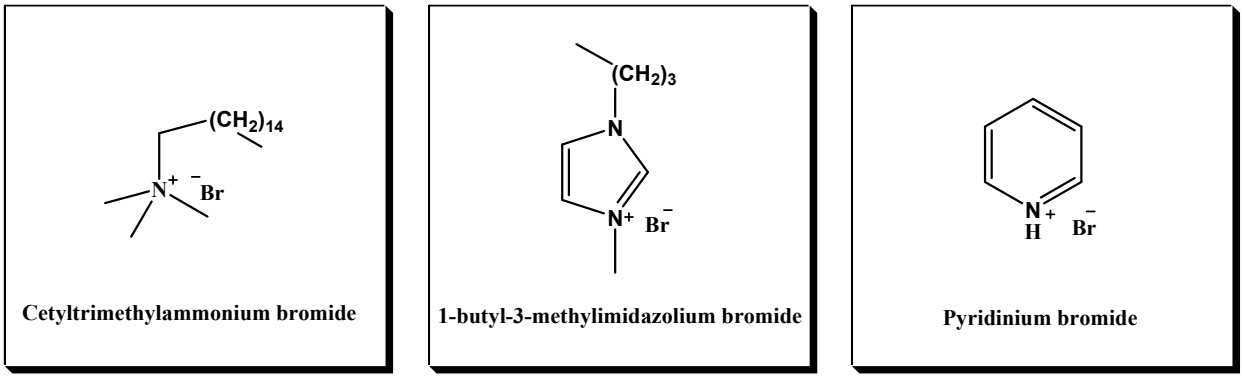
Electronic Supporting Information

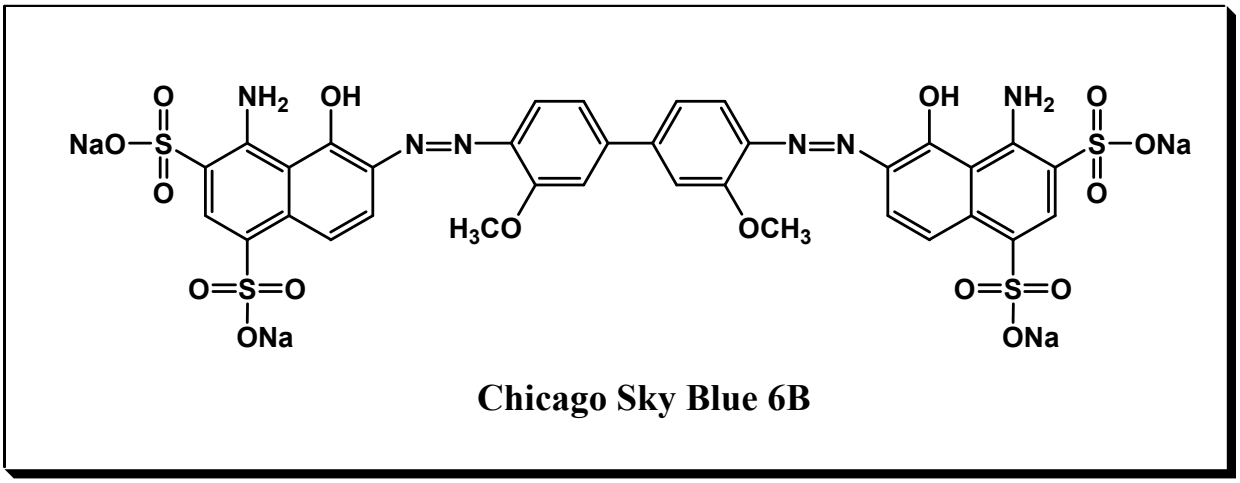
Ligand-assisted Soft-Chemical Synthesis of Self-assembled Shaped Mesoporous Co_3O_4: Efficient Visible Light Photocatalyst

Mouni Roy, Sourav Ghosh, and Milan Kanti Naskar*

Sol-Gel Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700 032, India



A B C



D

Fig. S1: The chemical structure of (A) CTAB, (B) 1-butyl-3-methylimidazolium bromide, (C) pyridinium bromide, and (D) Chicago sky blue 6B.

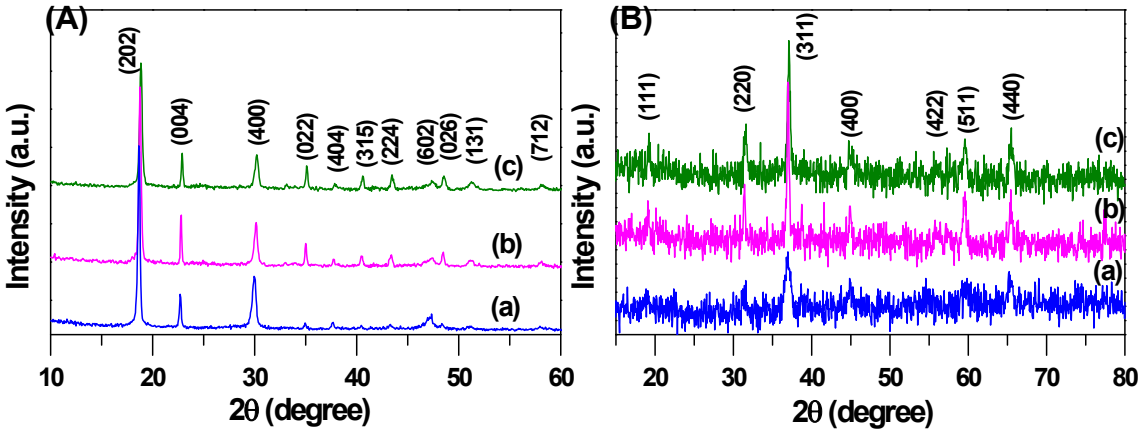


Fig. S2: XRD patterns of (A) as-prepared and (B) calcined samples synthesized using (a) CTAB, (b) IB and (c) PB with molar ratio of template : Co^{2+} as 0.2.

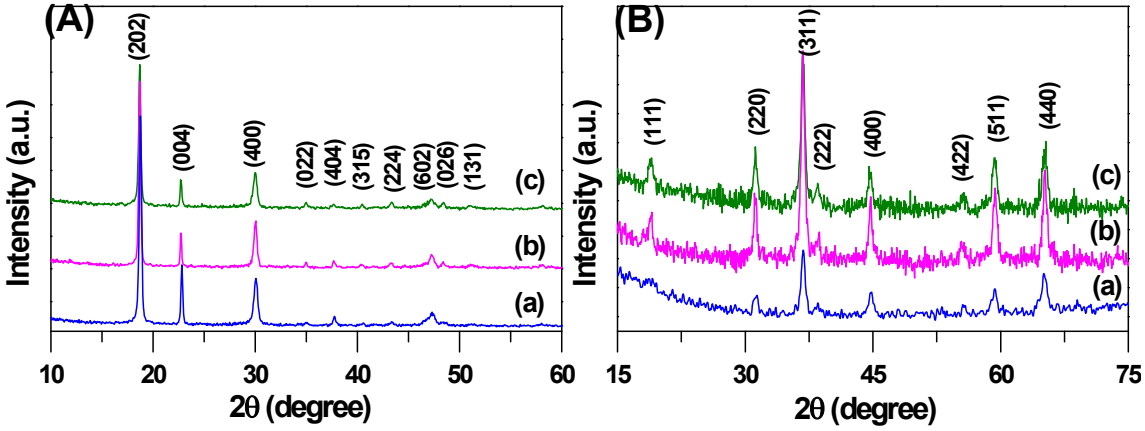


Fig. S3: XRD patterns of (A) as-prepared and (B) calcined samples synthesized using (a) CTAB, (b) IB and (c) PB with molar ratio of template : Co^{2+} as 0.4.

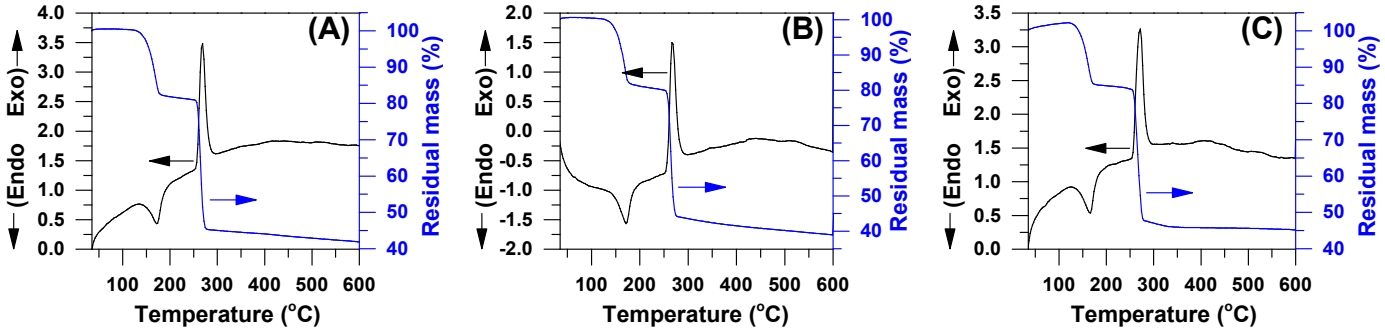


Fig. S4: The DTA and TG curves of the as-prepared (uncalcined) samples prepared using (A) CTAB, (B) IB (C) PB with molar ratio of template : Co^{2+} = 0.3.

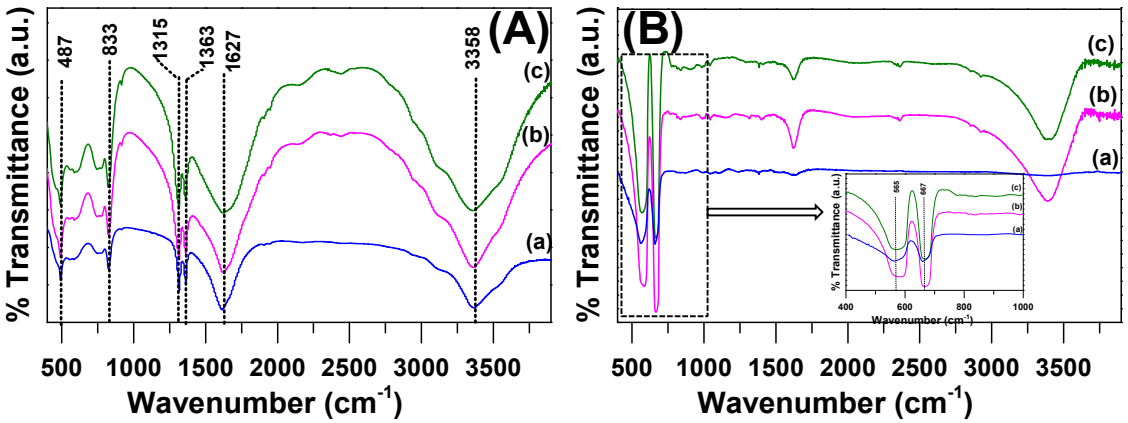


Fig. S5: FTIR spectra of (A) as-prepared and (B) calcined samples synthesized using (a) CTAB, (b) IB and (c) PB with molar ratio of template : Co^{2+} as 0.2.

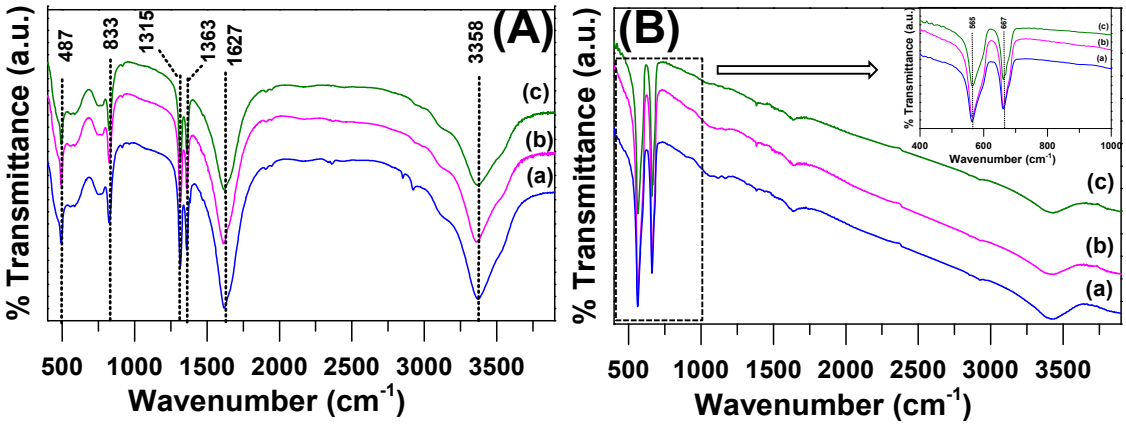


Fig. S6: FTIR spectra of (A) as-prepared and (B) calcined samples synthesized using (a) CTAB, (b) IB and (c) PB with molar ratio of template : Co^{2+} as 0.4.

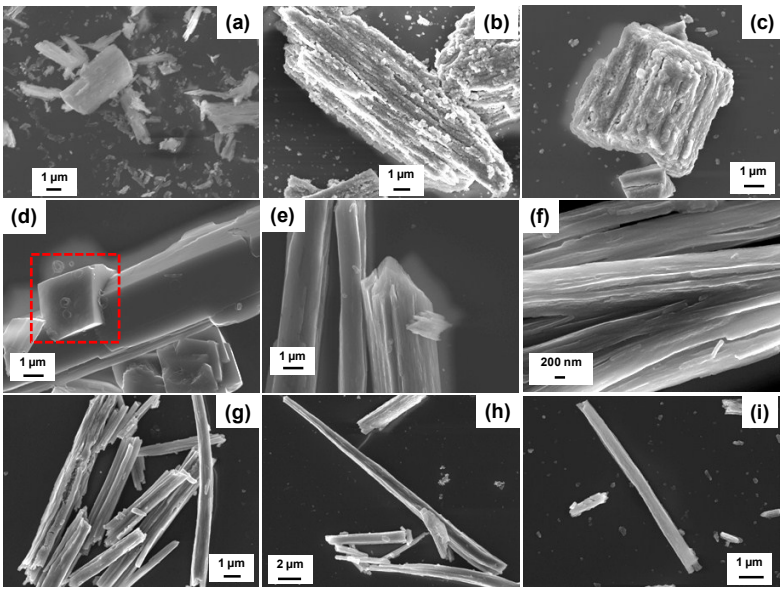


Fig. S7: FESEM micrographs (higher magnification images) of the calcined samples synthesized using CTAB, IB and PB with different concentrations: (a) CTAB-0.2, (b) IB-0.2, (c) PB-0.2, (d) CTAB-0.3, (e) IB-0.3, (f) PB-0.3, (g) CTAB-0.4, (h) IB-0.4, and (i) PB-0.4.

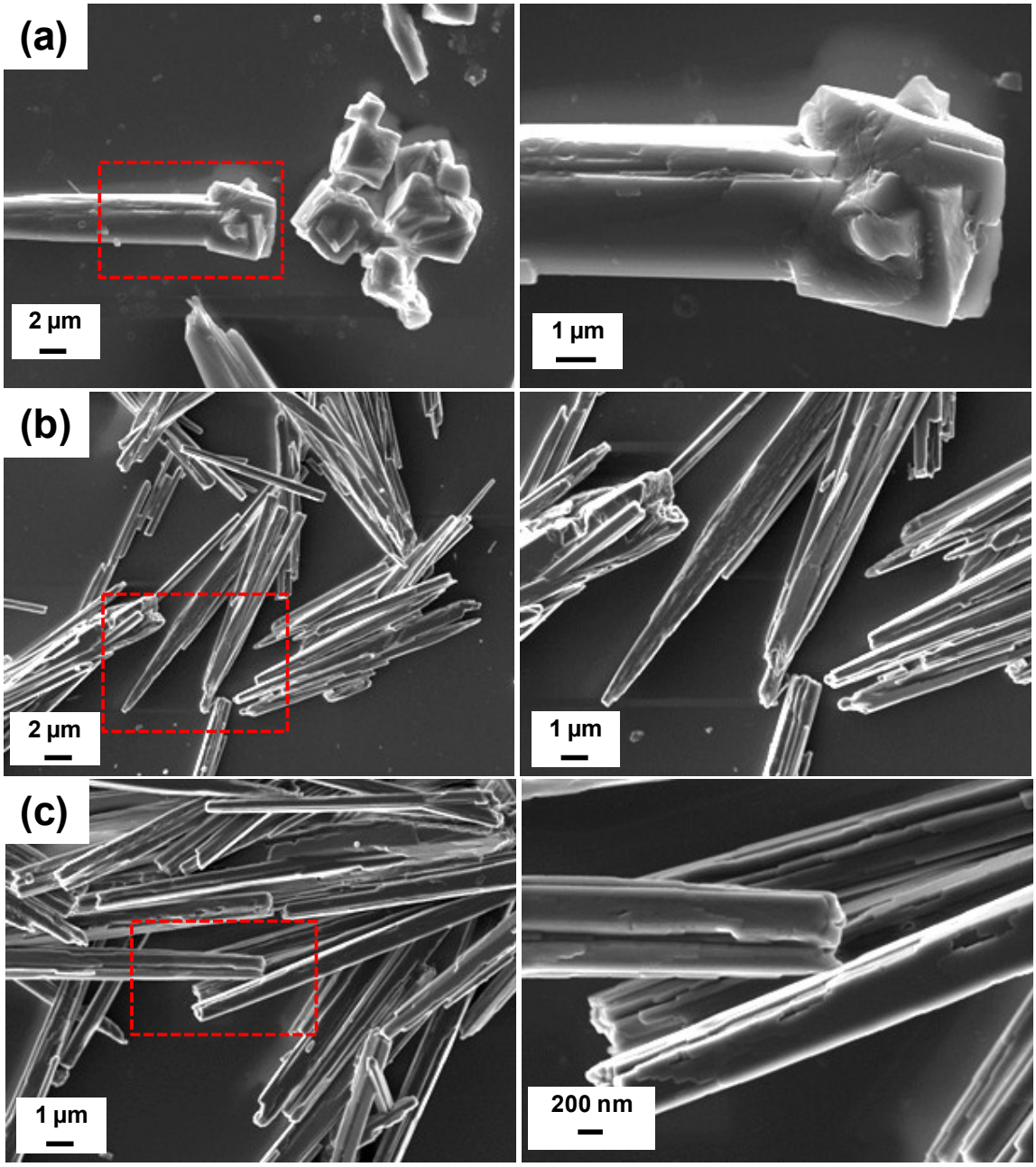


Fig. S8: FESEM micrographs of the as-prepared (uncalcined) samples prepared using (a) CTAB, (b) IB (c) PB with molar ratio of template : Co^{2+} = 0.3.

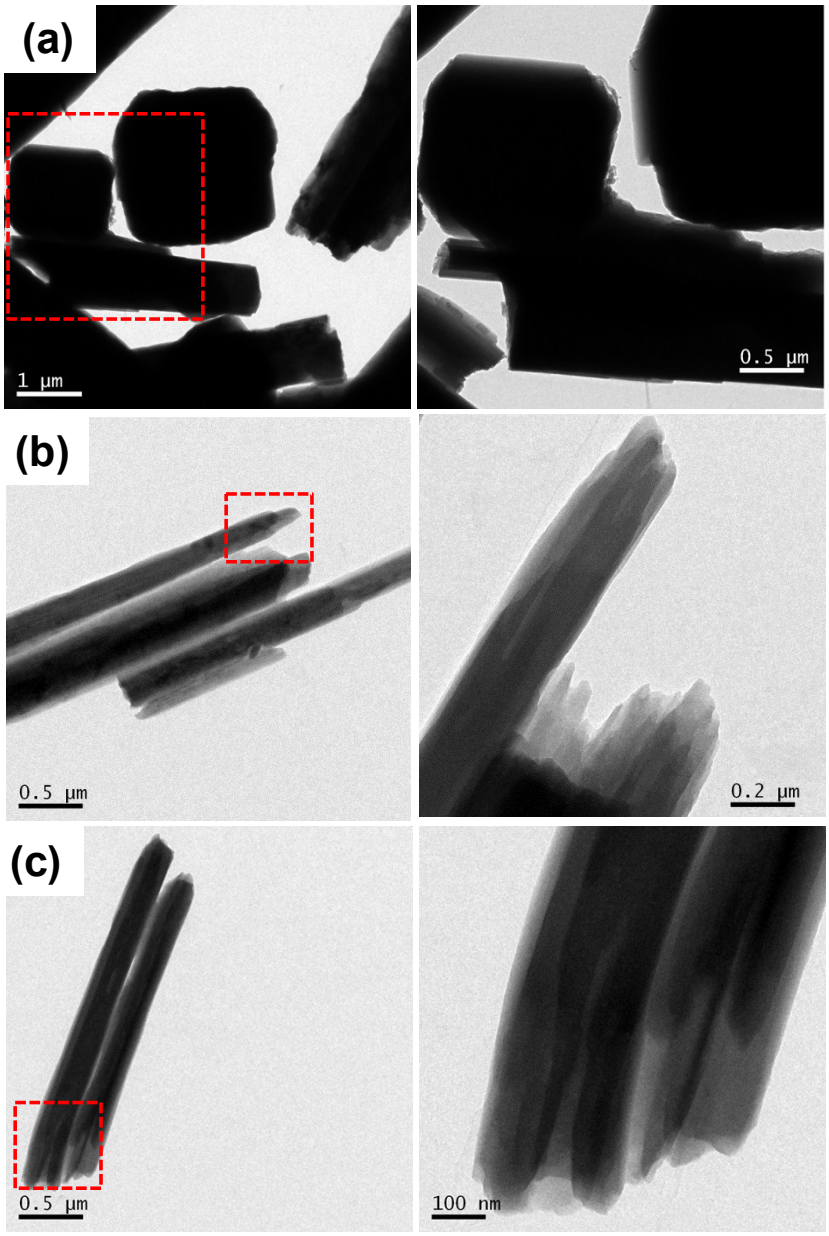


Fig. S9: TEM images of the as-prepared (uncalcined) samples prepared using (a) CTAB, (b) IB (c) PB with molar ratio of template : Co^{2+} = 0.3.

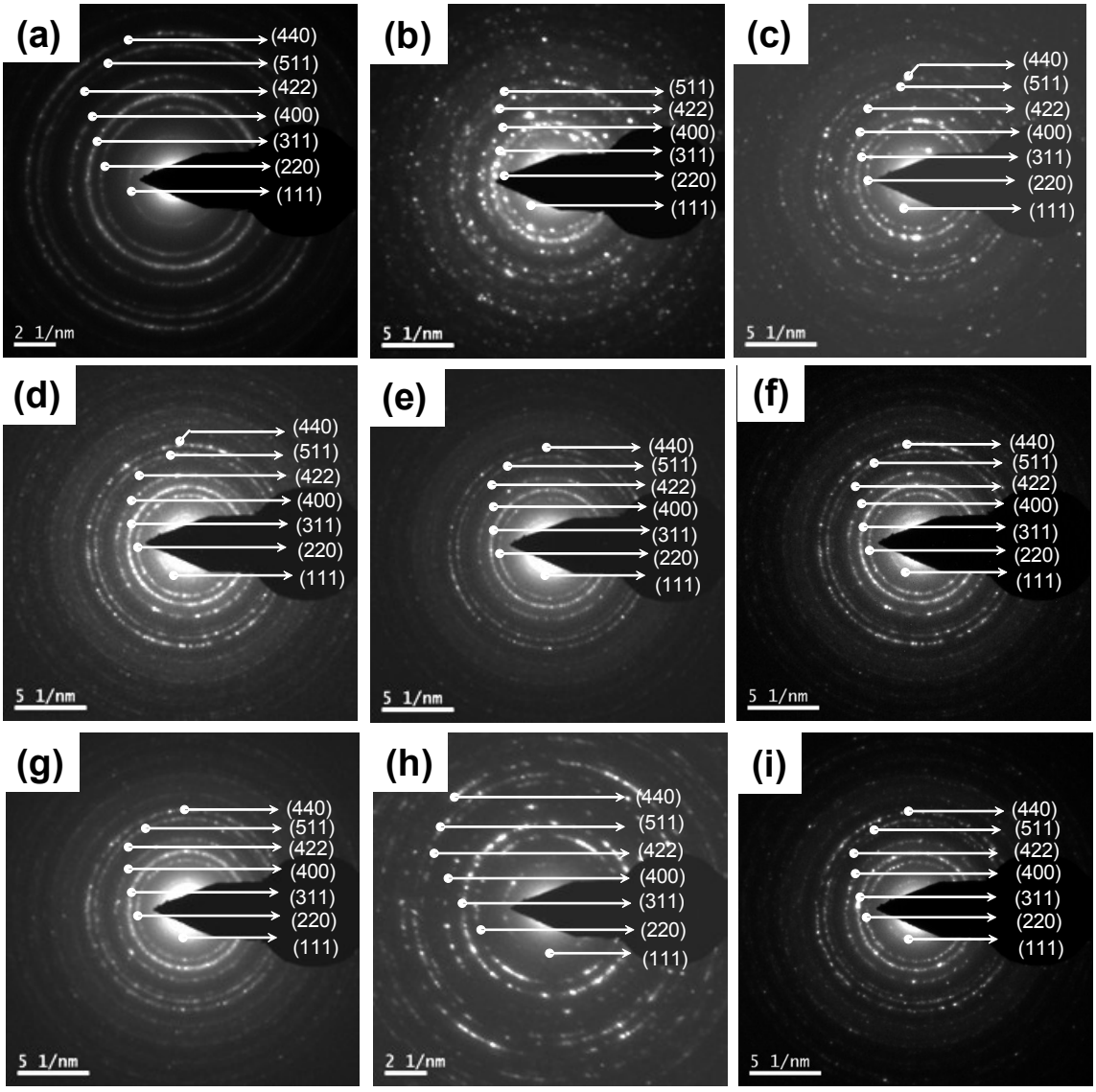


Fig. S10: The selected area electron diffraction (SAED) patterns of the calcined samples synthesized using CTAB, IB and PB with different concentrations: (a) CTAB-0.2, (b) IB-0.2, (c) PB-0.2, (d) CTAB-0.3, (e) IB-0.3, (f) PB-0.3, (g) CTAB-0.4, (h) IB-0.4, and (i) PB-0.4.

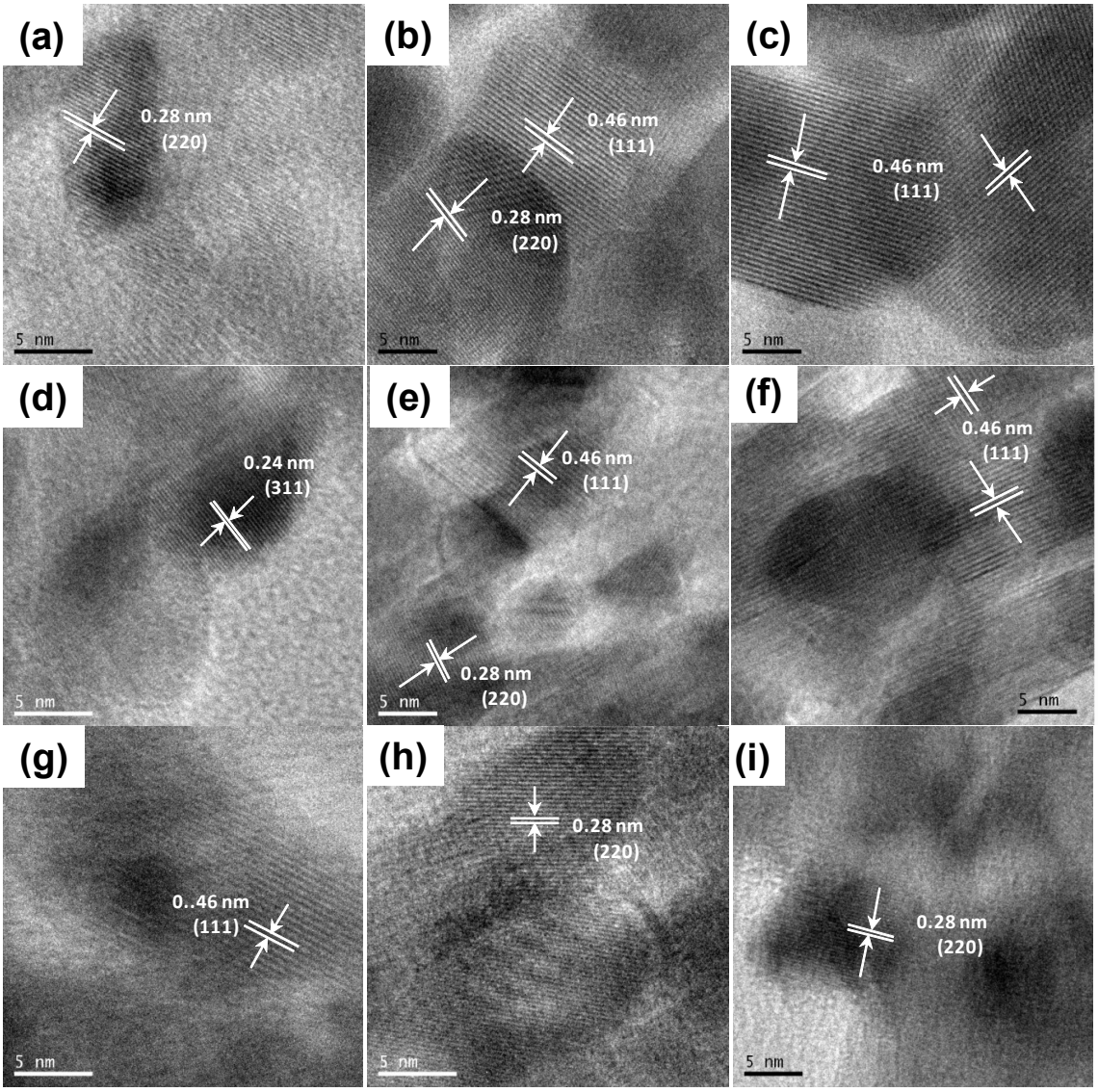


Fig. S11: HRTEM images of the calcined samples synthesized using CTAB, IB and PB with different concentrations: (a) CTAB-0.2, (b) IB-0.2, (c) PB-0.2, (d) CTAB-0.3, (e) IB-0.3, (f) PB-0.3, (g) CTAB-0.4, (h) IB-0.4, and (i) PB-0.4.

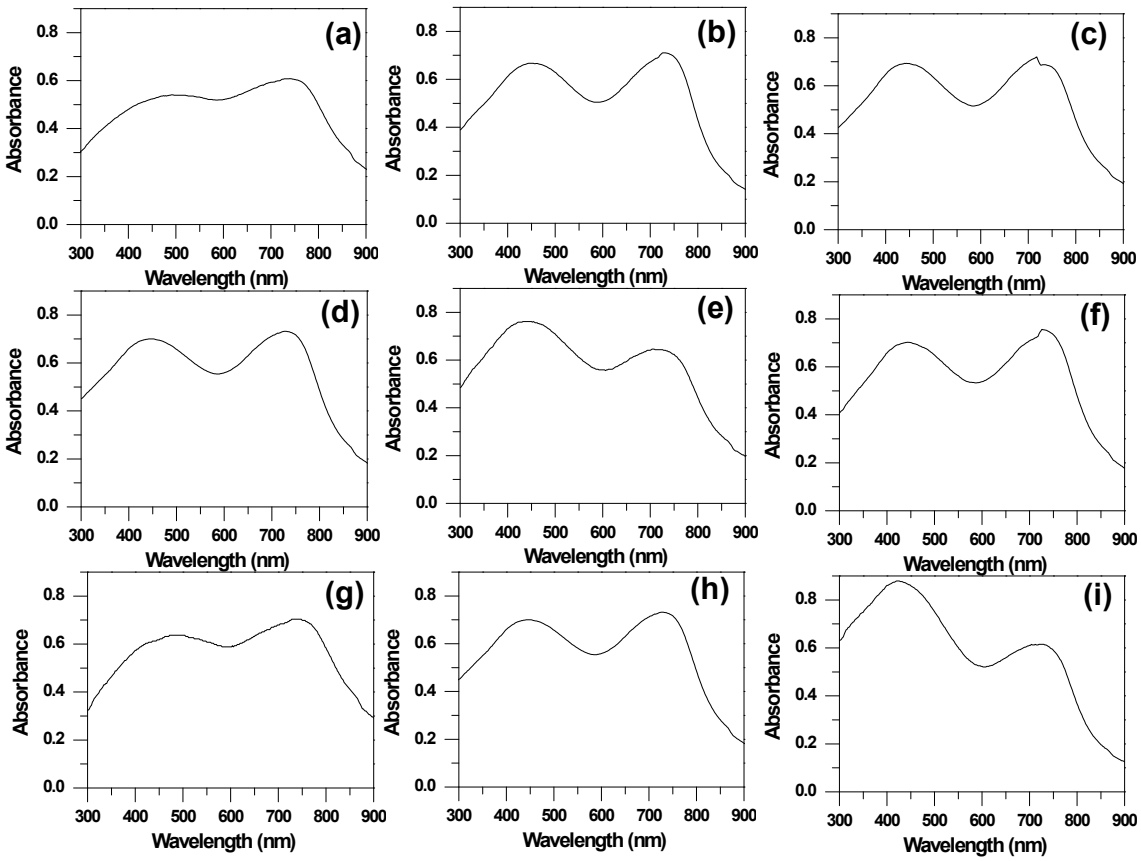


Fig. S12: Optical absorption spectra of synthesized Co_3O_4 particles, (a) CTAB-0.2, (b) IB-0.2, (c) PB-0.2, (d) CTAB-0.3, (e) IB-0.3, (f) PB-0.3, (g) CTAB-0.4, (h) IB-0.4, and (i) PB-0.4.

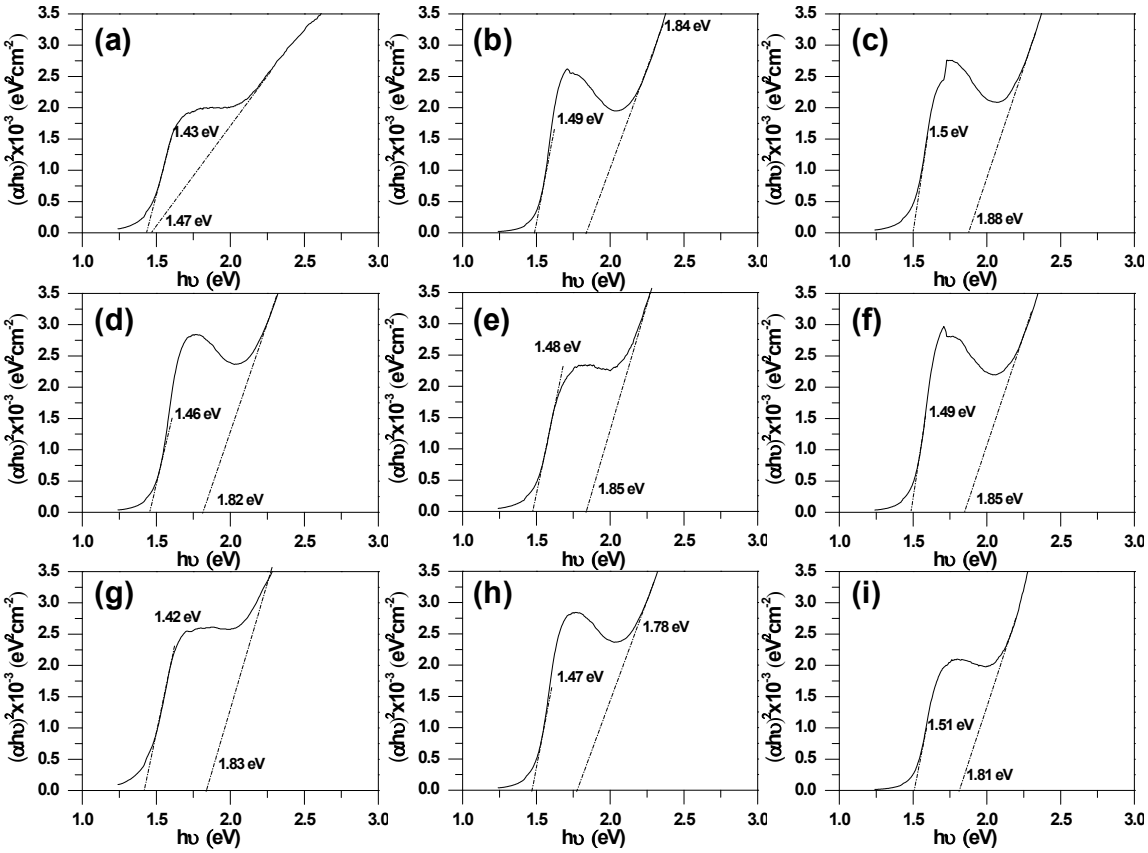


Fig. S13: $(\alpha h\nu)^2$ versus hν for different Co_3O_4 particles, (a) CTAB-0.2, (b) IB-0.2, (c) PB-0.2, (d) CTAB-0.3, (e) IB-0.3, (f) PB-0.3, (g) CTAB-0.4, (h) IB-0.4, and (i) PB-0.4.

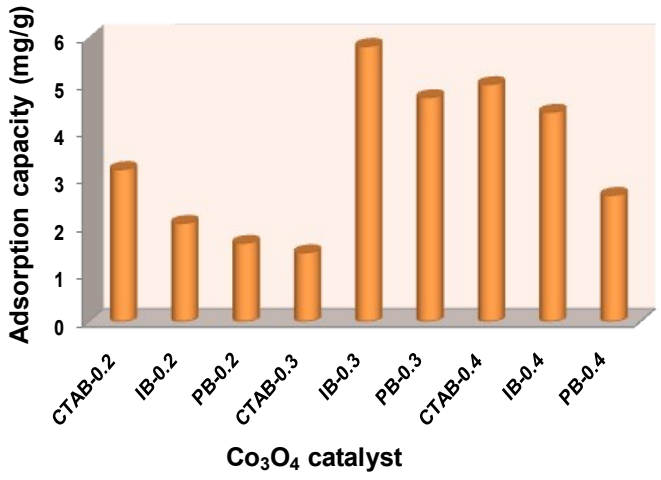


Fig. S14: Dye adsorption capacity (mg/g) of different Co_3O_4 samples.

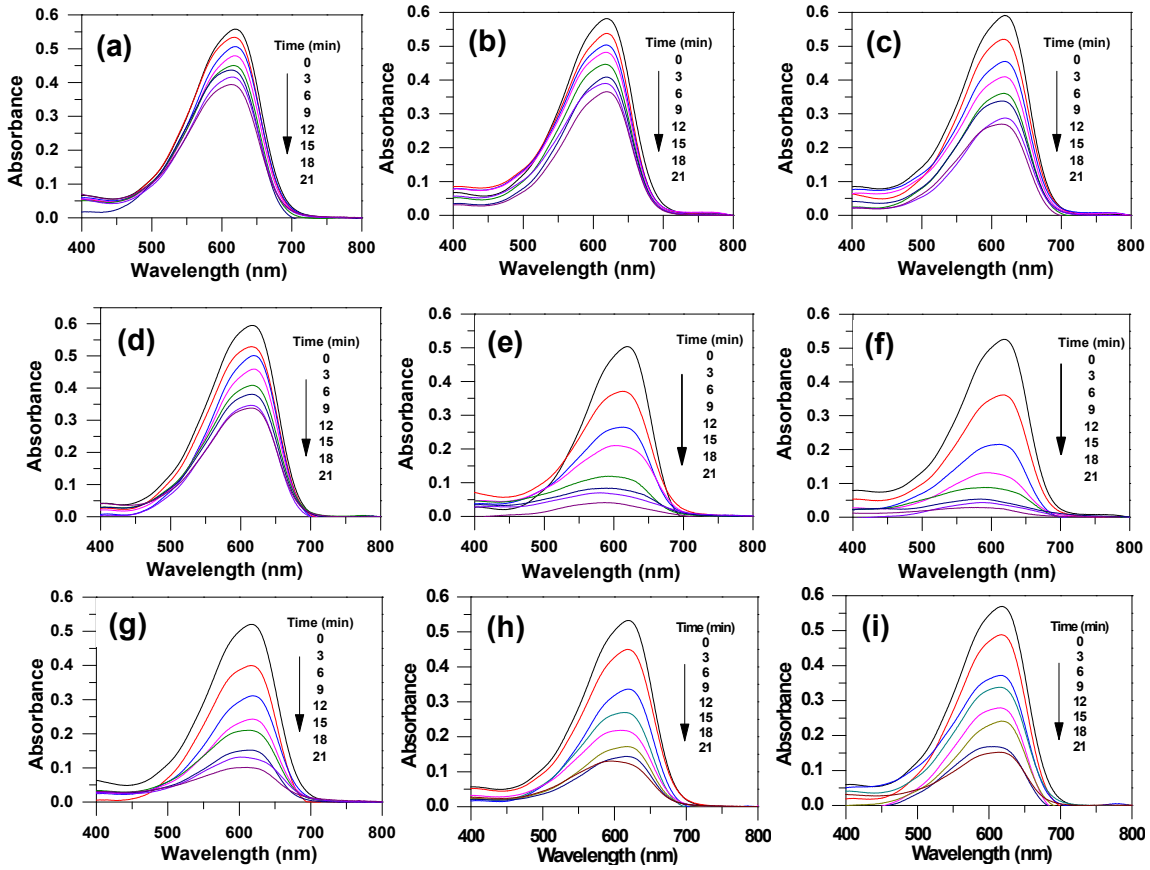


Fig. S15: Successive UV-vis absorption spectra with time for the photocatalytic degradation of Chicago sky blue 6B dye at 25 °C: for the calcined samples synthesized using CTAB, IB and PB with different concentrations: (a) CTAB-0.2, (b) IB-0.2, (c) PB-0.2, (d) CTAB-0.3, (e) IB-0.3, (f) PB-0.3, (g) CTAB-0.4, (h) IB-0.4, and (i) PB-0.4.

Table S1: The textural properties of Co_3O_4 particles

Sample ID	Surface area (S_{BET}) m^2/g	Pore Volume (V_p) cc/g	Pore Diameter (D) nm
CTAB-0.2	77.6	0.41	21.2
IB-0.2	32.0	0.42	53.2
PB-0.2	39.1	0.39	40.3
CTAB-0.3	48.9	0.33	27.0
IB-0.3	73.6	0.35	19.2
PB-0.3	88.7	0.44	19.6
CTAB-0.4	72.8	0.41	22.3
IB-0.4	67.6	0.44	26.0
PB-0.4	58.8	0.36	24.2

Table S2: The optical band gap energies of synthesised Co_3O_4 particles.

Sample ID	Morphology	E_{g1} (eV)	E_{g2} (eV)
CTAB-0.2	Flake	1.43	1.47
IB-0.2	Dice	1.49	1.84
PB-0.2	Dice	1.50	1.88
CTAB-0.3	Dice + rod	1.46	1.82
IB-0.3	Rod	1.48	1.85
PB-0.3	Rod	1.49	1.85
CTAB-0.4	Rod	1.42	1.83
IB-0.4	Rod	1.47	1.78
PB-0.4	Rod	1.51	1.81

Table S3: Morphology, surface area, and rate constants for dye degradation of Co_3O_4 particles

Sample Name	Morphology	Surface area (S_{BET}) m^2/g	Rate constant (min^{-1})
CTAB-0.2	Flake	77.6	0.0218
IB-0.2	Dice	32.0	0.022
PB-0.2	Dice	39.1	0.0377
CTAB-0.3	Dice + Rod	48.9	0.0284
IB-0.3	Rod	73.6	0.1205
PB-0.3	Rod	88.7	0.1431
CTAB-0.4	Rod	72.8	0.0781
IB-0.4	Rod	67.6	0.0725
PB-0.4	Rod	58.8	0.0640

Table S4: The degradation rate of various dyes in the presence of different photocatalyst

Co_3O_4 photocatalyst	Dye	Light source	Time (min)	% Degradation rate	Ref.
Co_3O_4 on glass by Pulsed laser deposition	Methylene Blue	Visible light source using 100 W Tungsten Halogen lamp	240	15-20	28
Cube shaped Co_3O_4	Methyl Violet	300 W mercury lamp	360	80-90	29
Co_3O_4 nanorod	Reactive Turquoise Blue K-NR	300 W high-pressure mercury lamp	120	90	30
Rod-like Co_3O_4	Methyl Orange	Visible light from 200 W incandescent lamp	180	8.1	31
Rod-like Co_3O_4	Chicago Sky Blue 6B	Two visible light (λ= 465 nm) lamps (each of 18 W)	21	95	This work