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# Photoinduced Oxygen Prompted Iron-Iron Oxide Catalyzed Clock Reaction: Mimic of Blue Bottle Experiment

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## General

### 1. Materials

Ferrous sulphate heptaydrate [$FeSO_4 \cdot 7H_2O$], Sodium borohydride [$NaBH_4$], citric acid, ethanol (EtOH) and methylene blue (MB), nile blue (NB), crystal violet (CV) and rhodamine B (RhB) were all analytical grade and used without further purifications. Double distilled water was employed throughout the experiments.

### 2. Catalysts preparation

Iron nanoparticles were prepared through simple one-pot synthesis method, using citric acid as stabilizing agent. In typical experiment, 100 ml water was added in round bottom flask containing ferrous sulphate hepta-hydrate [$FeSO_4 \cdot 7H_2O$] (2500 mg, 9mmol) and citric acid (165mg, 0.75 mmol). The mixture was stirrer for 10 min. Then Sodium borohydride [$NaBH_4$] (600 mg, 15 mmol) was portion-wise added to a stirring solution, act as reducing agent and vigorous stirring was continued for another 10 min. The solution kept to 30 min and when it settled down, it was filtered and washed with ethanol and water at least three times. The residue finally collected after dried under high vacuum [**zero-valent iron FNP-0**]. This zero-valent iron was kept in open atmosphere for 30days for aerial oxidation that produces mixed-valent iron-iron oxide (**FNP-30**). This is our active catalyst for the clock reaction. $Fe_3O_4$ and $\alpha$-$Fe_2O_3$ NPs was prepared in hydrothermal synthesis as reported earlier.

### 3. Characterizations of catalyst

X-ray powder diffraction study was carried out on a Rigaku X-Ray diffractometer at a voltage of 10 KV using Cu Kα radiations ($\lambda$=0.15418 nm) at scanning rate of 0.50°/minute in the 2θ range 10-80°. SEM images were obtained from a Hitachi S-4800 microscope at an operating voltage of 15Kv. HR-TEM image were obtain from a FEI-TecnaiG2,F30 microscope at an accelerating potential of 300Kv. Surface Analysis by XPS is accomplished by irradiating a sample with monoenergetic soft X-ray, Mg Kα (1253.6 eV) using the ESCA probe TPD system in an ultra-high vacuum system. The sample was coated with platinum for effectual imaging before being charged. UV-vis spectra were recorded in UV-Vis spectrophotometers of Shimadzo UV-2550 and Jasco V-760 using standard 1 cm quartz cuvette.

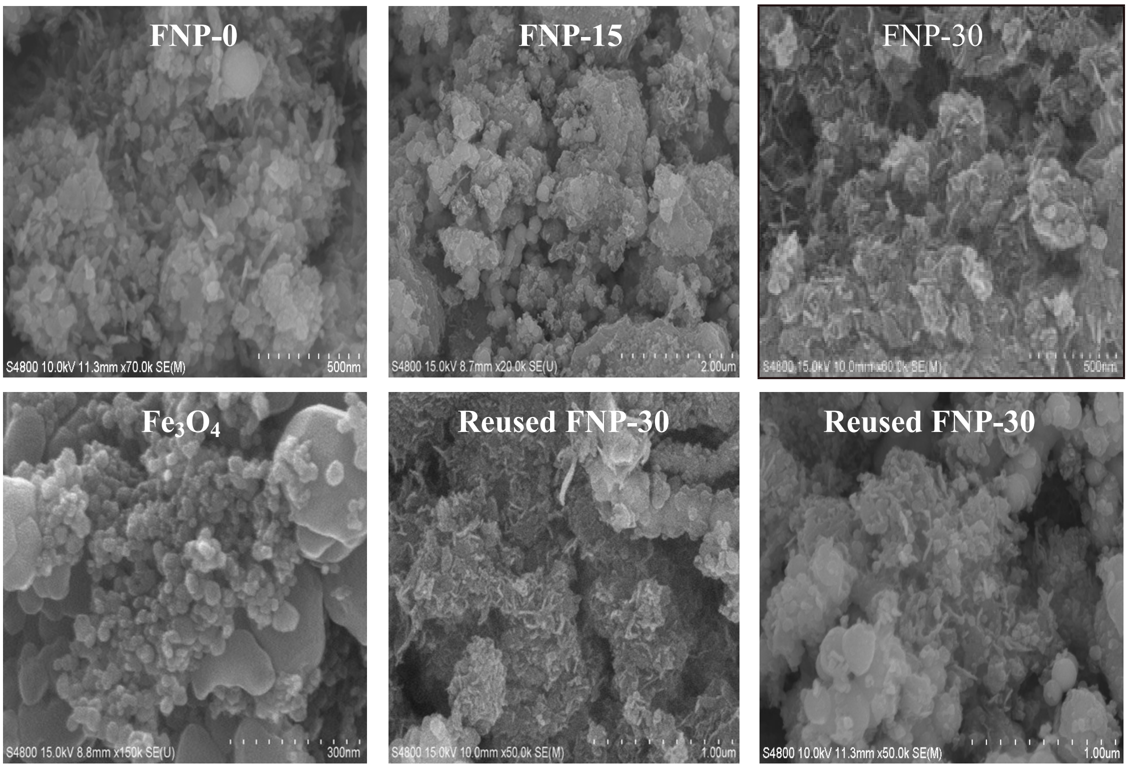


**Figure S1** FE-SEM image of prepared FNP-0, FNP-15, FNP-30, $Fe_3O_4$ and reused FNP-30

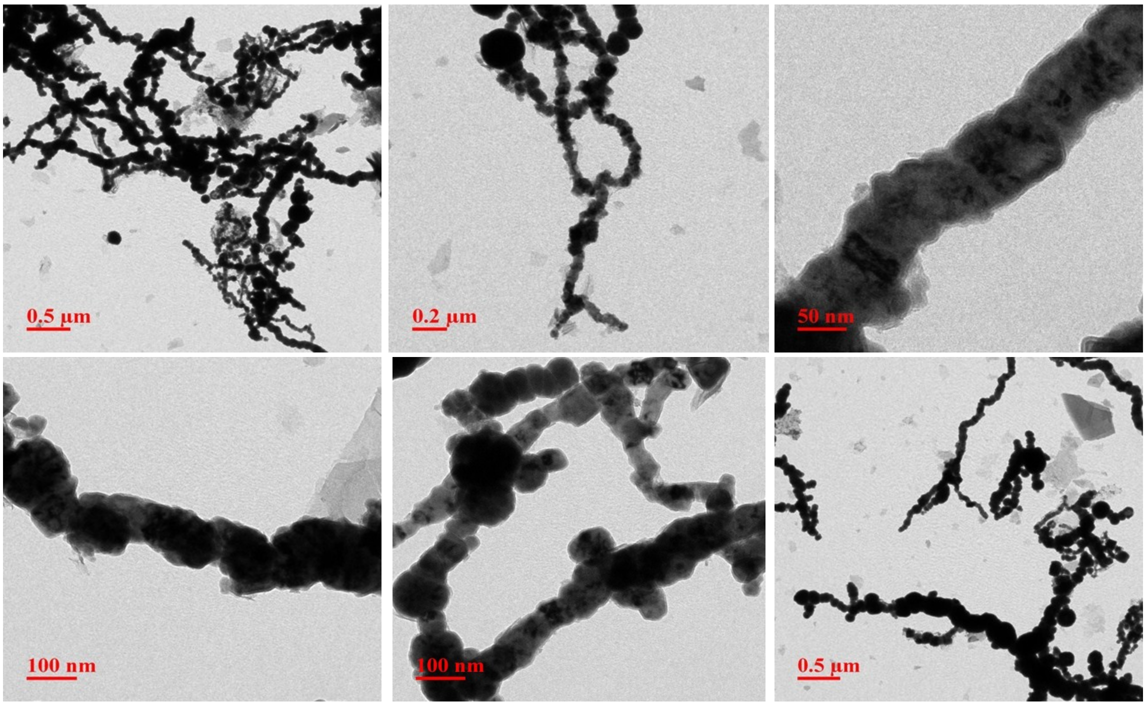


**Figure S2.** HRTEM of FNP-30.

**Table S1:** Distribution of elements from EDX analysis

| Sl | Catalyst | Element Weight (%) | |
|---|---|---|---|
| | | Iron | Oxygen |
| 01 | **FNP-0**<br>[freshly prepared] | 100 | --- |
| 02 | **FNP-15**<br>[aerially oxidized for 15days] | 75.31 | 24.69 |
| 03 | **FNP-30**<br>[aerially oxidized for 30 days] | 66.30 | 33.70 |
| 04 | **$Fe_3O_4$**<br>[Hydrothermal synthesis] | 63.14 | 36.86 |

**Table S2:** Characterization of FNP-30 mixed valence state.

| Sl | Compound | Fe (eV) | | | | Fe (eV) |
|---|---|---|---|---|---|---|
| | | $2P_{3/2}$ | Satellite | $2P_{1/2}$ | Satellite | 3P |
| 1 | $Fe_2O_3$ Standard | 711.0 | 718.8 | 724.6 | 729.5 | 55.6 |
| | $Fe_3O_4$ | 710.6 | | 724.1 | | |
| 2 | nanoscale zero valent iron | 707 ($Fe^0$)<br>711 ($Fe^{3+}$) | | | | |
| 3 | Fe–Cu bimetal nanoparticles | 707.0<br>($Fe^0$)<br>711.5<br>($Fe^{3+}$) | | | | |
| 4 | (In0.97□xFexSn0.03)2O3 films | 709<br>($Fe^{2+}$)<br>710.6<br>($Fe^{3+}$) | 724.7<br>($Fe^{3+}$)<br>722.9<br>($Fe^{2+}$) | | | |

1. *T. Yamashita et al, 2008, 254, 2441–2449.*
2. *Keyla T. Soto Hidalgo et al, RSC Adv., 2015, 5, 2777.*
3. *S. Hinokuma, Catal. Sci. Technol., 2015, 5, 3945.*
4. *D. Yang RSC Adv., 2014, 4, 33680.*

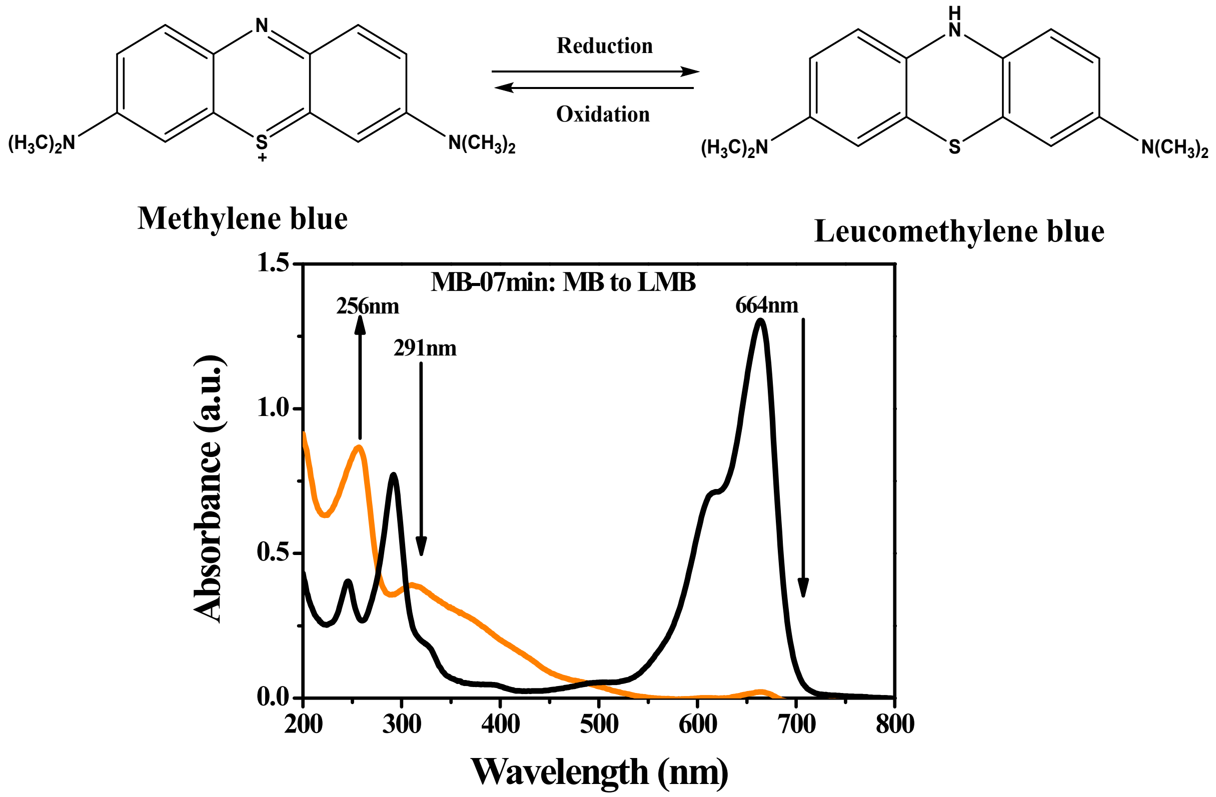


**Figure S3.** Reduction of MB to LMB with FNP-30.

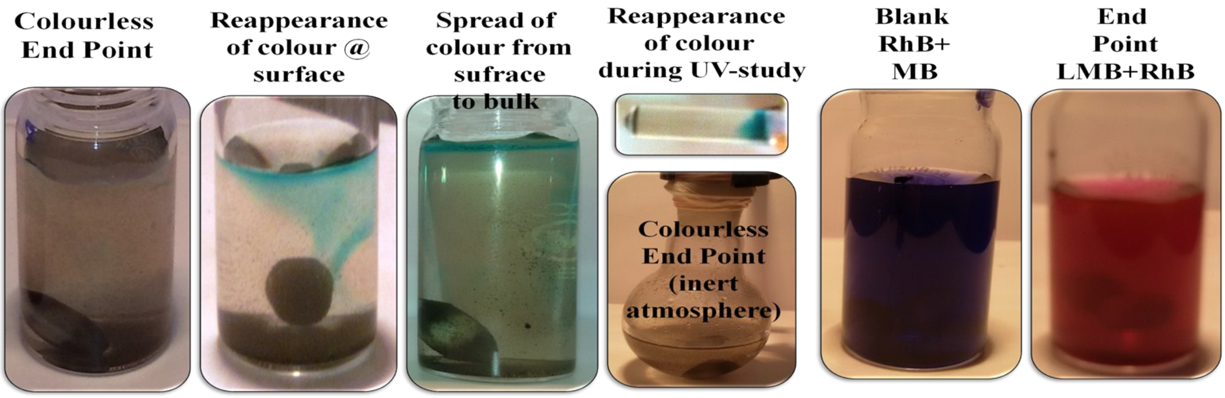
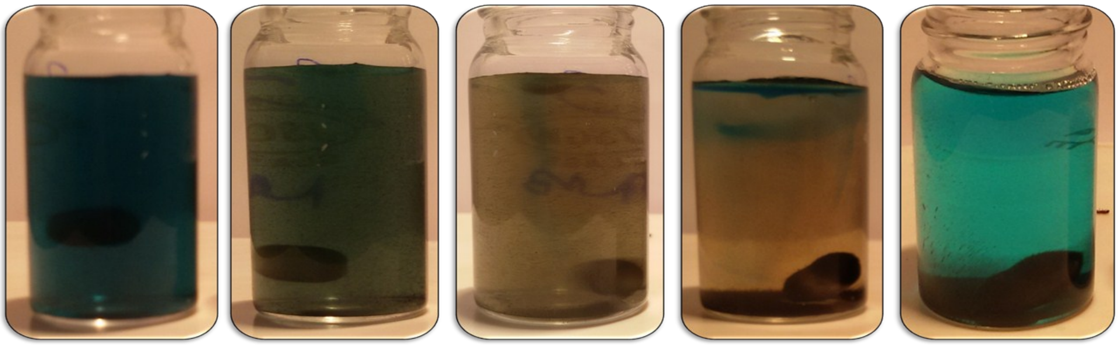
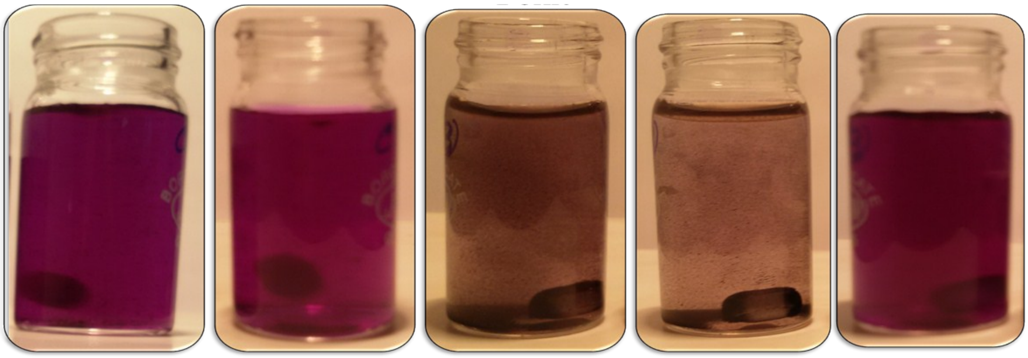


**Figure S4.** Fate of MB and mix dyes in presence of FNP-30 during clock reaction.



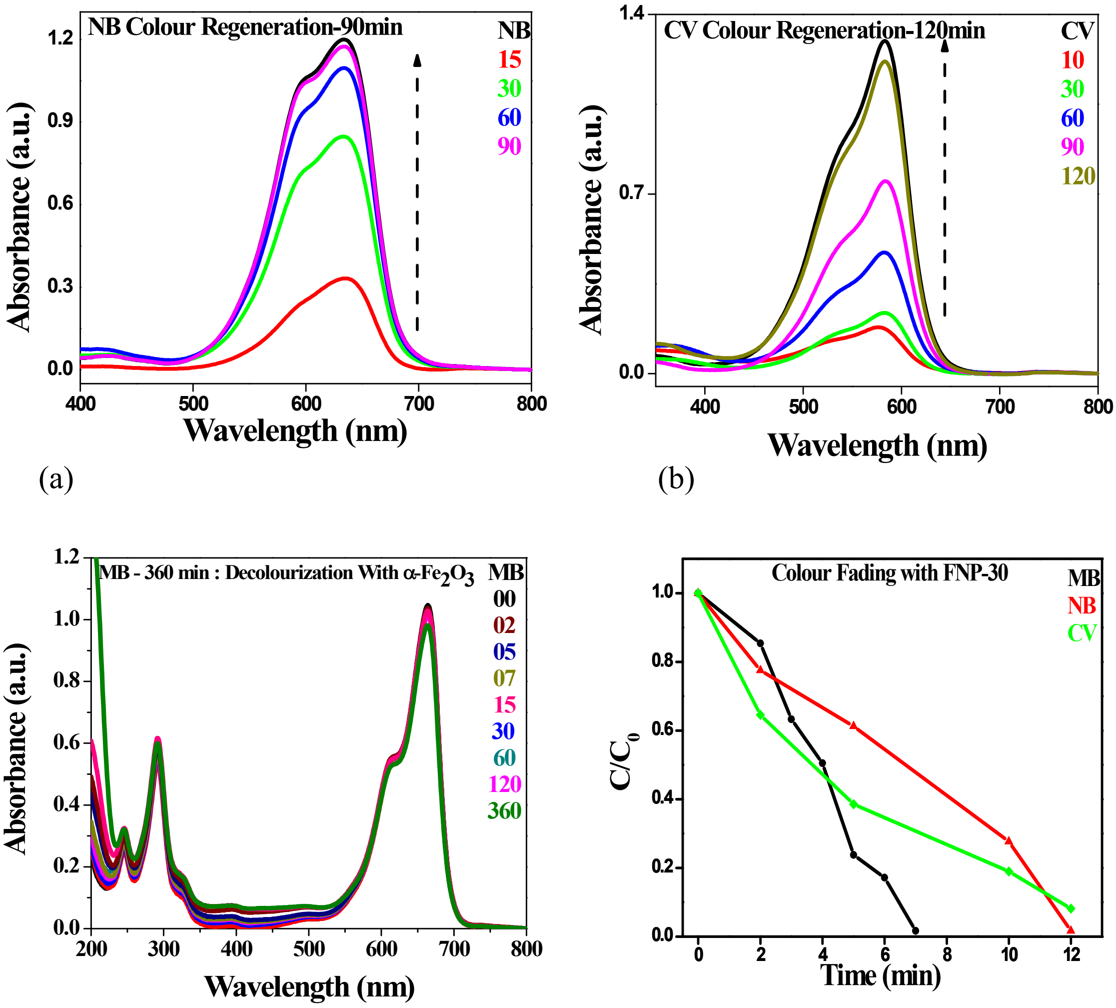
**Decolourization Start** | **Decolourization** | **Colourless End Point** | **Reappearance of Colour@surface** | **Regeneration of complete colour**

**Figure S5.** Decolourization and regeneration of NB in presence of FNP-30 during clock reaction



**Decolourization Start** | **Decolourization** | **Colourless End Point** | **Reappearance of Colour start** | **Regeneration of complete colour**

**Figure S6.** Decolourization-Regeneration of CV in presence of FNP-30 during clock reaction



(a) (b)

(c) (d)

**Figure S7.** UV-vis Spectra of (a) Colour regeneration of NB with FNP-30, (b) Colour regeneration of CV with FNP-30 (c) Decolourization of MB with α-$Fe_2O_3$ NPs in inert medium, (d) Relative concentration of MB, CV and NB with progress of time in the presence of FNP-30.

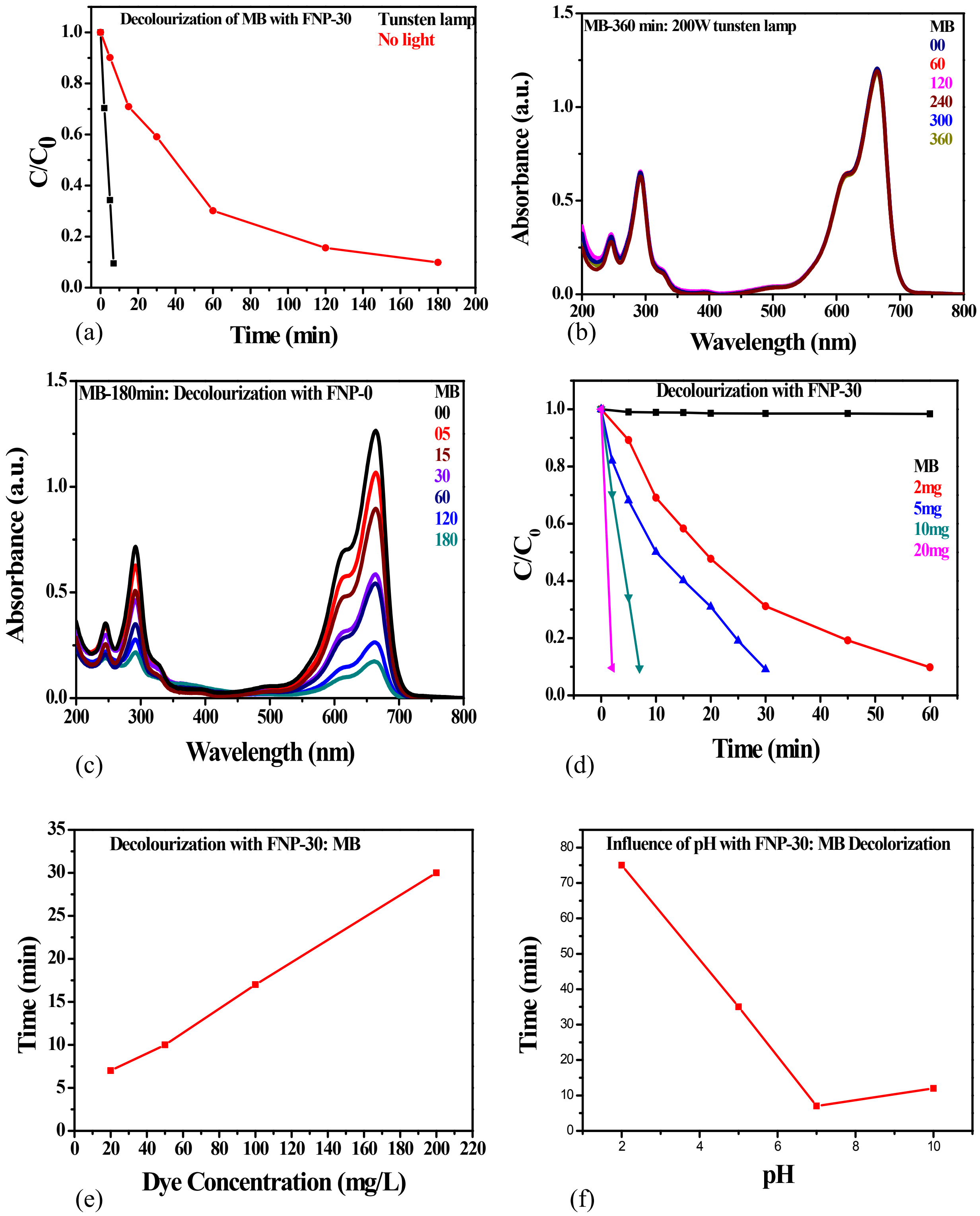
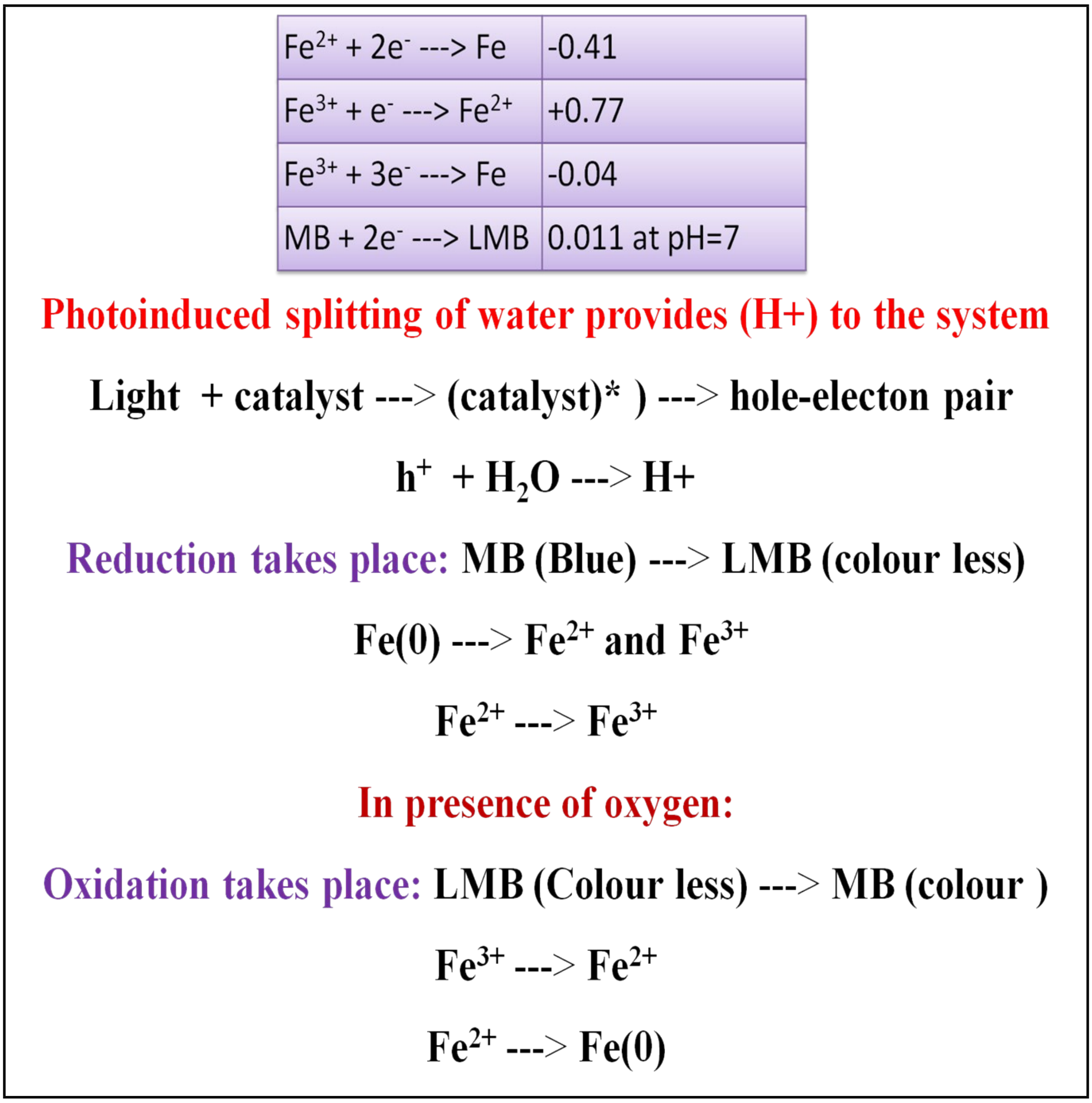


**Figure S8.** UV-vis spectra of (a) Decolourization of MB in light and no light condition with FNP-30, (b) MB with tungsten lamp, (c) Decolourization of MB with FNP-0 in non-inert condition, (d) Effect of amount of catalyst for MB decolourization, (e) Dye Concentration effect for MB decolourization, (f) Influence of pH for decolourization of MB.



| | |
|---|---|
| $Fe^{2+} + 2e^{-}$ ---> Fe | -0.41 |
| $Fe^{3+} + e^{-}$ ---> $Fe^{2+}$ | +0.77 |
| $Fe^{3+} + 3e^{-}$ ---> Fe | -0.04 |
| MB + $2e^{-}$ ---> LMB | 0.011 at pH=7 |

**Photoinduced splitting of water provides (H+) to the system**

**Light + catalyst ---> (catalyst)* ) ---> hole-electon pair**

**$h^{+}$ + $H_2O$ ---> H+**

**Reduction takes place: MB (Blue) ---> LMB (colour less)**

**Fe(0) ---> $Fe^{2+}$ and $Fe^{3+}$**

**$Fe^{2+}$ ---> $Fe^{3+}$**

**In presence of oxygen:**

**Oxidation takes place: LMB (Colour less) ---> MB (colour )**

**$Fe^{3+}$ ---> $Fe^{2+}$**

**$Fe^{2+}$ ---> Fe(0)**

**Figure S9.** Proposed mechanism for iron clock reaction.