Supporting Information for

Developed a dual surface inorganic molecularly imprinted Bi_2WO_6-CuO/Ag_2O heterostructured with enhanced activity-selectivity towards photocatalytic degradation of target contaminants

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Experimental Section

Instrumentation

The absorbance of MG and AO binary mixture of dyes was measured using a UV–Vis spectrophotometer (model PG 180 + instrument, England). The pH of solutions was adjusted and measured using dilute HCl or NaOH applying a pH-meter (Metrohm 691 pH meter, Switzerland). A Hermle Labortechnik GmbH centrifuge model Z206A (Germany) was used to accelerate the phase separation. The morphology of photocatalyst samples was investigated by field emission scanning electron microscopy (SEM: T3 Tescan) under an acceleration voltage of 26.00 KV. X-ray diffraction (XRD, Philips PW 1880, Philips, Amsterdam, Netherland) was applied to characterize the phase and structure of the photocatalysts using CuKα radiation (40 KV and 40 mA). An ultrasonic bath with a heating system (Tecno-GAZ SPA Ultra Sonic System) at 40 kHz frequency and 130 W power was used for the ultrasound-assisted synthesis procedure. The FT-IR spectra of compounds were recorded on a FT/IR-680 instrument (JASCO- Japan) in the range of 400-4000 cm^{-1} using KBr pellet with ratio of 1:100 for samples to KBr. Other equipment, software and chemical reagents were used according to manufacturer recommendations similar to our previous publications [21-23].

Experimental design and photocatalytic performance test

The central composite design (CCD) was applied to minimize number of experiments and to investigate the combined effect of operational parameters together. This approach leads to the reduction in reagents consumption and operating costs, save time, and also reduce systematic errors. The CCD operates based on the response surface methodology which is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes [24]. The preliminary studies showed the significant effects of operational parameters including initial dyes concentration, pH, photocatalyst mass and irradiation time on the degradation efficiency. Response surface methodology was applied to evaluate the individual as well as the mutual effects of operational parameters on dyes degradation. RSM provides a combination of experimental conditions at which maximum degradation of dyes occurs. The levels of the operational parameters and experimental runs which were provided using CCD are given in Table S1. Based on the experiment design during the process, each sample in triplicate was harvested, extracted and analyzed using UV-spectrophotometer for quantitative analysis of dyes residues. For statistical analysis, a quadratic polynomial equation (S1) was used to fit the experimental data based on the Analysis of variance (ANOVA).

$$R = \beta_0 + \sum_{i=1}^{5} \beta_i X_i + \sum_{i=1}^{5} \sum_{j=1}^{5} \beta_{ij} X_i X_j + \sum_{i=1}^{5} \beta_{ii} X_i^2 + \varepsilon \qquad (1)$$

where R indicates the predicted photocatalytic degradation percentage as response, while X_i and X_j are the independent parameters, ε is the residual term and β_0, β_i, β_{ii} and β_{ij} are the model coefficients corresponded to the model constant, linear coefficient, quadratic coefficient and the cross-product coefficient respectively. The statistical significance of the quadratic model was evaluated using a set of statistical and mathematical tests including, P-value, F-test, lack of fit, the predicted residual error sum of squares (PRESS), statistical coefficient of determination R-squared (R^2), adjusted R-squared ($R^2_{adj.}$) and predicted R-squared ($R^2_{pred.}$).

In the total organic carbon (TOC) test, 20 mg of DIMI-Bi_2WO_6/CuO/Ag_2O was added into binary MG and AO solution (6.0 and 3.0 mg L^{-1}, 20 mL, respectively). Before illumination, the solution was stirred in the dark for 20 min to achieve an adsorption-desorption equilibrium. Then suspension was intervals under visible light for 50 min. Carbon content of different suspensions was recorded after filtration by a TOC analyzer (TOC/TNb Analyzer/Elementar, Germany).

The trapping experiment of the active species have similarities with the former photocatalytic activity tests. Different scavengers, including 2-propanole (2-P), benzoquinone (BQ), silver nitrate (SN) and glycerol (Gly) made an addition

to the RhB/Cr(VI) solution to trap the hydroxyl radical (•OH), superoxygen radicals ($\bullet O_2^-$), the electrons (e^-) and the holes (h^+), respectively.

During EIS experiment, 10 mg sample and 5.0 mg conductive carbon past were added into the mixed solution consisting of 1.0 mL H2O and 0.5 mL NMP. Then the mixed solution was treated by ultrasound for 20 minutes. 0.05 mL Nafion was dropped into the above solution and then treated by ultrasound for 20 min. EIS test was conducted in a standard three-electrode system: 0.2 mL of above suspension was dropped onto glassy carbon electrode which was as working electrode, Ag/AgCl electrode was as reference electrode, platinum wire was as counter electrode, 50 mL KCl (1 M) solution containing 0.1 mol/L ascorbic acid (electron donor) was used as electrolyte.

Mechanism Eqs:

$$Bi_2WO_6 - CuO - Ag_2O - MIP + h\vartheta \rightarrow Bi_2WO_6 - CuO - Ag_2O - MIP\left(h^+\right) + \left(e^-\right) \quad (2)$$

$$Bi_2WO_6 - CuO - Ag_2O - MIP\left(e^-\right) + O_2 \rightarrow Bi_2WO_6 - CuO - Ag_2O - MIP + \cdot O_2^- \quad (3)$$

$$\cdot O_2^- + 2H_2O \rightarrow 2OH^- + H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + Bi_2WO_6 - CuO - Ag_2O - MIP(e^-) \rightarrow \cdot OH + OH^- + Bi_2WO_6 - CuO - Ag_2O - MIP \quad (5)$$

$$\cdot OH + \cdot O_2^- + h^+ + AO/MG \rightarrow Products \quad (6)$$

Kinetics investigation

$$-\frac{dC}{dt} = k_{obs}\, C \quad (8)$$

where k_{obs} *(min^{-1})* refers to observed first-order rate constant, *C* is the concentration and t is the reaction time. Integration of Eq. (8) gives a concentration–time equation as follows:

$$\ln\left(\frac{C_0}{C_t}\right) = k_{obs}t \quad (8)$$

where C_0 and C_t are the dye concentrations at the time *0* and *t*, respectively.

$$\frac{1}{R} = \frac{1}{k_r K_A C_0} + \frac{1}{k_r} \quad (9)$$

where *kr (mg.min^{-1}. L^{-1})* is the apparent photodegradation rate constant, while K_A *(L.mg^{-1})* defines as $K_A = \frac{K}{1 + K_s C_s}$.

Table S1. Experimental factors and levels in the central composite design.

Factor	Name	Units	Minimum	Maximum	Coded	Values	Mean	
A	pH	-	3.00	9.00	4.50	7.50	6.06	
B	Photocatalyst mass	g	0.008	0.016	0.010	0.014	0.012	
C	Irradiation Time	min	90.00	150.00	105.00	135.00	120.58	
D	Concentration of MG	mg/L	4.00	12.00	6.00	10.00	8.080	
E	Concentration of AO	mg/L	2.00	6.00	3.00	5.00	4.04	

Run	A	B	C	D	E	Actual R% MG	Predicted R% MG	R% AO	Predicted R% AO
1	4.50	0.014	105.00	10.00	5.00	83.56	83.47	59.71	59.82
2	6.00	0.012	120.00	8.00	4.00	72.42	*72.52*	77.78	77.85
3	7.50	0.010	135.00	6.00	5.00	57.23	57.14	50.71	50.82
4	7.50	0.014	135.00	6.00	3.00	80.15	80.06	91.14	91.25
5	6.00	0.012	90.00	8.00	4.00	41.68	41.82	36.84	36.67
6	3.00	0.012	120.00	8.00	4.00	39.57	39.71	33.83	33.66
7	6.00	0.012	120.00	8.00	4.00	72.55	*72.52*	77.38	77.85
8	6.00	0.012	120.00	4.00	4.00	59.78	59.92	87.21	87.04
9	6.00	0.012	120.00	8.00	2.00	76.74	76.88	75.39	75.22
10	9.00	0.012	120.00	8.00	4.00	84.15	84.29	80.52	80.35
11	7.50	0.014	105.00	10.00	3.00	50.73	50.64	70.37	70.48
12	4.50	0.014	135.00	10.00	3.00	60.5	60.41	54.81	54.92
13	4.50	0.010	135.00	10.00	5.00	63.19	63.10	57.03	57.14
14	7.50	0.010	135.00	10.00	3.00	31.08	30.99	26.5	26.61
15	6.00	0.016	120.00	8.00	4.00	95.33	95.47	96.45	96.28
16	6.00	0.012	120.00	12.00	4.00	62.64	62.78	47.18	47.01
17	6.00	0.012	120.00	8.00	4.00	72.63	*72.52*	78.13	77.85
18	6.00	0.008	120.00	8.00	4.00	30.09	30.23	36.15	35.98
19	6.00	0.012	150.00	8.00	4.00	85.79	85.93	86.32	86.15
20	4.50	0.014	135.00	6.00	5.00	68.71	68.62	55.21	55.32
21	6.00	0.012	120.00	8.00	4.00	72.37	*72.52*	77.73	77.85
22	7.50	0.014	105.00	6.00	5.00	48.37	48.28	77.86	77.97
23	6.00	0.012	120.00	8.00	6.00	68.67	68.81	48.73	48.56
24	6.00	0.012	120.00	8.00	4.00	72.92	*72.52*	77.89	77.85
25	4.50	0.010	105.00	6.00	3.00	67.67	67.48	56.57	56.80
26	7.50	0.010	105.00	10.00	5.00	73.68	73.59	48.71	48.82

Table S2. Sequential Model Sum of Squares for MG degradation.

R% MG						
Sequential Model Sum of Squares						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	1.101E+005	1	1.101E+005			
Linear vs Mean	1823.12	5	364.62	1.41	0.2623	
2FI vs Linear	4642.09	10	464.21	8.94	0.0009	
Quadratic vs 2FI	518.46	5	103.69	978.79	< 0.0001	Suggested
Cubic vs Quadratic	0.34	1	0.34	7.23	0.0547	Aliased
Residual	0.19	4	0.047			
Total	1.171E+005	26	4504.63			
Lack of Fit Tests						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Linear	5160.89	16	322.56	6838.16	< 0.0001	
2FI	518.80	6	86.47	1833.10	< 0.0001	
Quadratic	0.34	1	0.34	7.23	0.0547	Suggested
Cubic	0.000	0				Aliased
Pure Error	0.19	4	0.047			
Model Summary Statistics						
Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	16.06	0.2610	0.0763	-0.4200	9917.92	
2FI	7.20	0.9257	0.8142	-3.3392	30305.95	
Quadratic	0.33	0.9999	0.9996	0.9725	192.24	Suggested
Cubic	0.22	1.0000	0.9998		+	Aliased

Table S3. Sequential Model Sum of Squares for AO degradation.

R% AO						
Sequential Model Sum of Squares						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Mean vs Total	1.068E+005	1	1.068E+005			
Linear vs Mean	4921.45	5	984.29	4.35	0.0077	
2FI vs Linear	3155.68	10	315.57	2.30	0.1031	
Quadratic vs 2FI	1373.86	5	274.77	1714.79	< 0.0001	Suggested
Cubic vs Quadratic	0.50	1	0.50	6.79	0.0597	Aliased
Residual	0.30	4	0.074			
Total	1.162E+005	26	4470.12			
Lack of Fit Tests						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Linear	4530.05	16	283.13	3812.14	< 0.0001	
2FI	1374.37	6	229.06	3084.17	< 0.0001	
Quadratic	0.50	1	0.50	6.79	0.0597	Suggested
Cubic	0.000	0				Aliased
Pure Error	4530.05	16	283.13	3812.14	< 0.0001	
Model Summary Statistics						
Source	**Std. Dev.**	**R-Squared**	**Adjusted R-Squared**	**Predicted R-Squared**	**PRESS**	
Linear	15.05	0.5207	0.4009	0.1701	7843.88	
2FI	11.72	0.8546	0.6364	-12.0251	1.231E+005	
Quadratic	0.40	0.9999	0.9996	0.9699	284.20	Suggested
Cubic	0.27	1.0000	0.9998		+	Aliased

Table S4. Analysis of variance (ANOVA) results for quadratic model of degradation process.

		R% of MG					R% of AO			
Source	**df**	**Sum of Squares**	**Mean Square**	**F Value**	**p-value Prob > F**		**Sum of Squares**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	20	6983.68	349.18	3296.06	< 0.0001		9450.99	472.55	2949.07	< 0.0001
A	*1*	*993.69*	*993.69*	*9379.76*	*< 0.0001*		*1089.98*	*1089.98*	*6802.28*	*< 0.0001*
B	*1*	*2128.13*	*2128.13*	*20088.13*	*< 0.0001*		*1818.04*	*1818.04*	*11345.97*	*< 0.0001*
C	*1*	*972.85*	*972.85*	*9183.02*	*< 0.0001*		*1224.14*	*1224.14*	*7639.53*	*< 0.0001*
D	*1*	*4.09*	*4.09*	*38.61*	*0.0016*		*801.20*	*801.20*	*5000.09*	*< 0.0001*
E	*1*	*32.56*	*32.56*	*307.37*	*< 0.0001*		*355.38*	*355.38*	*2217.83*	*< 0.0001*
AB	*1*	*329.24*	*329.24*	*3107.81*	*< 0.0001*		*0.30*	*0.30*	*1.86*	*0.2311*
AC	*1*	*179.16*	*179.16*	*1691.20*	*< 0.0001*		*798.45*	*798.45*	*4982.91*	*< 0.0001*
AD	*1*	*0.13*	*0.13*	*1.27*	*0.3102*		*6.08*	*6.08*	*37.92*	*0.0016*
AE	*1*	*243.83*	*243.83*	*2301.56*	*< 0.0001*		*118.87*	*118.87*	*741.82*	*< 0.0001*
BC	*1*	*16.55*	*16.55*	*156.24*	*< 0.0001*		*377.08*	*377.08*	*2353.29*	*< 0.0001*
BD	*1*	*67.45*	*67.45*	*636.71*	*< 0.0001*		*204.35*	*204.35*	*1275.32*	*< 0.0001*
BE	*1*	*253.99*	*253.99*	*2397.53*	*< 0.0001*		*138.60*	*138.60*	*864.94*	*< 0.0001*
CD	*1*	*0.23*	*0.23*	*2.20*	*0.1984*		*4.63*	*4.63*	*28.90*	*0.0030*
CE	*1*	*414.75*	*414.75*	*3914.98*	*< 0.0001*		*9.13*	*9.13*	*56.99*	*0.0006*
DE	*1*	*2890.32*	*2890.32*	*27282.70*	*< 0.0001*		*2058.99*	*2058.99*	*12849.62*	*< 0.0001*
A^2	*1*	*189.22*	*189.22*	*1786.12*	*< 0.0001*		*743.15*	*743.15*	*4637.81*	*< 0.0001*
B^2	*1*	*159.88*	*159.88*	*1509.15*	*< 0.0001*		*234.98*	*234.98*	*1466.42*	*< 0.0001*
C^2	*1*	*127.78*	*127.78*	*1206.16*	*< 0.0001*		*462.28*	*462.28*	*2885.00*	*< 0.0001*
D^2	*1*	*213.33*	*213.33*	*2013.66*	*< 0.0001*		*200.47*	*200.47*	*1251.06*	*< 0.0001*
E^2	*1*	*0.18*	*0.18*	*1.71*	*0.2483*		*435.69*	*435.69*	*2719.02*	*< 0.0001*
Residual	5	0.53	0.11				0.80	0.16		
Lack of Fit	*1*	*0.34*	*0.34*	*7.23*	*0.0547*		*0.50*	*0.50*	*6.79*	*0.0597*
Pure Error	*4*	*0.19*	*0.047*				*0.30*	*0.074*		
Cor Total	25	6984.21					9451.80			

Table S5. Statistical supplementary results of quadratic model.

	R% AO		R% MG
Std. Dev.	0.40		0.33
Mean	64.08		65.08
C.V. %	0.62		0.50
PRESS	284.20		192.24
-2 Log Likelihood	-16.69		0.9999
R-Squared	0.9999		0.9996
Adj R-Squared	0.9996		0.9725
Pred R-Squared	0.9699		0.9999
Adeq Precision	193.642		223.029
BIC	51.73		40.97
AICc	256.31		245.55

Table S6. Kinetics Parameters

	Kinetics parameters					
	k_{obs}	**R^2**	**k_r**	**R^2**	**K_A**	**R^2**
AO	0.035	0.99	0.162	0.99	0.062	0.99
MG	0.030	0.99	0.111	0.99	0.159	0.99

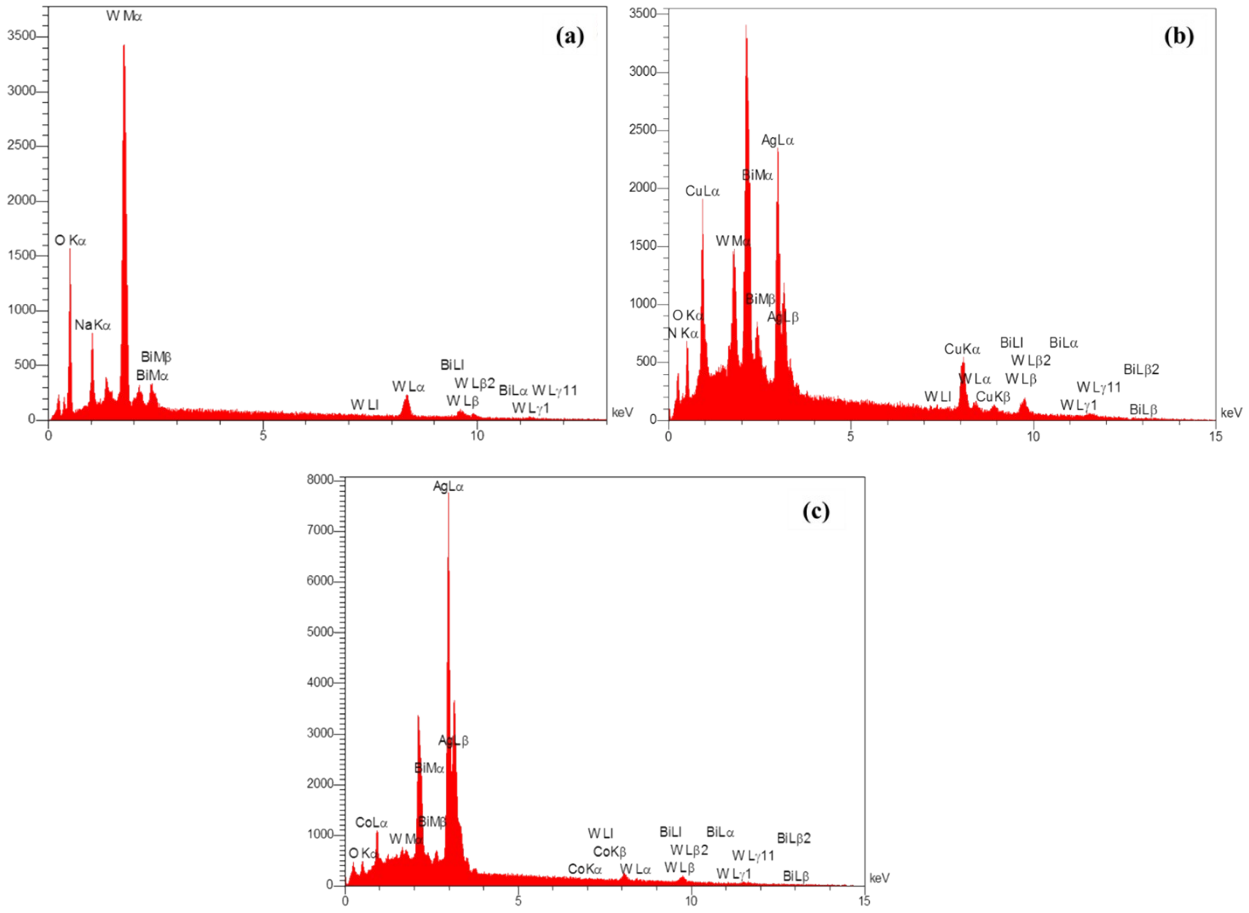

Fig. S1. EDS spectra of (a) Bi_2WO_6 and DIMI-Bi_2WO_6/CuO/Ag_2O before (b) and after (c) MG and AO extraction

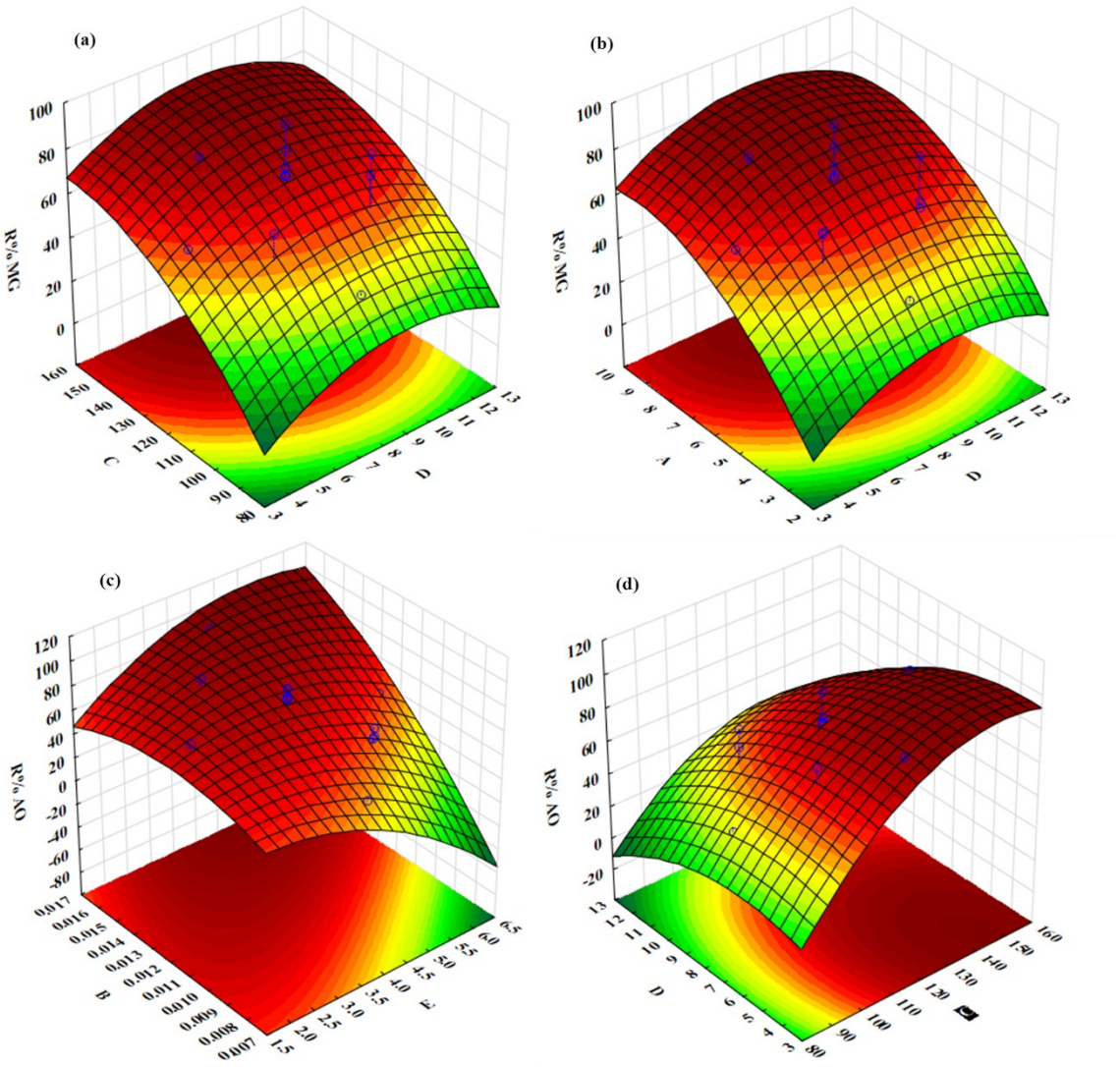

Fig. S2. 3D plots of RSM at optimal conditions.

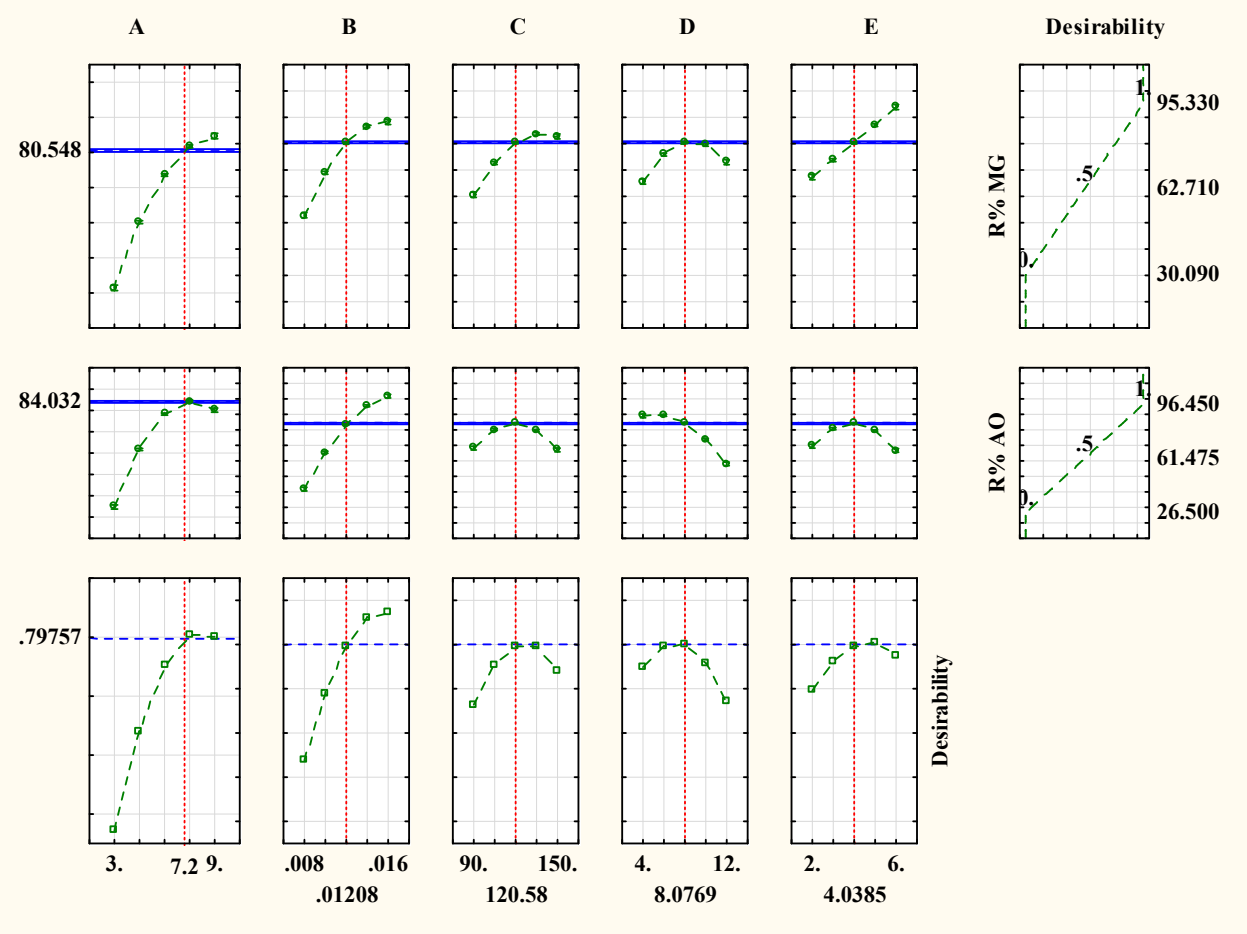

Fig. S3. Profiles for predicated values and desirability function for photocatalytic degradation process. Dashed line shows optimum values.

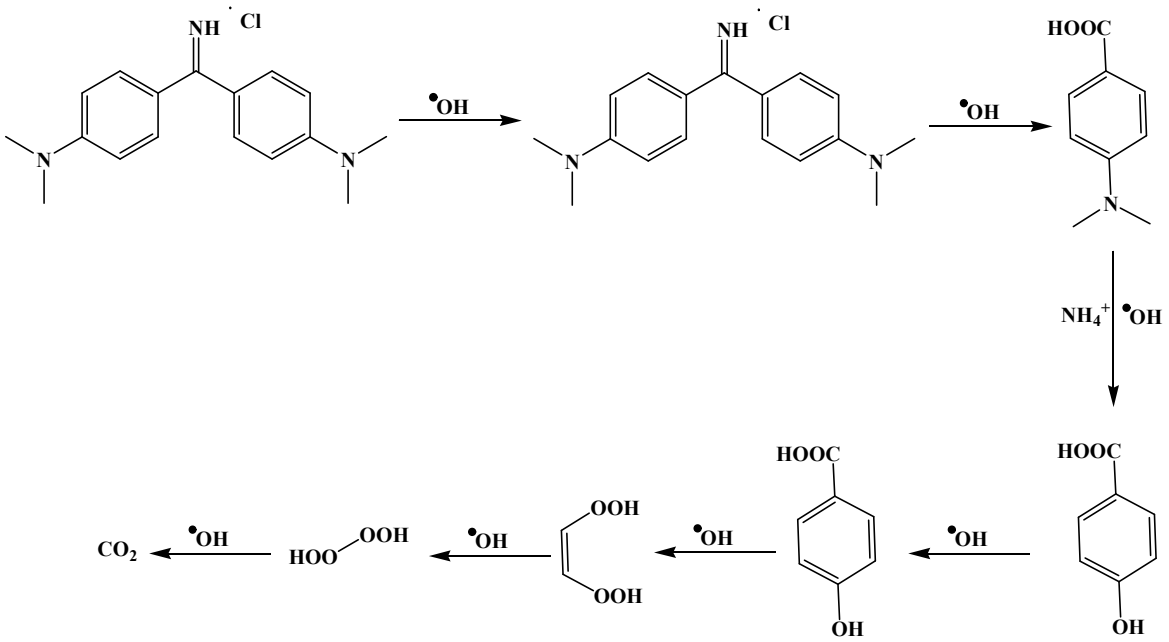

Fig. S4. Schematic diagram of the possible reaction mechanism for photocatalytic degradation of AO.

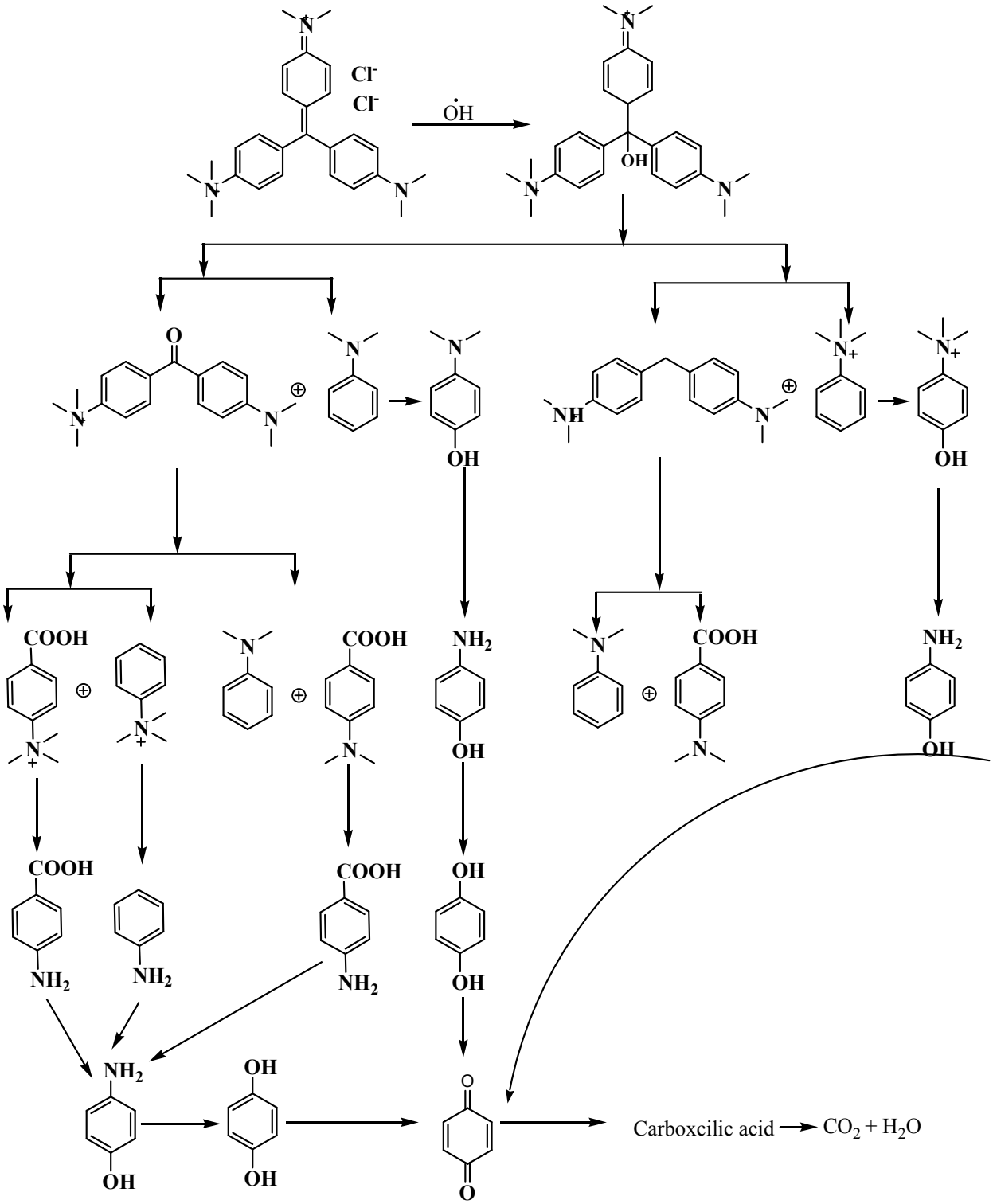

Fig. S5. Schematic diagram of the possible reaction mechanism for photocatalytic degradation of MG.

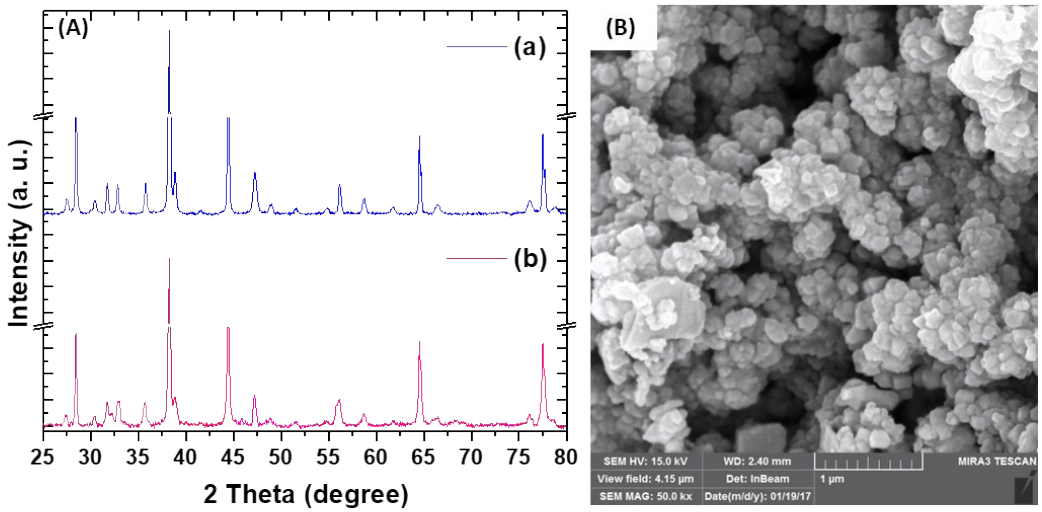

Fig. S6. XRD pattern (A) and SEM images of before and after photocatalysis over DIMI-Bi_2WO_6/CuO/Ag_2O composite photocatalyst