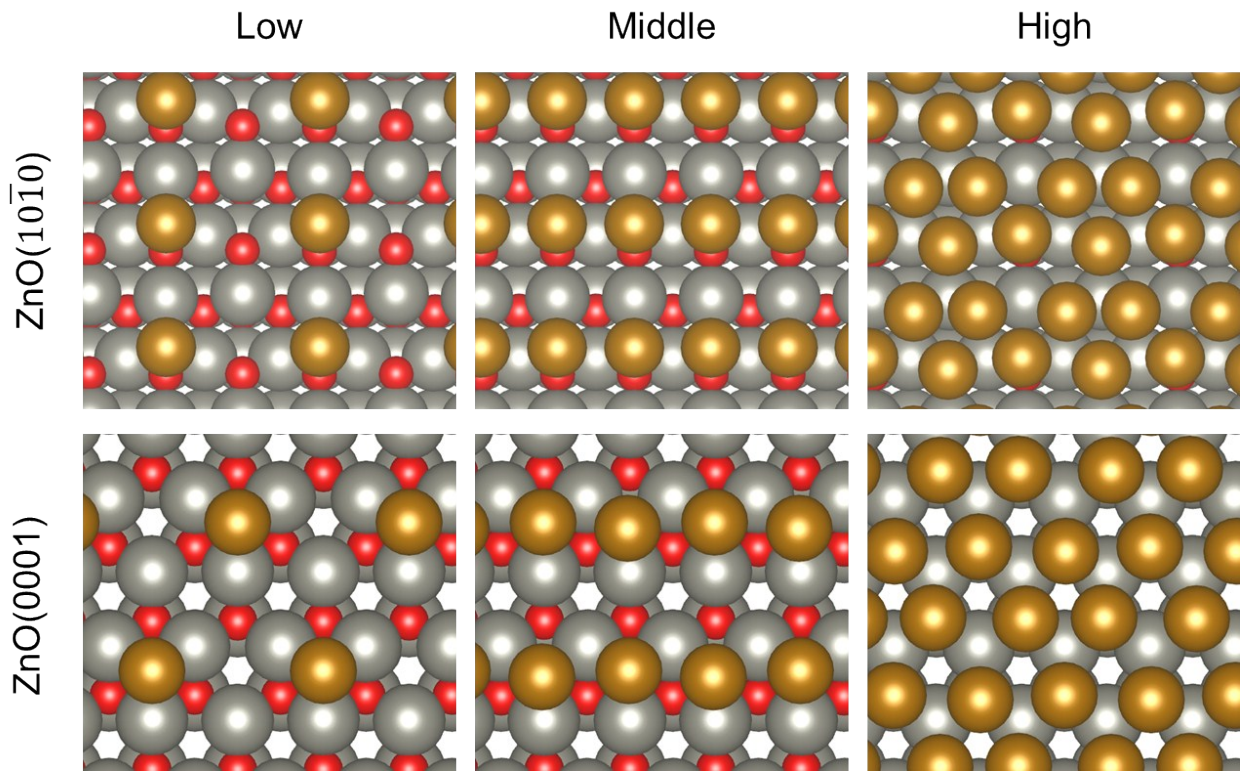

Fig. S15 DFT simulation data.

DFT-optimized structures of adsorbed configurations of Fe cations on ZnO(0001) and ($10\bar{1}0$) as a function of surface coverage. Zn atoms are shown as grey spheres, O atoms as red spheres, Fe atoms as ocher spheres, respectively.

Table S1

Inductively coupled plasma (ICP) result of irregular shaped particles.

Element	Weight (ppm)
Zn	1.73
Ti	1.41

Table S2

Adsorption energies of various cations on ZnO(0001) and $(10\bar{1}0)$ with and without NH_3^+.

	Adsorption energy (eV)			
	Without NH_3^+		With NH_3^+	
	(0001)	$(10\bar{1}0)$	(0001)	$(10\bar{1}0)$
Ca	-1.50	-3.26	0.14	-1.85
Mg	-0.84	-1.64	0.73	-0.57
K	-1.35	-1.99	0.66	-0.35
Ti	-3.52	-4.52	-2.02	-3.65
Mn	-1.84	-2.22	-0.22	-1.24
Fe	-2.72	-2.70	-1.22	-1.73

Table S3

Adsorption energies (eV) of Fe cations on different surface coveragies of ZnO(0001) and $(10\bar{1}0)$.

	(0001)		$(10\bar{1}0)$	
Coverage	Surface Area (atom/Å^2)	Adsorption Energy (eV/atom)	Surface Area (atom/Å^2)	Adsorption Energy (eV/atom)
High	0.1203	-3.96	0.1118	-3.98
Middle	0.0601	-3.27	0.0559	-3.46
Low	0.0301	-2.99	0.0280	-3.21

Table S4

C_3H_6/C_3H_8 binary gas permeance performance of ZIF-8 membranes prepared the etched ZnO layer (etched367), 2 times dip-coating ZnO layer (dip-coated356), and 3 times dip-coating layer (dip-coated577).

Method & Thickness of ZnO layers (nm)	**Thickness of membrane (nm)**	**C_3H_6 Permeance (10^{-10}mol/s m^2 Pa)**	**C_3H_6/ C_3H_8 Selectivity[a]**
Dip-coated 356	1229	325.04	10.54
Etched 367	1218	225.64	55.98
Dip-coated 577	1494	120.36	53.21

[1]Selectivity was calculated by dividing the permeance of C_3H_6 by the permeance of C_3H_8.