Supporting Information

Lattice variations in $CaTiO_3$ cubes and cuboids and their use in photocatalytic benzimidazole formation

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Synthesis of small $CaTiO_3$ cubes and cuboids

To grow 212 nm cubes, 0.041 mL of $TiCl_4$ was added to 20 mL of H_2O/EtOH cosolvent in a vial under vigorous stirring for 5 min, then 0.314 mL of 1.187 M $CaCl_2 \cdot 2H_2O$ solution was added and stirred for another 5 min. Next, 0.5 mL of 5 M KOH solution was slowly introduced with stirring for 30 min. Finally, 0.1 mL of 1.187 M KCl solution was added to the mixed solution and kept stirring for 1 min. A Teflon autoclave containing the final suspension was heated at 200 ºC in an oven for 3 h. After the reaction, the solution was washed several times with 2 M HNO_3 solution, distilled water, and ethanol. To prepare 156 nm $CaTiO_3$ cuboids, the steps are the same as described above. However, the KCl solution added is 2 mL.

Photodegradation of rhodamine B using $CaTiO_3$ crystals

For fair comparison of photocatalytic activity, the total surface area for each $CaTiO_3$ shape should be kept the same. Table S3 provides the calculated weights of different samples needed for the photodegradation experiment. For rhodamine B (RhB) photodegradation reaction, $CaTiO_3$ crystals were weighed and placed inside a quartz cell measuring 4 cm × 4 cm × 4 cm. Subsequently, 45 μL of the RhB solution was added, and the volume was adjusted to 45 mL with water. The quartz cell was then positioned 30 cm away from a xenon lamp with a power density set at 1 W/cm^2, and stirred on a hot plate. At regular time intervals, 1 mL of the solution was extracted and promptly centrifuged for spectral measurements.

Benzimidazole synthesis using recycled photocatalyst

Using 2.7 mg of micron-sized $CaTiO_3$ cubes for the first cycle of the benzimidazole synthesis produced a yield of approximately 67%. After the reaction, the cubes were recovered by centrifugation and rinsed twice with ethanol to remove any possible impurities from the reaction mixture. The remaining solid was dried in vacuum environment for 12 h. Because of the loss of some particles sticking to the centrifuge tube, the used particles were combined to obtain another 2.7 mg of catalyst for the next reaction cycle.

Electron paramagnetic resonance measurement

Due to the common presence of impurities in commercially available DMPO (5,5-dimethyl-1-pyrroline-N-oxide), it is essential to purify it using activated carbon prior to utilization. First, 30 mg of DMPO was dissolved in 6 mL of methanol. Following the addition of activated carbon, the mixture underwent sonication for 2 min to facilitate the removal of DMPO impurities by the activated carbon. Subsequently, the mixture was subjected to centrifugation to separate the activated carbon, resulting in the acquisition of a pure DMPO solution.

Under atmospheric conditions, 2.7 mg of $CaTiO_3$ cuboids was added to the DMPO solution in a 15 mL oven-dried quartz tube. After sonication for 1 min, the mixture underwent 2 min of exposure to Xe lamp radiation. Subsequently, the irradiated mixture was transferred to an Eppendorf tube, covered with aluminum foil, and promptly delivered to the EPR laboratory for measurement.

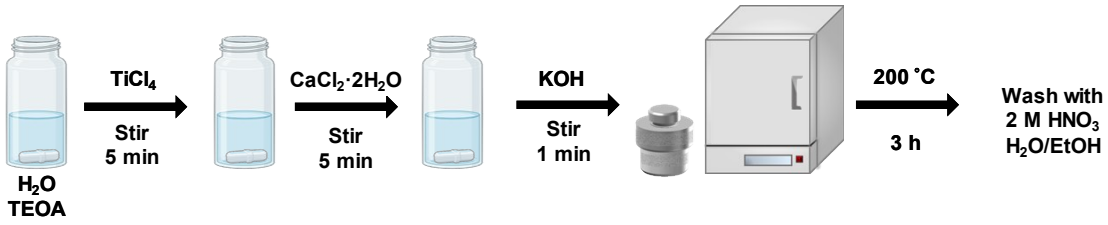


Fig. S1 Procedure for synthesizing large $CaTiO_3$ cubes and cuboids.

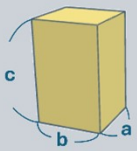
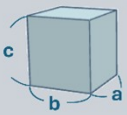
Table S1 Reagent amounts used to grow large $CaTiO_3$ cubes and cuboids.

886 nm Cube	H_2O	TEOA	99% $TiCl_4$	1.187 M $CaCl_2·2H_2O$	5 M KOH	Temperature	Time
	4.033 mL	2 M 15.7 mL	0.041 mL	0.314 mL	0.5 mL	200 °C	3 h
695 nm Cube	H_2O	TEOA	99% $TiCl_4$	1.187 M $CaCl_2·2H_2O$	5 M NaOH	Temperature	Time
	4.033 mL	2 M 15.7 mL	0.02775 mL	0.236 mL	0.5 mL	200 °C	3 h
393 nm Cube	Butanol	TEOA	99% $TiCl_4$	1.187 M $CaCl_2·2H_2O$	5 M NaOH	Temperature	Time
	4.033 mL	1.8 M 15.7 mL	0.02775 mL	0.236 mL	0.5 mL	190 °C	3 h
725 nm Cuboid	Hexanol	TEOA	99% $TiCl_4$	1.187 M $Ca(NO_3)_2·4H_2O$	5 M KOH	Temperature	Time
	2.017 mL	1.78 M 7.85 mL	0.01388 mL	0.118 mL	0.25 mL	190 °C	2.5 h

Table S2 Reagent amounts used to grow small $CaTiO_3$ cubes and cuboids.

	H_2O	Ethanol	99% $TiCl_4$	1.187 M $CaCl_2 \cdot H_2O$	5 M KOH	1.187 M KCl	Temperature	Time
 212 nm Cube	10.5 mL	9.5 mL	0.041 mL	0.314 mL	0.5 mL	0.1 mL	200 °C	3 h
	H_2O	Ethanol	99% $TiCl_4$	1.187 M $CaCl_2 \cdot H_2O$	5 M KOH	1.187 M KCl	Temperature	Time
 90 nm Cube	10.5 mL	9.5 mL	0.041 mL	0.314 mL	0.5 mL	0.3 mL	200 °C	3 h
	H_2O	Ethanol	99% $TiCl_4$	1.187 M $CaCl_2 \cdot H_2O$	5 M KOH	1.187 M KCl	Temperature	Time
 156 nm Cuboid	10.5 mL	9.5 mL	0.041 mL	0.314 mL	0.5 mL	2 mL	200 °C	3 h

Table S3 Calculations for weights of $CaTiO_3$ crystals needed for rhodamine B photodegradation.

$CaTiO_3$	725 nm cuboids	695 nm cubes	156 nm cuboids	212 nm cubes
model				
length of a side (nm)	a = 440 b = 465 c = 725	a = 647 b = 666 c = 695	a = 106 b = 119 c = 156	a = 168 b = 192 c = 212
A (nm^2)	1721450	2686874	112285	217152
V (nm^3)	148335000	299476890	1929942	6838272
weight of single particle (g)	5.90373×10^{-13}	1.19192×10^{-12}	2.72163×10^{-14}	7.68117×10^{-15}
fixed total surface area (nm^2)	3×10^{16}	3×10^{16}	3×10^{16}	3×10^{16}
number of particles	17427168956	11165391455	1.38152×10^{11}	2.67177×10^{11}
weight (mg)	10.3	13.3	3.8	2.1

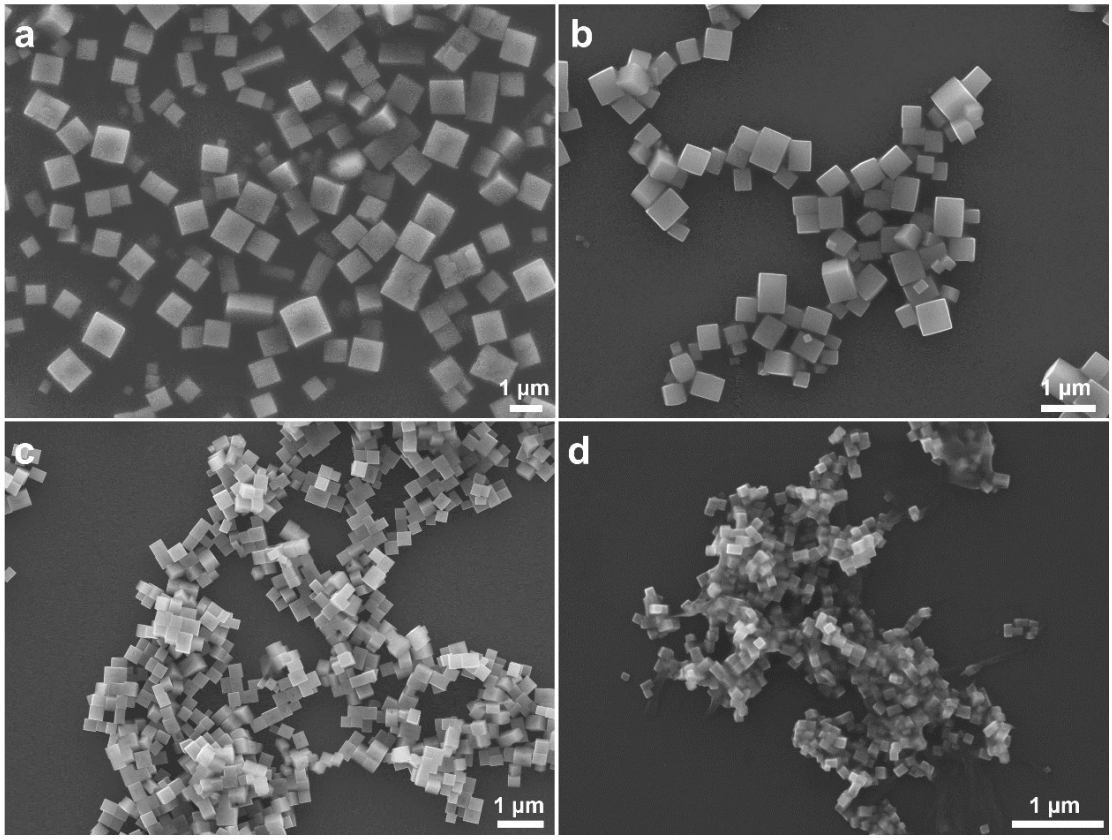


Fig. S2 SEM images of (a) 886, (b) 393, (c) 253, and (d) 90 nm $CaTiO_3$ cubes.

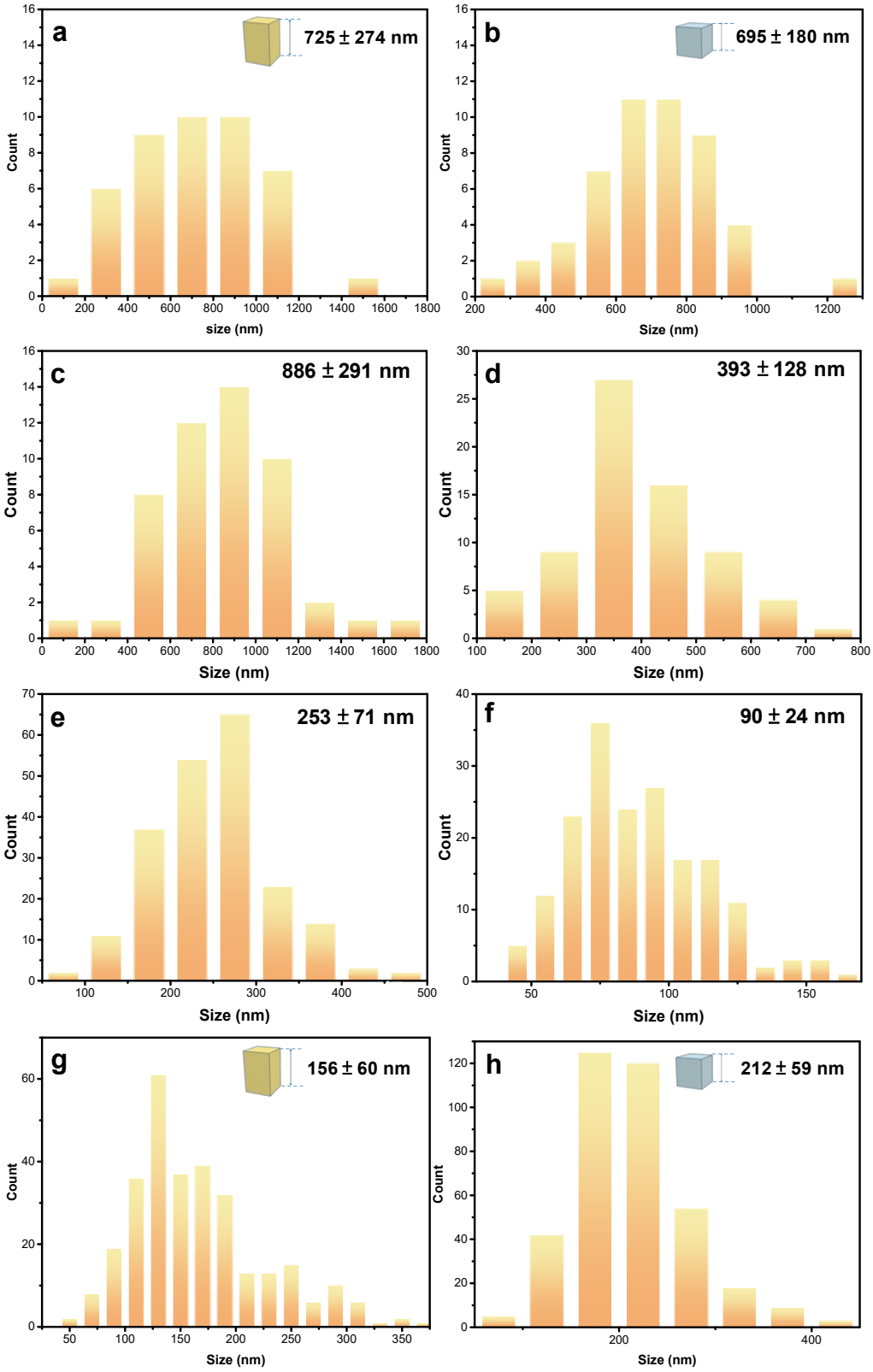


Fig. S3 Size distribution histograms of $CaTiO_3$ (a, g) cuboids and (b, c–f, h) cubes.

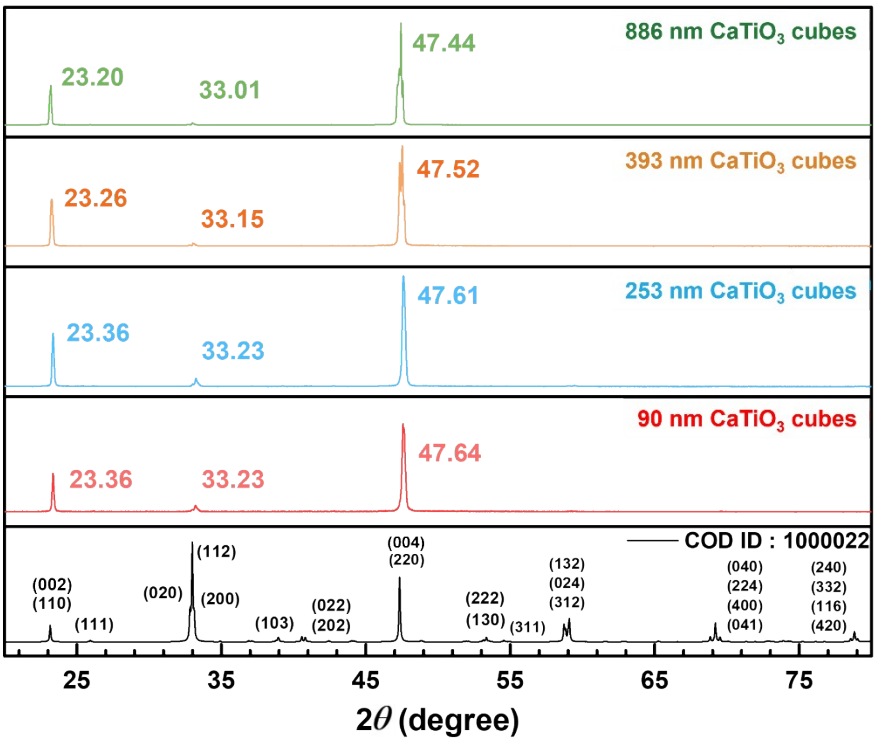


Fig. S4 XRD patterns of size-tunable $CaTiO_3$ cubes and a reference pattern.

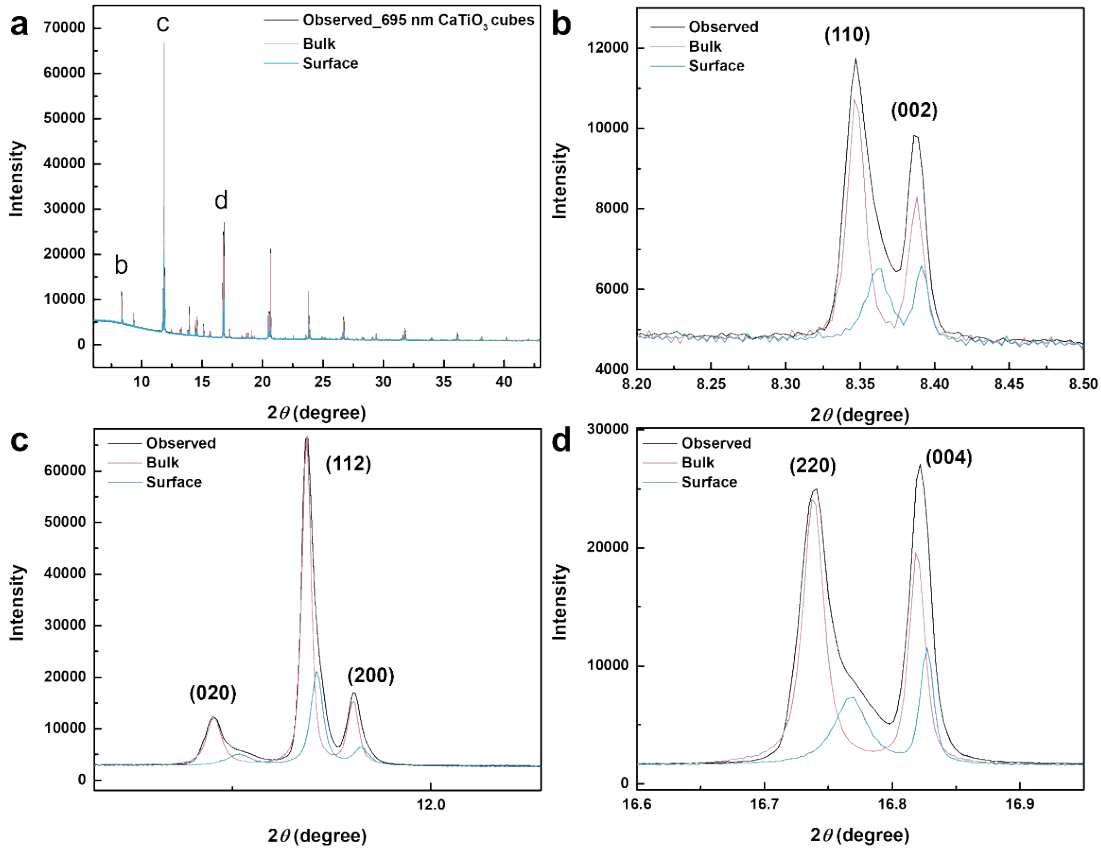


Fig. S5 (a–d) Rietveld refinement of 695 nm $CaTiO_3$ cubes into bulk and surface lattice components.

Table S4 Crystallographic data of $CaTiO_3$ cuboids and cubes.

Morphology	**725 nm Cuboids**		**695 nm Cubes**	
Formula	$CaTiO_3$			
Radiation source	TPS 19A			
Wavelength (Å)	0.56025			
Crystal system	Orthorhombic			
Space group	P b n m (62)			
Z (repeat unit)	4			
2θ range (°)	6.0 to 43.0			
Rietveld refinement	GSAS II (*J. Appl. Cryst.* **2013**, *46*, 544–549)			
d-spacing resolution (Å)	0.764			
Zero-point shift (°)	0.0001		0.0014	
Phases	**Bulk**	**Surface**	**Bulk**	**Surface**
a (Å)	5.40394(5)	5.39734(6)	5.40417(3)	5.39952(8)
b (Å)	5.48185(7)	5.46818(8)	5.48464(3)	5.47024(2)
c (Å)	7.66070(7)	7.65866(6)	7.66205(3)	7.65850(5)
V (Å^3)	226.938(5)	226.035(5)	227.103(3)	226.206(7)
α, β, γ (°)	90			
c/*a*	1.4176	1.4190	1.4178	1.4184
Weight percentage (%)	46.0(6)	54.0 (6)	72.3(5)	27.7(5)
Mean μ strain (Δd/d)	0.002644	0.003167	0.002367	0.003373
R(F^2) (%)	9.288	9.095	9.296	9.930
wR (%)	5.234		3.678	

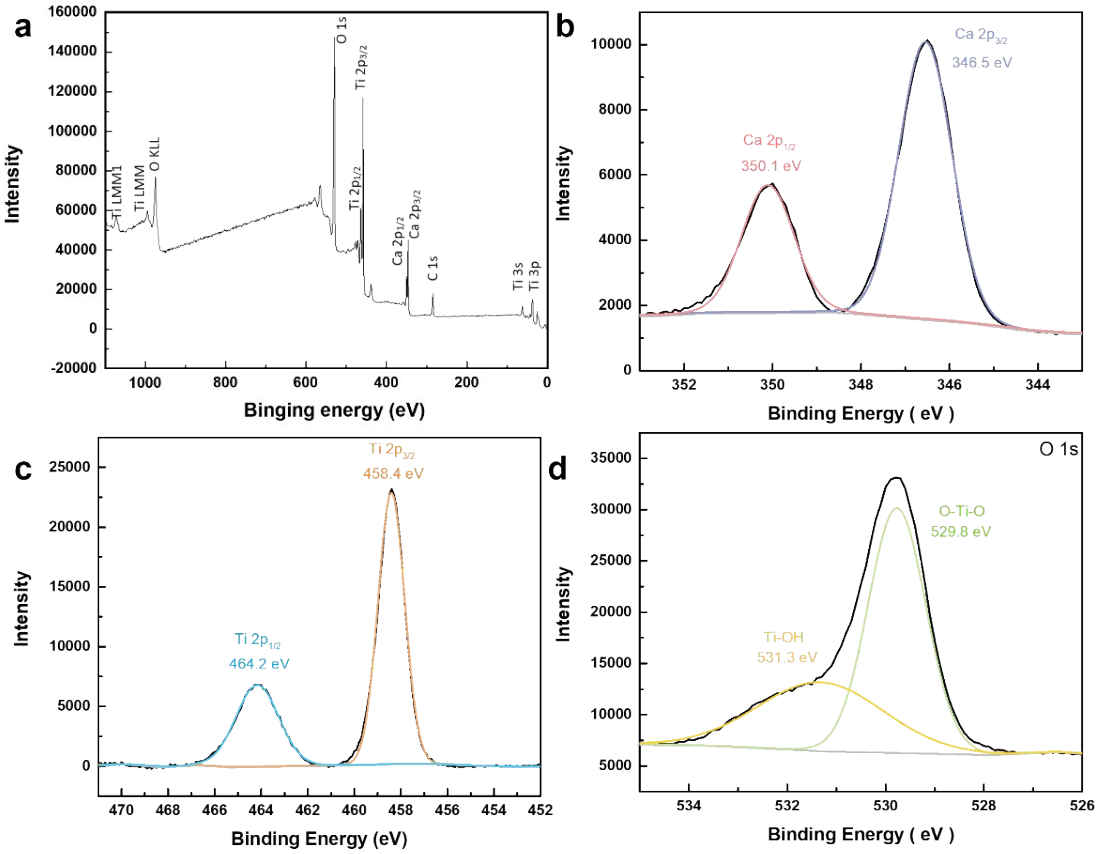


Fig. S6 XPS spectra of 725 nm $CaTiO_3$ cuboids. (a) Full XPS spectra. (b–d) Expanded HR-XPS spectra of the (b) Ca 2p, (c) Ti 2p, and (d) O 1s peaks. The C 1s peak is utilized for instrument error calibration.

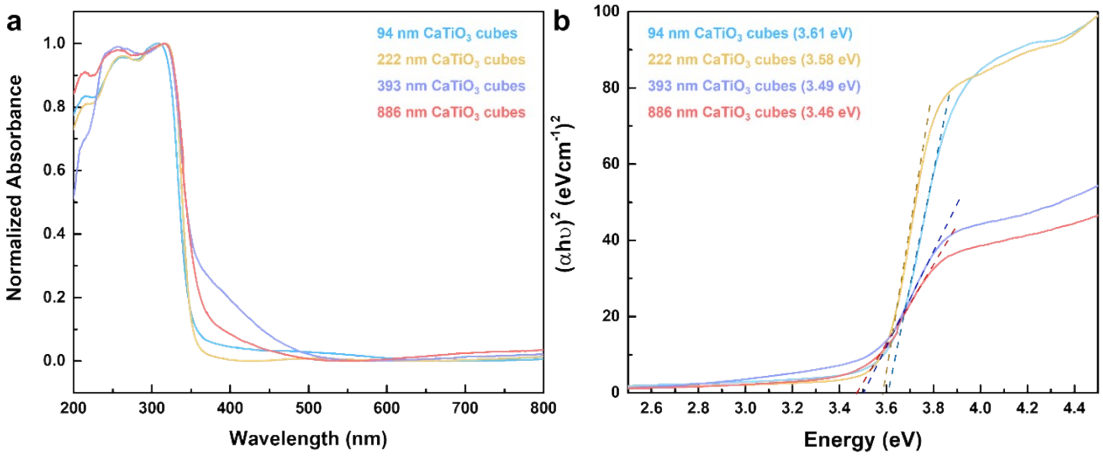


Fig. S7 (a) Diffuse reflectance spectra of size-tunable $CaTiO_3$ cubes and (b) the corresponding Tauc plot.

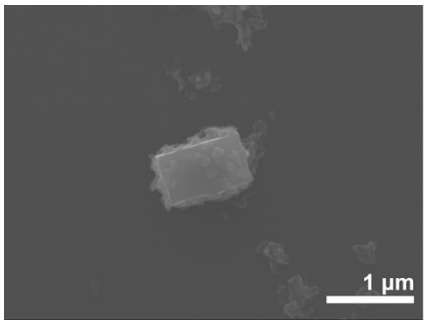


Fig. S8 SEM image of a $CaTiO_3$ cuboid after the photodegradation experiment.

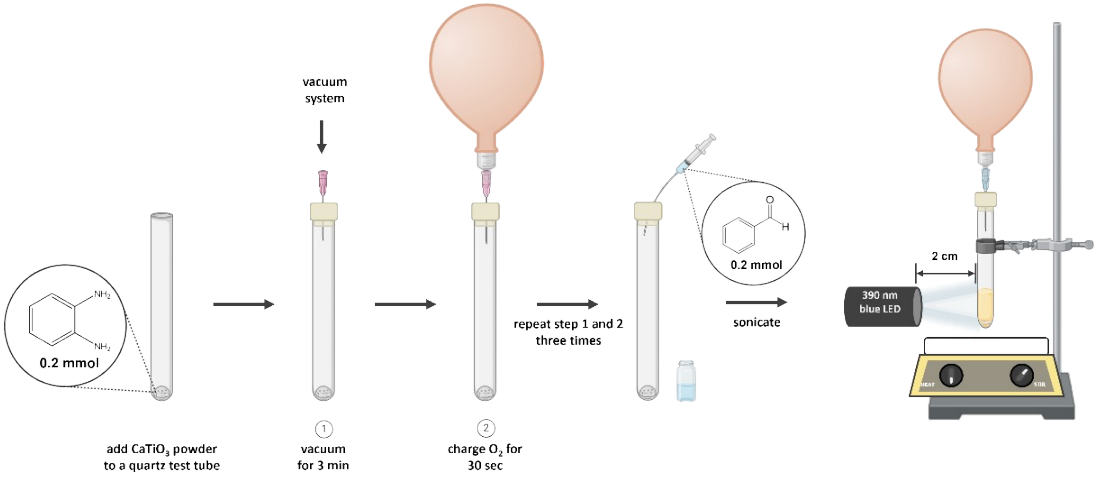


Fig. S9 Procedure for the synthesis of benzimidazoles.

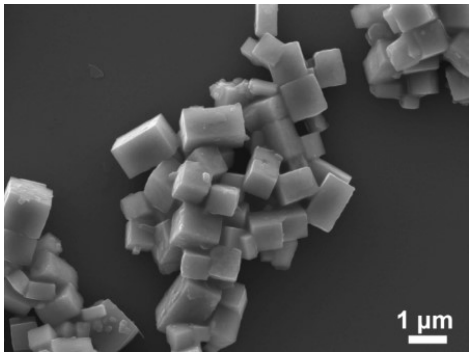


Fig. S10 SEM image of $CaTiO_3$ cuboids after the benzimidazole synthesis experiment.

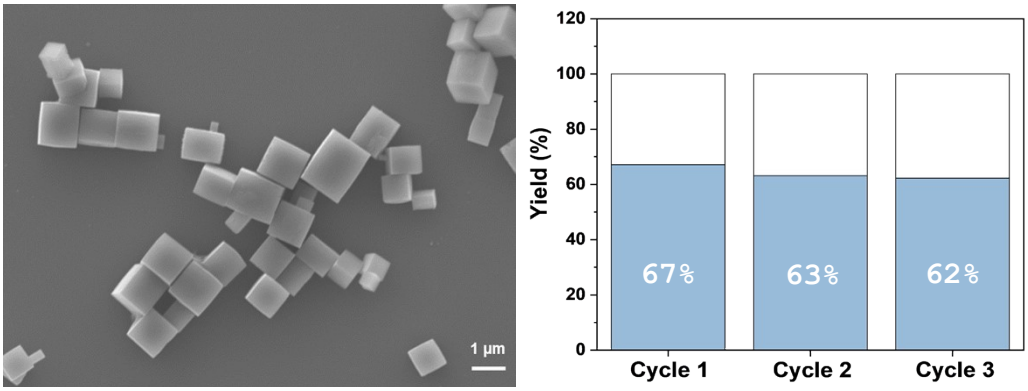


Fig. S11 Benzimidazole synthesis with 3 cycles of reactions using 2.7 mg of micron-sized $CaTiO_3$ cubes as the catalyst.

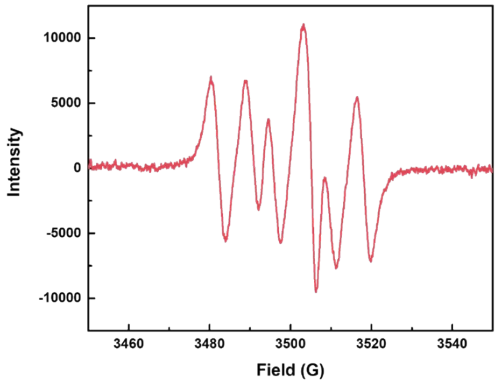
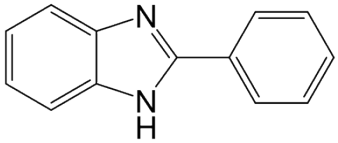


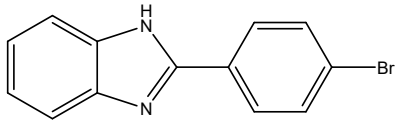
Fig. S12 EPR spectrum of photoirradiated $CaTiO_3$ cuboids dispersed in methanol.

Spectroscopic Data



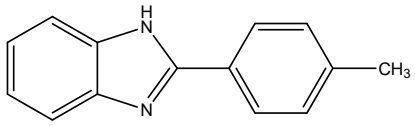
2-phenyl-1H-benzo[d]imidazole

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 12.92 (s, 1H, NH), 8.19–8.16 (*d*, 2H, Ar–H, *J* = 4.0 Hz), 7.58–7.44 (m, 5H, Ar–H), 7.19–7.16 (m, 2H, Ar–H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 151.6, 130.0, 129.31, 126.9.



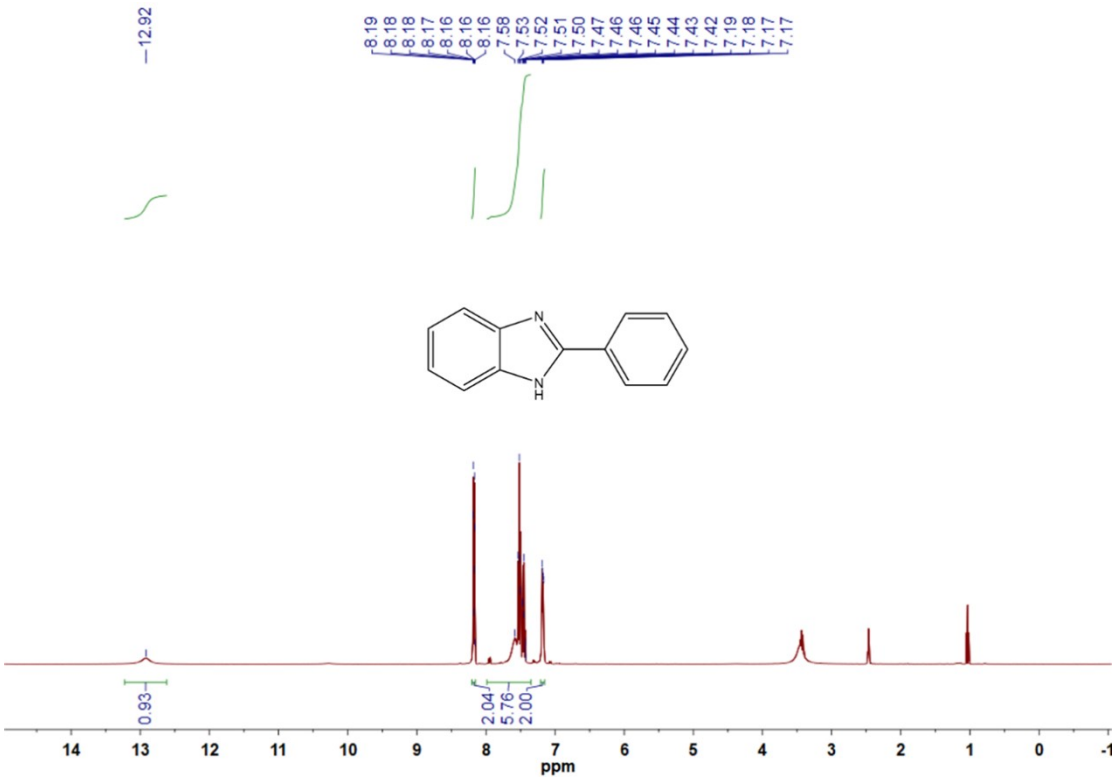
2-(4-bromophenyl)-1H-benzimidazole

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm), 8.12 (*d*, 2H, *J* = 7.8 Hz), 7.76 (d, 2H, J = 8.4 Hz), 7.60 (s, 2H).

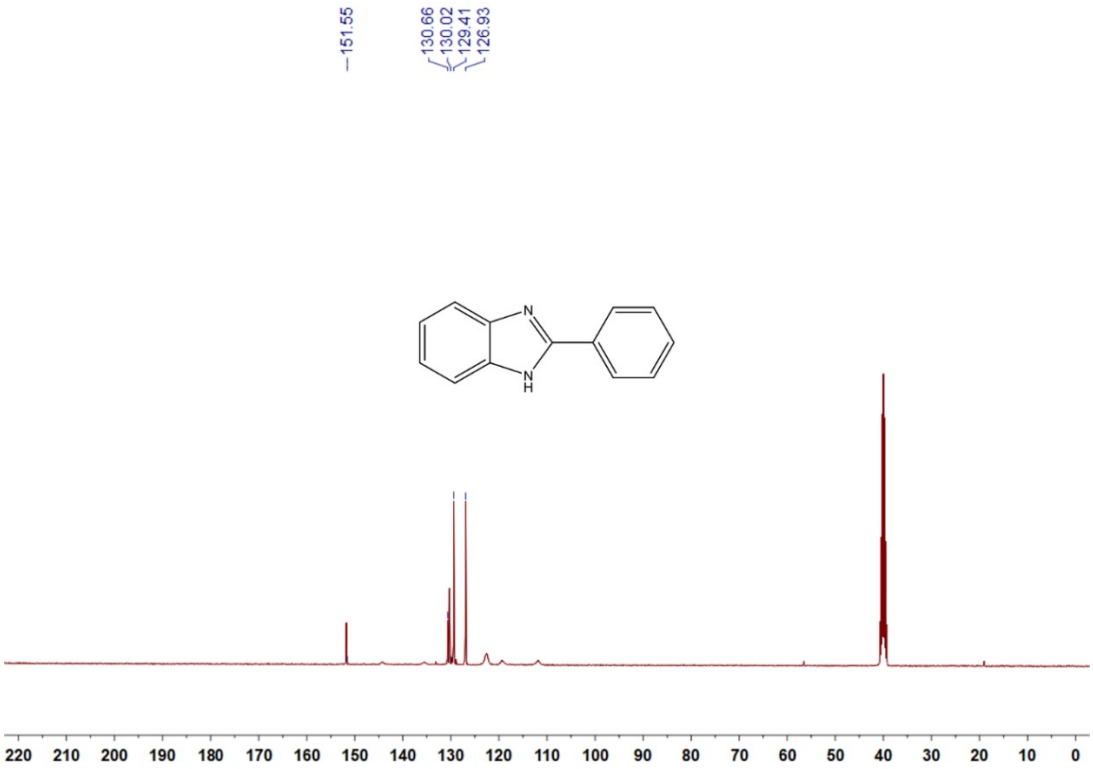


2-(4-methylphenyl)-1H-benzimidazole

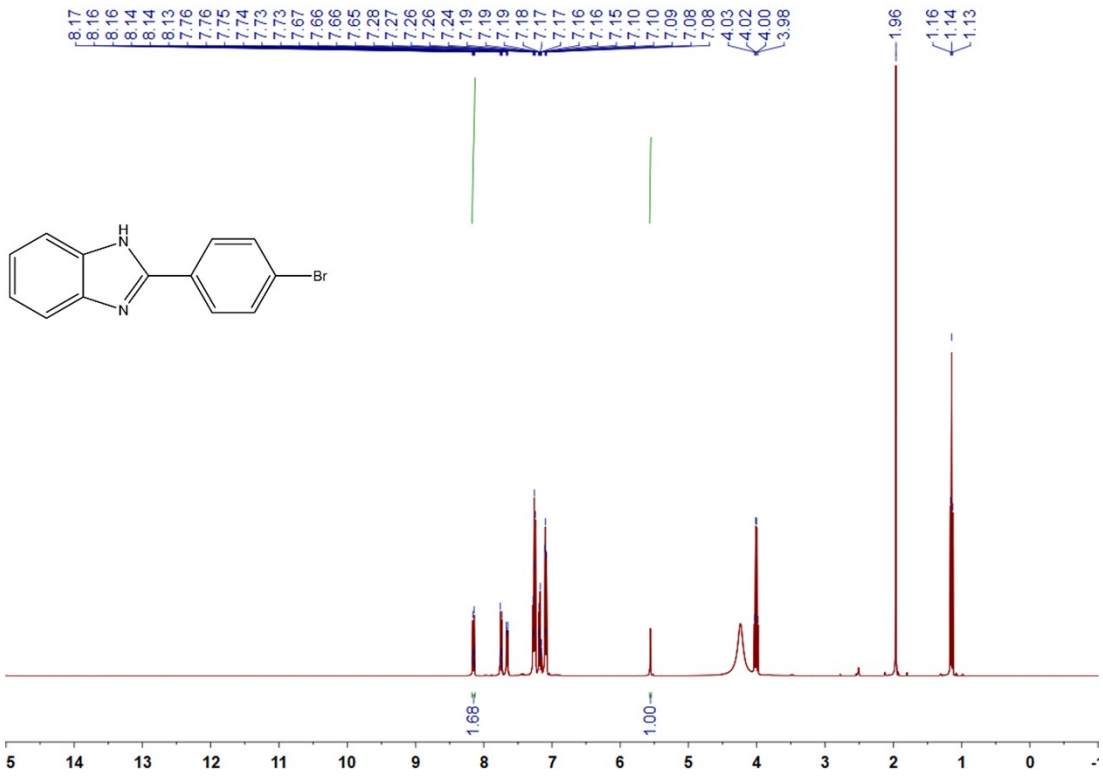
^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 12.89 (br, 1H), 8.14 (*d*, 2H, *J* = 8.0 Hz), 7.50 (d, 2H, Ar–H), 7.27–7.11 (m, 4H, Ar–H).



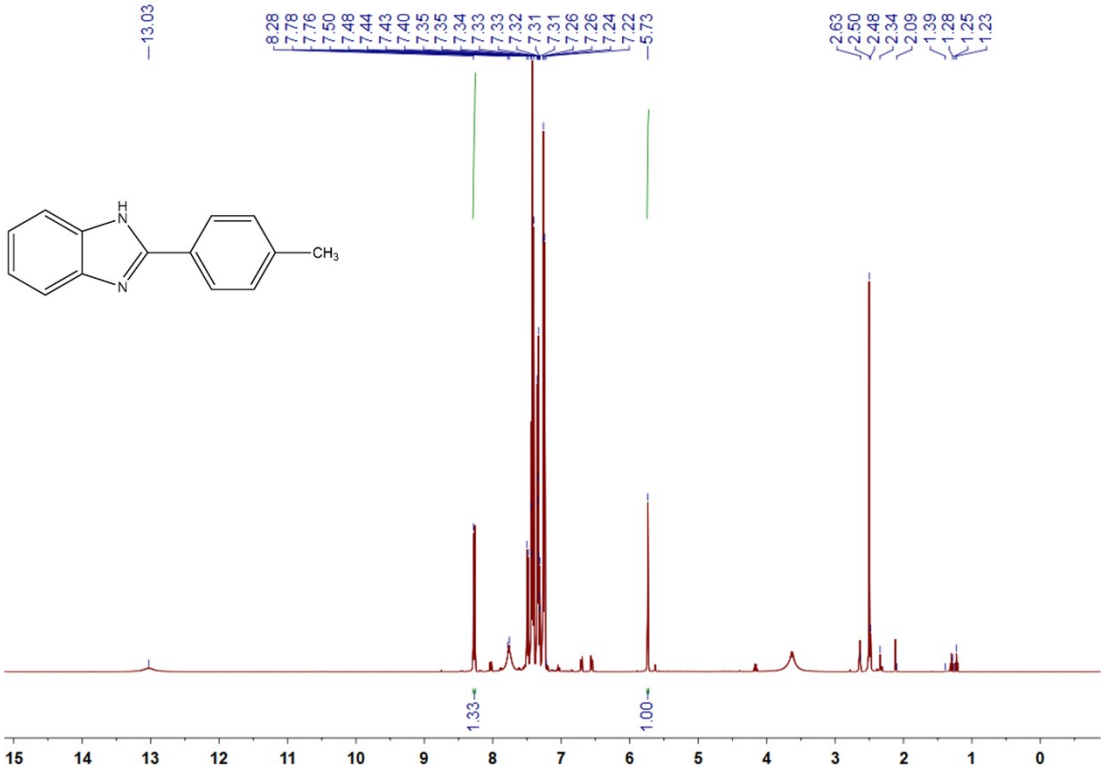
Spectrum S1. Crude ^{1}H NMR spectrum of 2-phenyl-1H-benzo[d]imidazole (d_6-DMSO, 400 MHz).



Spectrum S2. ^{13}C NMR spectrum of 2-phenyl-1H-benzo[d]imidazole (d_6-DMSO, 100 MHz).



Spectrum S3. Crude ^{1}H NMR spectrum of 2-(4-bromophenyl)-1H-benzimidazole (d_6-DMSO, 400 MHz).



Spectrum S4. Crude ^{1}H NMR spectrum of 2-(4-methylphenyl)-1H-benzimidazole (d_6-DMSO, 400 MHz).