Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting information

Synergism of Co/Na in $BiVO_4$ microstructures for visible-light driven degradation of toxic dyes in water†

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Section 1: Experimental

Synthesis of Na-$BiVO_4$: For the synthesis of Na-$BiVO_4$, an optimized amount of $BiVO_4$ (~175 mg) powder was transfer into a three necks round bottom flask followed by addition of 50 mL of high purity deionized water (PIAS-GW1-Z) to produce the slurry. For depositing the Na, optimized amount of Na^+ ions (NaOH solution) were introduced into $BiVO_4$ slurry stirrer for 5 h followed by 30 min sonication. The precipitate of Na-$BiVO_4$ was filtered using vacuumed filtration and finally the product was calcined at 350 ℃ for 3 h to converts Na^+ into Na_2O.

Synthesis of Co-$BiVO_4$: The synthesis of Co-$BiVO_4$ microstructures, an optimized amount of $BiVO_4$ (~255 mg) powder was transfer into a three necks round bottom flask followed by addition of 50 mL of high purity deionized water to produce uniform suspension. This suspension was then purge with high purity argon gas, to deposit the Co, $Co(NO_3)_2.6H_2O$ solution were introduced into $BiVO_4$ slurry. The Co metal ions were then in-situ reduced over $BiVO_4$ using freshly prepared cold alkaline borohydride solution (~10 ℃). The final suspension was filtered, thoroughly washed and dried at 94 ℃. The product was calcined at 350 ℃ for 3 h.

Cobalt reduction: It is reported that, reducing the Co with $NaBH_4$ generate proton (H^+) that promotes the hydrolysis of borohydride. The existence of NaOH that produce the hydroxyl ions ^-OH further favors the cobalt reduction. Moreover, the efficiency of cobalt reduction increases with decreasing temperature of borohydride solution and increasing pH, which neutralizes the released H^+ during cobalt reduction [1, 2].

Table S1: EDX Analysis Weight and Atomic percentage of elements in as-synthesized Co@Na-$BiVO_4$.

Elements	Weight %	Atomic %
Bi	55.81	11.85
V	16.31	13.95
O	23.62	64.30
Co	1.29	0.95
Na	1.16	2.26
C	1.81	6.69
Totals	100.00	

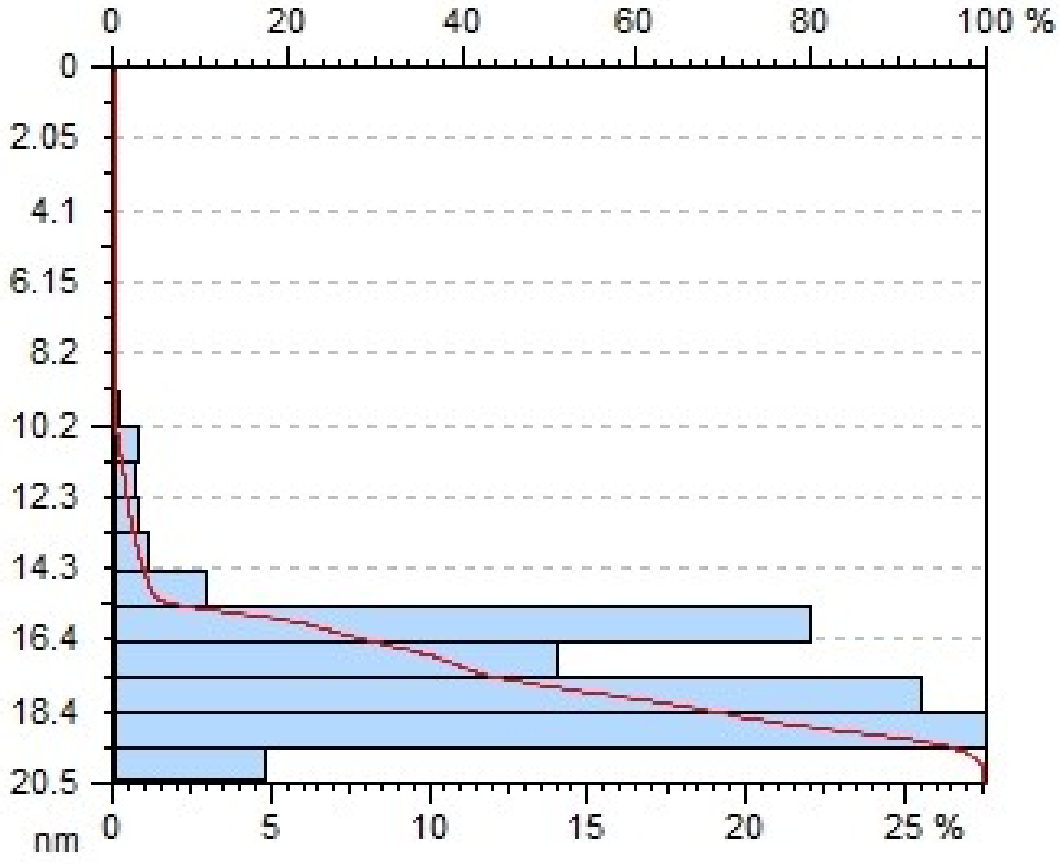

Figure S1: Particle size distribution of Co@Na-$BiVO_4$.

Table S2: Comparative analysis of MB, CR, and RhB dye degradation efficiency of previously reported metal doped-photocatalysts with currently synthesized Co@Na-$BiVO_4$ photocatalysts.

Materials	Dye	% efficiency	Time (min)	(%/min) efficiency	Source	Ref.
$BiVO_4$	MB	50 %	120 min	0.41	UV-Visible	[3]
Paint coated $BiVO_4$	MB	72 %	240 min	0.30	Visible	[4]
$BiVO_4/TiO_2$	MB	85 %	120 min	0.70	Visible	[5]
Polycrystalline $BiVO_4$	CR	55 %	60 min	0.91	Visible	[6]
m-$BiVO_4$	RhB	64.8 %	210 min	0.31	Visible	[7]
$BiVO_4$ (biscuits)	RhB	68 %	270 min	0.25	Visible	[8]
$ZnO/BiVO_4$	RhB	72.7 %	150 min	0.48	Visible	[9]
TiO_2-$BiVO_4$	RhB	79.3 %	300 min	0.26	Sunlight	[10]
Co@Na-$BiVO_4$	MB	88 %	60 min	1.46	Sun-light	Current work
Co@Na-$BiVO_4$	CR	85 %	60 min	1.41	Sun-light	Current work
Co@Na-$BiVO_4$	RhB	60 %	60 min	1.0	Sun-light	Current work

Table S3 Recyclability test of Co@Na-$BiVO_4$ microstructures for degradation of MB, CR and RhB dyes

Dye	Photocatalyst Co@Na-$BiVO_4$	Absorbance of selected dyes with time intervals						Degradation efficiency (%)
		Time (min)						
		10	20	30	40	50	60	
MB	1st Run	0.485	0.382	0.285	0.210	0.124	0.07	88 %
	2nd Run	0.488	0.385	0.288	0.214	0.130	0.077	86.8 %
	3rd Run	0.491	0.388	0.291	0.219	0.138	0.085	85.4 %
CR	1st Run	0.138	0.102	0.073	0.053	0.037	0.026	85.3 %
	2nd Run	0.140	0.105	0.078	0.057	0.040	0.029	83.6 %
	3rd Run	0.142	0.105	0.083	0.063	0.043	0.032	81.9 %
RhB	1st Run	0.817	0.684	0.589	0.513	0.455	0.385	60.2 %
	2nd Run	0.822	0.694	0.595	0.520	0.460	0.400	58.7 %
	3rd Run	0.828	0.699	0.599	0.535	0.47	0.415	57.1 %

Note: Absorbance was measured at the λ-max of each dye.

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