Synthesis of an Fe Rich Amorphous Structure with a Catalytic Effect To Rapidly Decolorize Azo Dye at Room Temperature

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Supporting Information

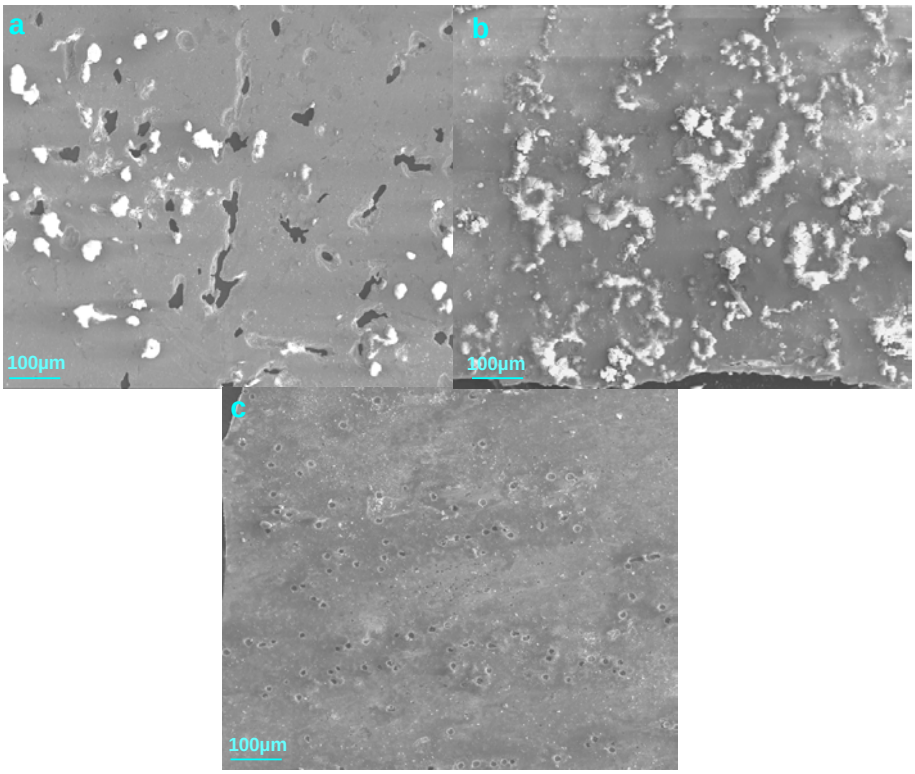

Figure S1. The SEM observations of $Fe_{79}B_{16}Si_5$ (a), $Fe_{11}Y_3$ (b), and $Fe_{66.7}B_{16.6}Y_{17.1}$ (c). after 180 min decolorization.

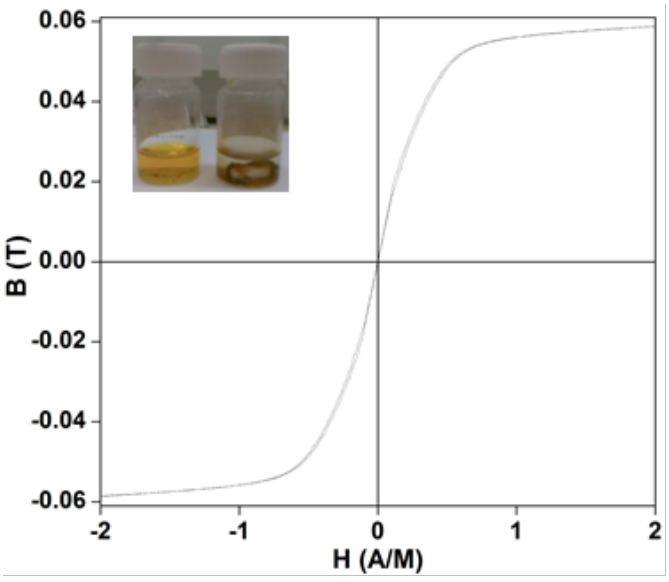

Figure S2. The Magnetization curve of $Fe_{66.3}B_{16.6}Y_{17.1}$ after 180 min decolorization.

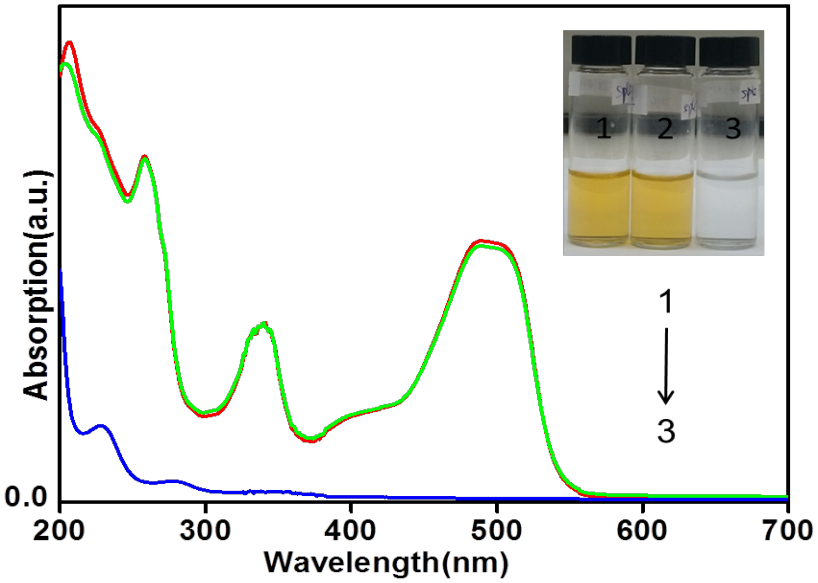

Figure S3. UV-vis spectrum of treated solutions after 180 min 1) OG (red), 2) B powder (green), 3) $Fe_{66.3}B_{16.6}Y_{17.1}$ (blue).

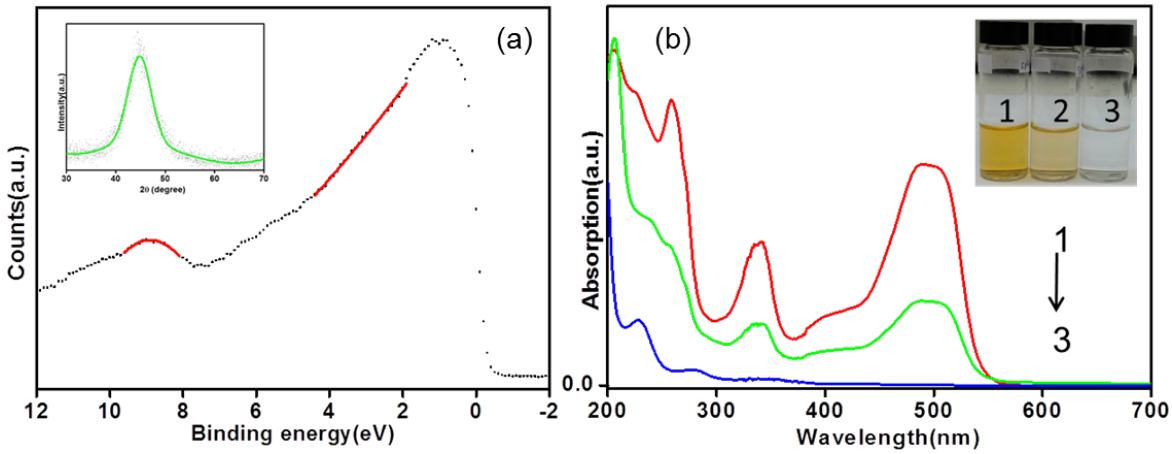

Figure S4. The decolorization of reported sample $Fe_{78}B_{14}Si_8$ in ref:[7] (a) Valence band XPS spectrum of $Fe_{78}B_{14}Si_8$ and the insert is the XRD for phase identification, (b) UV-vis spectrum of treated solutions after 180 min, 1) OG (red), 2) $Fe_{78}B_{14}Si_8$ (green), 3) $Fe_{66.3}B_{16.6}Y_{17.1}$ (blue).

We have made the amorphous foil with the reported composition $Fe_{78}B_{14}Si_8$ in ref.[7] Its XPS spectrum shows the strong Fe−B interaction, characterized by the hump at 8.9eV. The profile of Fe-3d peak does not have a shoulder. With the Fe−B interaction, its decolorization of OG was much inferior to the $Fe_{66.3}B_{16.6}Y_{17.1}$. The calculated efficiency of $Fe_{78}B_{14}Si_8$ is 61.7% and the calculated k value is 0.0053 min^{-1}. The k is closely to the 0.0044 min^{-1} of $Fe_{79}B_{16}Si_5$ but far below the 0.047 min^{-1} of $Fe_{66.3}B_{16.6}Y_{17.1}$.

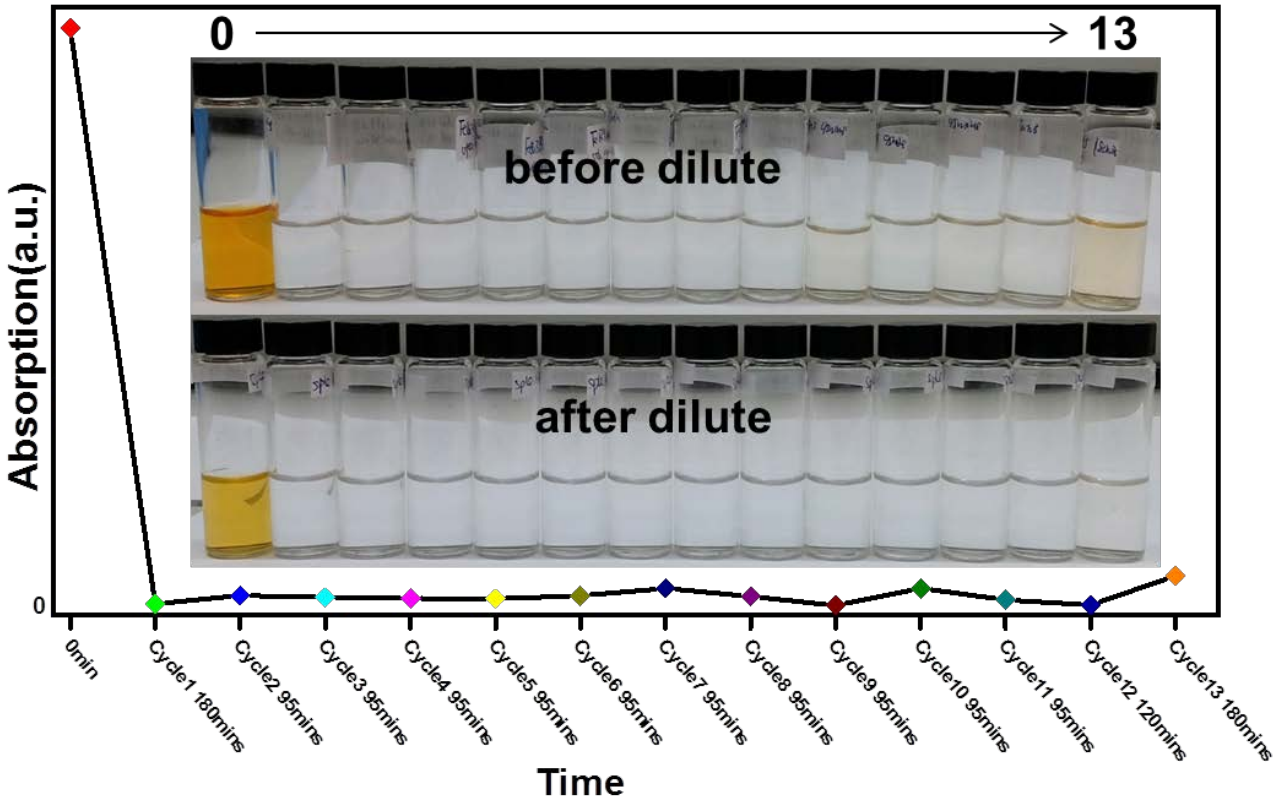

Figure S5. The UV-vis spectrum of treated solutions in cyclic decolorization testing.

After the 1st cycle, the decolorization time was fixed to 95 min until the 11th cycles. In the 12th cycles, the decolorization was not finished after 95 min, and then continued to 120 min. In the 13th cycles, the decolorization was not finished even continued to 180 min. For the filtrates obtained in the 9th, 10th, 11th cycles, the slight yellow color was appeared. But after dilution for UV-vis absorption spectroscopy, the absorption values were comparable to the previous 8 cycles. Overall, the fast decolorization could be observed until the 11th cycles and the cyclic decolorization testing was conducted up to 13 cycles. The reported $Fe_{78}Si_8B_{14}$ has 8 cycles reusability,[7] so the $Fe_{66.3}B_{16.6}Y_{17.1}$ has longer usable life.

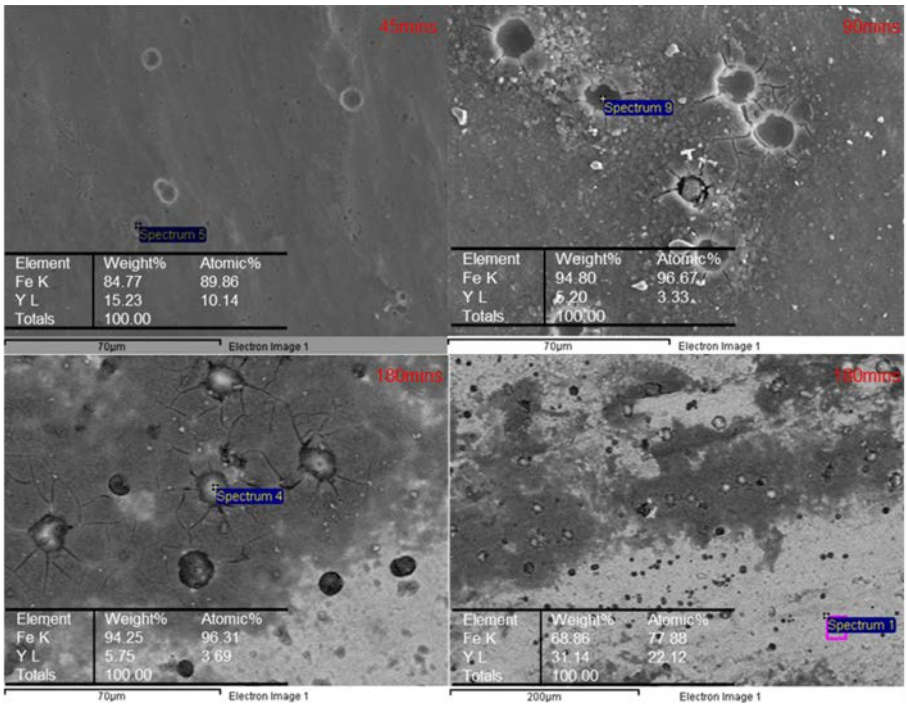

Figure S6. The EDS of selected holes of $Fe_{66.3}B_{16.6}Y_{17.1}$ during decolorization.

Table S1. The element analysis of $Fe_{66.3}B_{16.6}Y_{17.1}$ in cyclic decolorization.

Items	EDS			XRF			ICP		
	Fe(at%)	Y(at%)	Fe/Y(at%)	Fe(at%)	Y(at%)	Fe/Y(at%)	Fe^{2+}/Fe^{3+} (mg/L)	B^{3+}(mg/L)	Y^{3+}(mg/L)
$Fe_{66.3}B_{16.6}Y_{17.1}$(as raw)	79.44	20.56	3.86	——	——	——	——		——
$Fe_{66.3}B_{16.6}Y_{17.1}$(after 1st cycle)	78.58	21.42	3.52	——	——	——	——		——
Colourless Filtrate(after 1st cycle)	——	——	——	——	——	——	0.0866±0.0210	21.0740±0.0267	0.0259±0.0186
Red Sediments(after 1st cycle)	71.46	28.54	2.50	97.7636±0.28	2.2364±1.59	43.64	——	——	——
Colourless Filtrate(after 2nd cycles)	——	——	——	——	——	——	0.1148±0.0210	17.4770±0.0267	0.0199±0.0186
Red Sediments(after 2nd cycles)	——	——	——	95.4111±0.44	4.5889±1.65	20.79	——	——	——
Colourless Filtrate(after 3rd cycles)	——	——	——	——	——	——	0.0191±0.0210	18.3750±0.0267	0.0043±0.0186
Red Sediments(after 3rd cycles)	75.57	24.43	3.09	95.6604±0.28	4.3396±1.34	22.04	——	——	——
Colourless Filtrate(after 4rd cycles)	——	——	——	——	——	——	0.0779±0.0210	14.9850±0.0267	0.0155±0.0186
Red Sediments(after 4th cycles)	——	——	——	95.8189±0.31	4.1811±1.23	22.92	——	——	——
Colourless Filtrate(after 5th cycles)	——	——	——	——	——	——	0.0814±0.0210	19.9190±0.0267	0.0198±0.0186
Red Sediments(after 5th cycles)	——	——	——	94.8677±0.30	5.1323±1.07	18.49	——	——	——
Colourless Filtrate(after 6th cycles)	——	——	——	——	——	——	0.0784±0.0210	18.6190±0.0267	0.0199±0.0186
Red Sediments(after 6th cycles)	73.86	26.14	2.83	95.4407±0.48	4.5593±1.96	20.93	——	——	——
Colourless Filtrate(after 7th cycles)	——	——	——	——	——	——	0.0121±0.0210	16.6690±0.0267	0.0024±0.0186
Red Sediments(after 7th cycles)	——	——	——	92.5885±0.56	7.4115±1.67	12.48	——	——	——
Colourless Filtrate(after 8th cycles)	——	——	——	——	——	——	0.0293±0.0210	16.7770±0.0267	0.0077±0.0186
Red Sediments(after 8th cycles)	72.09	27.91	2.58	95.7913±0.50	4.2087±2.10	22.75	——	——	——
Colourless Filtrate(after 9th cycles)	——	——	——	——	——	——	0.0520±0.0210	17.0760±0.0267	0.0061±0.0186
Red Sediments(after 9th cycles)	——	——	——	96.6446±0.31	3.3554±1.41	28.76	——	——	——
Colourless Filtrate(after 10th cycles)	——	——	——	——	——	——	0.0311±0.0210	16.5000±0.0267	0.0084±0.0186
Red Sediments(after 10th cycles)	——	——	——	95.4028±0.42	4.5972±1.68	20.74	——	——	——
Colourless Filtrate(after 11th cycles)	——	——	——	——	——	——	0.0391±0.0210	15.1800±0.0267	0.0134±0.0186
Red Sediments(after 11th cycles)	71.56	28.44	2.52	95.4888±0.44	4.5112±1.67	21.18	——	——	——
Colourless Filtrate(after 12th cycles)	——	——	——	——	——	——	0.0140±0.0210	14.1920±0.0267	0.0040±0.0186
Red Sediments(after 12th cycles)	——	——	——	97.0034±0.40	2.9966±2.01	32.33	——	——	——
Colourless Filtrate(after 13th cycles)	——	——	——	——	——	——	0.0659±0.0210	15.6150±0.0267	0.0100±0.0186
Red Sediments(after 13th cycles)	76.00	24.00	3.17	94.9087±0.36	5.0913±1.29	18.65	——	——	——
Average	——	——	——	——	——	——	0.0540±0.0210	17.1122±0.0267	0.0121±0.0186
$Fe_{66.3}B_{16.6}Y_{17.1}$(after 13th cycles)	79.16	20.84	3.80	85.9476±0.31	14.0524±0.46	6.12	——	——	——

According to the results, the Fe was took part in the redox and formed $Fe(OH)_3$, this explains the low concentration of Fe^{2+} /Fe^{3+} in the solution but high percentage of Fe in the sediments. The B was release into the water but it did not contributed to the decolorization (Figure S3). Compare with $Fe_{79}B_{16}Si_5$ (Table S2), the leached B of $Fe_{66.3}B_{16.6}Y_{17.1}$ was low. No Y was released into the solution. The Y was concentrated at the edge of the pits (Figure 7c and 7d) and then peeled from the foil as the atomic arrangement of Fe−B−Y is increasingly unstable. Finally, the Y was existed at the surface of the insoluble reaction products.

Table S2. The ICP tests of various samples for comparison.

Samples	H_2O	B+H_2O after180mins	B+OG after180mins	$Fe_{79}B_{16}Si_5$+OG after180mins
Fe^{2+},Fe^{3+} mg/L	-0.0002±0.0059	0.0609±0.0041	0.0106±0.0041	0.0057±0.0059
B^{3+} mg/L	0.0532±0.0373	3.7498±0.0946	6.2102±0.0946	29.41±0.0373
Y^{3+} mg/L	0.0000±0.0141	0.0013±0.0043	0.0027±0.0043	0.0007±0.0141

DI water was used without further treatment. The B was leached into the solution after being stirred with water and OG respectively. For $Fe_{79}B_{16}Si_5$, the concentration of iron ion was small but B ion was high. This result also demonstrates that the B was not related to the decolourization. We propose that with strong Fe-B hybridization, the Fe has low activity but B readily reacts with water.

Table S3. The decolorization efficiency of samples.

Items	Samples				
	Iron powder	$Fe_{79}B_{16}Si_5$	$Fe_{11}Y_3$	$Fe_{66.3}B_{16.6}Y_{17.1}$	$Fe_{78}B_{14}Si_8$
Efficiency(%)	11.8	51.5	57.5	99.7	61.7

Reference

(7) Zhang, C.; Zhu, Z.; Zhang, H.; Hu, Z. Rapid Decolorization of Acid Orange II Aqueous Solution by Amorphous Zero−Valent Iron. *J. Environ. Sci.* **2012**, *24*, 1021−1026.