Electronic Supplementary Material (ESI) for RSC Advances.

Unprecedented iron-assisted room temperature synthesis of AgCN using acetonitrile

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Experimental Section

Materials Used

$Fe(NO_3)_3$, $FeSO_4.7H_2O$ and $AgNO_3$ were purchased from E-Merck. HPLC-grade CH_3CN was purchased from E-Merck and was used in the synthesis of AgCN. H_2O_2 (30% (w/w)) was used as received from Merck. The commercially available AgCN was procured from Sigma-Aldrich.

Physical Measurements

The Fourier-transform infrared spectroscopy spectrum (FTIR) was recorded in the mid-IR range of 450–4000 cm^{-1} in a Frontier-MIR-FIR from Perkin-Elmer. Powder X-ray diffraction (PXRD) measurement was recorded in BRUKER AXS, D8 FOCUS instrument in a low angle measurement from 2θ values of 10–80°. The electronic absorption spectra (UV-Vis) were measured using a Hitachi U-3400 spectrophotometer.

Computational Details

The electronic structures of all species involved in Figure 3 are optimized using the ωB97XD density functional[1] method. We utilized 6-311++G(d,p) basis set for all the elements except Ag. Considering the strong relativistic effect of Ag-atom, we have employed the Los Alamos LanL2DZ basis set with an effective core potential[2] for Ag atom only. Furthermore, frequency calculations are performed for all optimized species using the same level of theory. The cartesian coordinates of all species are given in Table S1. All the stationary points have been characterized with real and positive vibrational frequency values, while the transition state has been characterized by only one imaginary frequency value. Harmonic vibrational frequencies of all species are given in Table S2. Intrinsic reaction coordinate (IRC)[3] calculation has also been performed to ascertain the minimum energy pathways (MEP) linking the reactant and product-like structures through the transition state along a reaction coordinate. All the electronic calculations are performed using Gaussian 09 program package.[4]

Procedure of the catalytic degradation of MB dye

The degradation of methylene blue (MB) dye commenced by employing a standard solution with a molar concentration of 1×10^{-5} M, 10 mg of the catalyst and 100 μL of 2 mM solution of sodium borohydride. The progression of the reaction was assessed through UV-vis spectrophotometric analysis, with samples collected from the reaction vessel at 3-minute intervals. A similar methodology was employed utilizing commercially available AgCN as the catalyst. Due to the observed lower activity of the commercially available AgCN compared to the synthesized counterpart, UV-Vis data interpretation necessitated sample collection every 8 minutes.

Table S1 Cartesian coordinates of all species obtained at ωB97XD/6-311++G(d,p)/LANL2DZ level of theory.

FeO_2 (I)

Z	X	Y	Z
26	0.000000000	-0.606968000	0.000000000
8	0.676957000	0.986457000	0.000000000
8	-0.676957000	0.986188000	0.000000000

IM

Z	X	Y	Z
26	0.661063000	-0.000002000	-0.009844000
8	1.172596000	1.407776000	0.324804000
8	1.172511000	-1.407824000	0.324760000
6	-2.440751000	0.000006000	0.630778000
1	-2.383146000	-0.886346000	1.263261000
1	-3.376341000	-0.000251000	0.069419000
1	-2.383411000	0.886650000	1.262883000
6	-1.312394000	0.000006000	-0.304625000
7	-0.755246000	0.000044000	-1.356150000

TS

Z	X	Y	Z
26	0.792328000	0.060917000	-0.028359000
8	0.553966000	1.578082000	-0.224556000
8	1.893388000	-0.833580000	0.560631000
6	-2.728120000	0.161879000	0.471907000
1	-2.718907000	-0.101410000	1.530014000
1	-3.648109000	-0.198652000	0.008082000
1	-2.656144000	1.244948000	0.362054000
6	-1.593667000	-0.447569000	-0.191686000
7	-0.746496000	-0.967227000	-0.790392000

II

Z	X	Y	Z
26	-0.405374000	0.150239000	-0.021582000
8	-1.924349000	-0.659094000	-0.589250000
8	-2.065936000	-0.045938000	0.681784000
6	2.753105000	-0.703881000	0.135255000
1	2.796470000	-1.187772000	1.114913000
1	3.611611000	-0.031595000	0.025264000
1	2.814451000	-1.495081000	-0.617074000
6	1.455870000	0.029357000	-0.005460000
7	1.140804000	1.213661000	-0.211573000

III

Z	X	Y	Z
26	-0.157752000	-0.079376000	0.125603000
8	-1.917593000	-0.315794000	0.527306000
8	-1.515845000	-0.843137000	-0.714073000
6	0.006775000	1.831747000	-0.176126000
1	0.506993000	1.986553000	-1.138504000
1	0.629222000	2.278422000	0.609586000
1	-0.990338000	2.281065000	-0.185294000
6	1.795612000	-0.378251000	0.005222000
7	2.944122000	-0.561685000	-0.004557000

IV

Z	X	Y	Z
26	-3.556246000	-0.065954000	-0.090360000
8	-4.681971000	-0.652277000	1.123690000
8	-5.299095000	-0.566310000	-0.132902000
6	-3.604158000	1.848286000	-0.384179000
1	-3.135605000	2.062413000	-1.354386000
1	-3.026776000	2.353287000	0.396850000
1	-4.643409000	2.184339000	-0.373076000
6	-1.583630000	-0.108566000	-0.050258000
7	-0.423992000	-0.141277000	-0.073712000
47	1.684161000	-0.215199000	-0.149727000
7	4.476956000	0.192611000	0.204137000

8	3.822935000	0.951521000	0.942084000
8	5.695135000	0.181893000	0.175054000
8	3.821572000	-0.610894000	-0.556576000

V

Z	**X**	**Y**	**Z**
26	1.401610000	0.042978000	0.116120000
8	3.081895000	-0.405809000	0.165178000
8	2.749965000	0.194717000	-1.000362000
6	-0.502189000	0.273014000	0.809035000
1	-0.933004000	0.963181000	1.536220000
1	0.210389000	-0.398019000	1.388217000
1	-0.123027000	0.951594000	-0.033689000
7	-2.645095000	-0.030360000	-0.167710000
8	-1.476260000	-0.650612000	0.337394000
8	-3.466354000	-0.814525000	-0.505416000
8	-2.647673000	1.168760000	-0.195557000

CH_3CN

Z	**X**	**Y**	**Z**
6	-1.175342000	0.000000000	0.000003000
1	-1.547487000	0.897918000	0.495287000
1	-1.547486000	-0.877905000	0.529953000
1	-1.547495000	-0.020016000	-1.025252000
6	0.280614000	0.000001000	-0.000001000
7	1.430119000	0.000000000	0.000000000

$AgNO_3$

Z	X	Y	Z
47	-1.067123000	-0.000008000	-0.000094000
7	1.652324000	-0.000017000	0.000099000
8	0.983325000	1.086172000	0.000548000
8	2.856409000	0.000244000	-0.000633000
8	0.983828000	-1.086351000	0.000548000

CH_3NO_3

Z	X	Y	Z
6	-1.754959000	-0.001247000	-0.000033000
1	-2.517220000	-0.777791000	-0.000541000
1	-1.836591000	0.616202000	0.894891000
1	-1.836147000	0.616884000	-0.894518000
7	0.613093000	0.046099000	-0.000010000
8	-0.531896000	-0.743652000	0.000064000
8	1.620769000	-0.591953000	-0.000030000
8	0.464635000	1.239292000	0.000020000

AgCN

Z	X	Y	Z
47	0.000000000	0.000000000	0.582652000
7	0.000000000	0.000000000	-2.640722000
6	0.000000000	0.000000000	-1.483265000

Table S2 Harmonic vibrational frequencies (in cm^{-1}) of all species obtained at ωB97XD/6-311++G(d,p)/LANL2DZ level of theory.

Species	**Frequencies (in cm^{-1})**										
FeO_2 (I)	731	857	1098								
IM	92	107	159	227	282	316	388	407	553	925	1047
	1064	1064	1106	1404	1465	1473	2103	3071	3164	3165	
TS	134*i*	44	77	179	205	276	308	380	453	925	1046
	1049	1062	1101	1404	1458	1468	2301	3070	3161	3166	
II	77	97	107	202	291	362	430	503	612	632	958
	988	1022	1110	1375	1477	1479	1795	3021	3102	3112	
III	82	118	140	154	170	276	363	384	474	541	619
	641	729	1013	1169	1438	1451	2231	3004	3093	3118	
IV	4	21	25	59	68	74	102	115	131	146	155
	171	188	269	331	406	450	481	543	624	643	732
	735	768	844	1022	1097	1180	1370	1434	1455	1579	2254
	3004	3095	3134								
V	]42	52	102	131	166	183	279	402	567	606	659
	700	785	845	895	1001	1061	1083	1170	1353	1411	1565
	1672	1802	2485	2651	3126						
CH_3CN	386	386	940	1064	1064	1414	1479	1479	2401	3070	3155
	3155										
$AgNO_3$	122	178	261	728	773	838	1083	1290	1625		
CH_3NO_3	133	210	358	607	705	796	918	1069	1177	1207	1375
	1475	1479	1505	1769	3070	3162	3188				
AgCN	220	220	393	2288							

Table S3 Total energy, Enthalpy and Gibb's free energy of all species obtained at ωB97XD/6-311++G(d,p)/LANL2DZ level of theory. All values are in Hartree.

Species	E_0	H	G
FeO_2 (I)	-1413.91341	-1413.909444	-1413.93899
CH_3CN	-132.696571	-132.692025	-132.720577
IM	-1546.746679	-1546.738448	-1546.77873
TS	-1546.73966	-1546.731475	-1546.77258
II	-1546.780715	-1546.772398	-1546.81381
III	-1546.791687	-1546.782512	-1546.82543
IV	-1972.911908	-1972.895838	-1972.9622
V	-1734.063757	-1734.054014	-1734.09992
$AgNO_3$	-426.039935	-426.034099	-426.070174
CH_3NO_3	-320.127539	-320.121705	-320.155542
AgCN	-238.572209	-238.567528	-238.597239

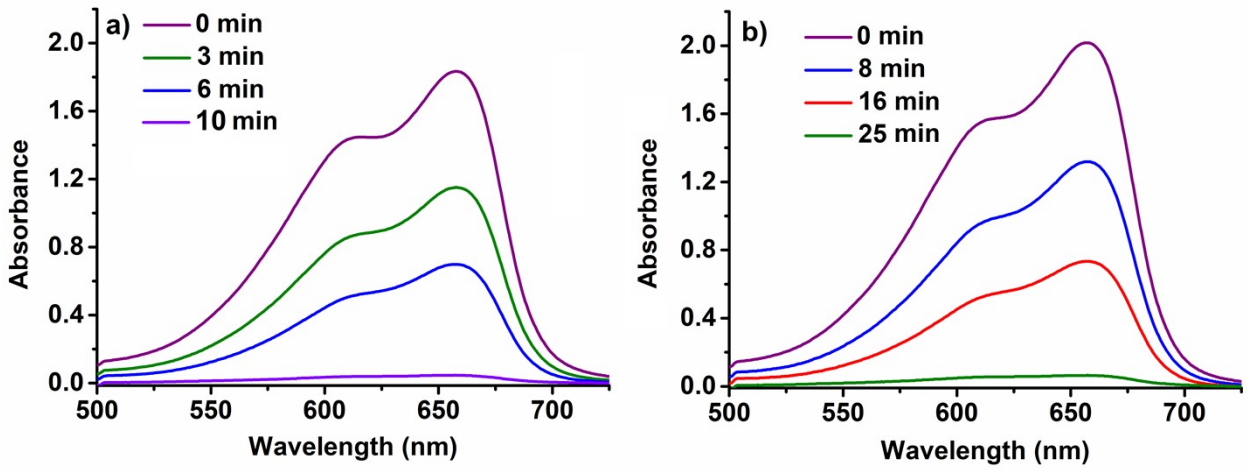

Fig. S1 UV-Vis spectra for the degradation of methylene blue (MB) using (a) synthesized AgCN, and (b) Commercially available AgCN

References

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