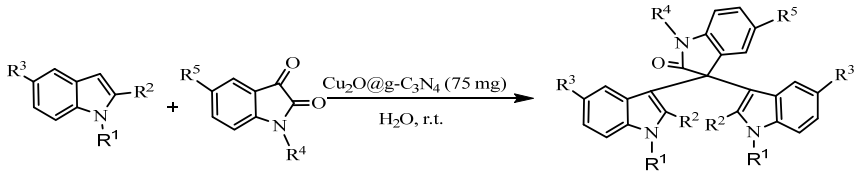
Table 4. Synthesis of di-indolyloxindoles catalyzed by SiO_2@g-C_3N_4 in water at room temperature.[a]



Yield: 80-95%

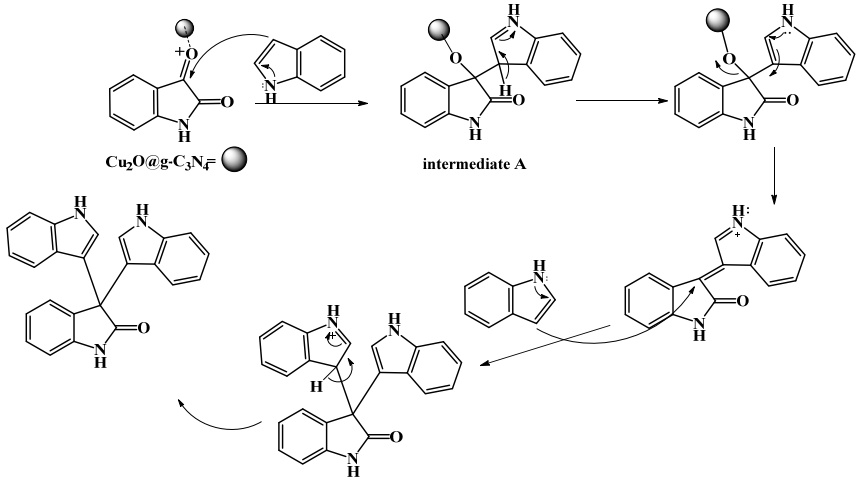
Entry	Indole			Isatin		Time (min)	Yield (%)[b]
	R^1	R^2	R^3	R^4	R^5		
1	H	H	H	H	H	60	95
2	Me	H	H	H	H	55	95
3	H	H	Br	H	H	75	80
4	H	H	H	H	Cl	55	94
5	H	Me	H	H	Cl	45	93
6	H	H	Br	H	Cl	75	88
7	Me	H	H	H	Br	60	87
8	Me	H	H	CH_2CH_3	Br	45	95
9	H	H	Br	H	Br	75	83
10	H	H	H	H	NO_2	70	95
11	H	Me	H	H	NO_2	65	95
12	H	H	Br	H	NO_2	75	94
13	H	H	H	$PhCH_2$	H	75	80
14	H	Me	H	$PhCH_2$	H	75	86
15	H	H	Br	$PhCH_2$	H	75	80
16	H	H	H	Me	H	75	89
17	H	Me	H	Me	H	75	90
18	H	H	Br	Me	H	75	81

[a]Reaction conditions: Isatin derivatives (1.0 mmol), indole derivatives (2 mmol), catalyst (75 mg) and water (3 mL).

The aqueous filtered phase was analyzed by atomic absorption to investigate leaching of CuO from the solid CuO@g-C_3N_4 catalyst and no leaching of Cu metal was detected in it. Therefore, the mesoporous graphitic carbon nitride containing CuO could serve as an efficient heterogeneous catalyst for the synthesis of oxindole derivatives. The reaction can be rationalized by assuming the following mechanism (Scheme 4). As shown in Scheme 3, CuO@g-C_3N_4 activates the carbonyl groups of isatin followed by the nucleophilic addition of indole to isatin to form the intermediate (A). This intermediate undergoes a further nucleophilic attack with the second indole molecule to afford di-indolyloxindole derivatives.

The efficiency of our method was also compared with some other published works in the literature [31,35,40,66-72]. As the results shown in Table 5, CuO@g-C_3N_4 showed sufficient efficiency compared to the other catalysts (Table 5, entry 11).

From an industrial perspective, long-term stability, recovery, and reusability are the main objects of using heterogeneous catalysts. For this purpose, under optimized conditions the model reaction was performed as previously described, followed by separating, washing and drying the catalyst and reusing in another four successive catalytic cycles under identical reaction conditions. The results showed excellent yields with a negligible decrease in a catalytic activity (The yields were 95, 94, 91, 88 and 88 %, respectively). So, the performance of CuO@g-C_3N_4 nanocomposite was consistent and validates its recyclability.



Scheme 4. A proposed mechanism for the synthesis of di-indolyloxindole catalyzed by CuO@g-C_3N_4.

4. Conclusions

In conclusion, a green and rapid hydrothermal method was introduced for the synthesis of CuO@g-C_3N_4 nanocomposites. Then, CuO@g-C_3N_4 nanocomposites was characterized by various techniques. The prepared CuO@g-C_3N_4 nanocomposites was applied for the synthesis of biologically active di-indolyloxindole derivatives in good to excellent yields (95 %). In addition, the reusability of nanocomposite was investigated and the results showed that the catalyst has good reusability after 5 cycles. This protocol provides a straightforward approach for deposition of CuO nanoparticles onto the g-C_3N_4 nanosheets and can be readily extended to the preparation of other classes of metal hybrids based on g-C_3N_4 nanosheets for technological and industrial applications.

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Table 5. The comparison of the efficiency of CuO@g-C_3N_4 with different catalysts.[a]

Entry	Catalyst	Solvent/Temp.(°C)	Time (min)	Yield (%)	Ref.
1	Cellulose sulfuric acid (5 mol %)	Solvent-free/ r.t.	120	88	[66]
2	Tungstic acid (10 mol %)	EtOH/ r.t.	360	92	[67]
3	Fe_3O_4–SO_3H (0.1 g)	CH_3CN/ 60°C	60	93	[68]
4	I_2 (10 mol %)	CH_2Cl_2/ r.t.	840	82	[69]
5	$LiClO_4$ (10 mol %)	EtOH/ 60°C	240	93	[70]
6	Nano-NiO (0.004 gr)	H_2O/ 70°C	30	98	[71]
7	SiO_2-OSO_3H (0.2 g)	CH_2Cl_2/ r.t.	120	94	[40]
8	Bi $(OTf)_3$	CH_3CN/ r.t.	180	92	[35]
9	Ceric ammonium nitrate	EtOH/ U.S.	180	95	[31]
10	PEG/OSO_3H	CH_3CN/ r.t.	150	93	[72]
11	CuO@g-C_3N_4	H_2O/ r.t.	50	95	This work

[a]Reaction conditions: Indole(2.0 mmol), isatin (1 mmol).

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