

Supplementary Information

Environmentally Benign Fabrication of Superparamagnetic and Photoluminescent Ce,Tb-codoped Fe₃O₄-gluconate Nanocrystals from Low-quality Iron Ore Intended for Wastewater Treatment†

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The supporting file contains five figures with respective captions and a table.

1. Experimental section

1.1. IOT treatment details

IOTs were collected from the tailing dams of the Donimalai iron ore mines (NMDC, Karnataka) and prior to performing its μ -XRF analysis, the samples were dried and grinded at ~ 100 °C. A laboratory ball milling machine (Lawrence & Mayo, Model No. LM-17-605, internal diameter and length- 300 mm each) was utilized for ball milling of IOT samples. The experiment was carried out at 65% of the critical speed of the instrument using 150 balls made of steel with varying their diameters (25/20/9.5 mm). The ore-to-ball ratio was fixed at 0.5 and ball-milling run time was set for 30 minutes to get the ultimate particle size ≤ 50 μ m.

1.2. Selective leaching of IOTs

Consistent with some earlier studies^{1,2}, a selective leaching process of the ball milled IOTs was conducted with the help of concentrated HCl (considering as the leaching solvent) to obtain the hydrolysate solution ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) for the synthesis of G24 and lanthanide doped G24. Approximately 10-12 g ball milled IOTs powder was added in a ~ 250 ml 38 weight% 12.4 M HCl (HCl/IOTs volume ratio is 20:1). The thermal treatment of the leachate solution was executed on a heating plate at 120 °C for 5-6 hrs. Although CaCl_2 and MgCl_2 can be formed and dissolved in HCl during the boiling stage owing to the presence of CaO and MgO in the IOTs (see Table 2 in the main manuscript), the related possibility was negligibly small as Mg and Ca-based minerals weight% were less compare to the standard value (1.5 %) for the chlorination process^{3,4}. According to the μ -XRF analysis, Mg and Ca-based minerals are also very less concerning the total Fe weight% (71.38 %). The trace elements like Mn, Cr, and V-based minerals having ≤ 0.13 weight% also nullifying the possibility of white pigment formation during leaching⁴. Afterward a precise filtration was done using Whatman 41 filter paper to separate the acid soluble hydrolysate (contains total Fe only) and insoluble residues (contain impurities like aluminum, silicon, magnesium, and calcium-based oxides and other trace element-based minerals). Finally, the deep brown colored hydrolysate solution was taken in a 500 ml stoppered bottle for use in further synthetic processes.

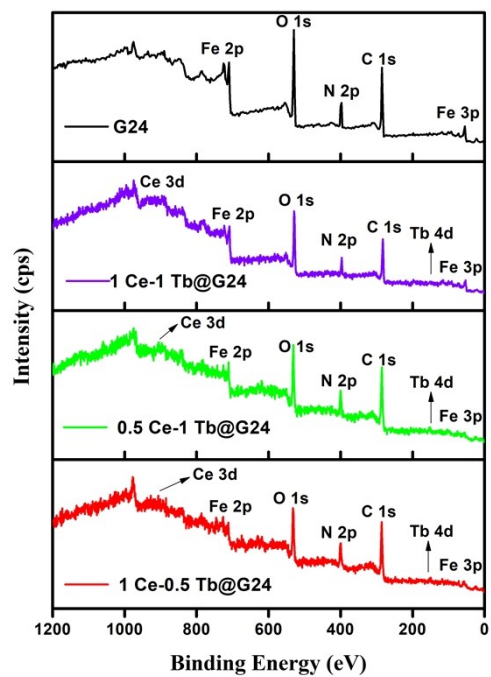


Fig. S1 XPS survey spectra comparison for all Ln doped G24 and pure G24 samples.

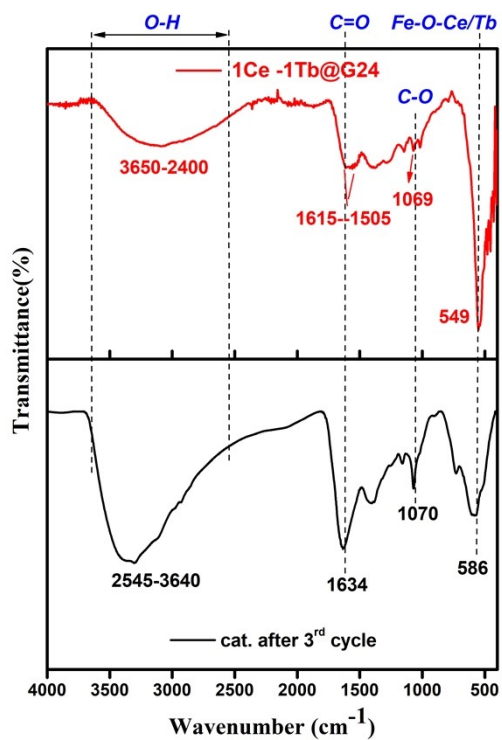


Fig. S2 FTIR data for both pre and post-catalytic 1Ce-1Tb@G24 sample.

Table S1 XPS atomic concentration data with the Relative Sensitivity Factors for all Ln doped G24 and pure G24 samples.

X P S D A T A C H A R T	Atomic Orbital peaks																			
	C 1s				O 1s				Fe 2p				Ce 3d				Tb 4d			
	G24	1Ce-0.5Tb	0.5Ce-1Tb	1Ce-1Tb	G24	1Ce-0.5Tb	0.5Ce-1Tb	1Ce-1Tb	G24	1Ce-0.5Tb	0.5Ce-1Tb	1Ce-1Tb	G24	1Ce-0.5Tb	0.5Ce-1Tb	1Ce-1Tb	G24	1Ce-0.5Tb	0.5Ce-1Tb	1Ce-1Tb
R S F	0.314	0.314	0.314	0.314	0.733	0.733	0.733	0.733	1.964	1.964	1.964	1.964	NA	7.343	7.343	7.343	NA	2.672	2.672	2.672
A t o m i c %	56.58	65.20	65.07	50.47	29.70	25.82	26.23	30.68	13.72	6.09	6.77	14.69	NA	1.82	0.98	3.75	NA	0.50	0.67	0.42

1.3. Comparison of physical and photochemical properties of IOT-derived 1Ce-1Tb@G24 with its common counterpart

We have productively synthesized the common counterpart of our best prepared photocatalyst (1Ce-1Tb@G24) by using pure anhydrous FeCl₃ (laboratory reagent). The synthetic method is kept entirely identical as that of IOTs-derived 1Ce-1Tb@G24. Subsequently both the synthesized samples were structurally characterized by HRTEM imaging and EDS analysis (**Fig. S3**). From the TEM analysis, both the samples show the amorphous nature and their elemental percentage curve (**Fig. S3 (c) and (f)**) authenticates the presence of dopant ions (Ce and Tb) with other major elements (Fe, O and C).

We have also estimated their optical band gaps to monitor their valence band to conduction band electron transition capabilities. From the K-M plot comparison (**Fig. S4 (b)**), it is observed that the band gap values are quite close to each other implying their identical light-inducing properties. The photocatalytic activity was also studied for both the IOTs-derived and FeCl₃-derived samples and it is found that almost 98% of rhodamine B dye can be fragmented by IOTs-derived sample whereas FeCl₃-derived sample can degrade up to ~95% of the dye (**Fig. S5**). So the results of the structural, spectroscopic and photocatalytic analysis confirm that both the sample remain roughly identical. Therefore it is unnecessary to prepare the as-reported photocatalyst by using a costly pathway (using lab chemicals) rather than preparing the same following a cheaper, simple, and environmentally sustainable method.

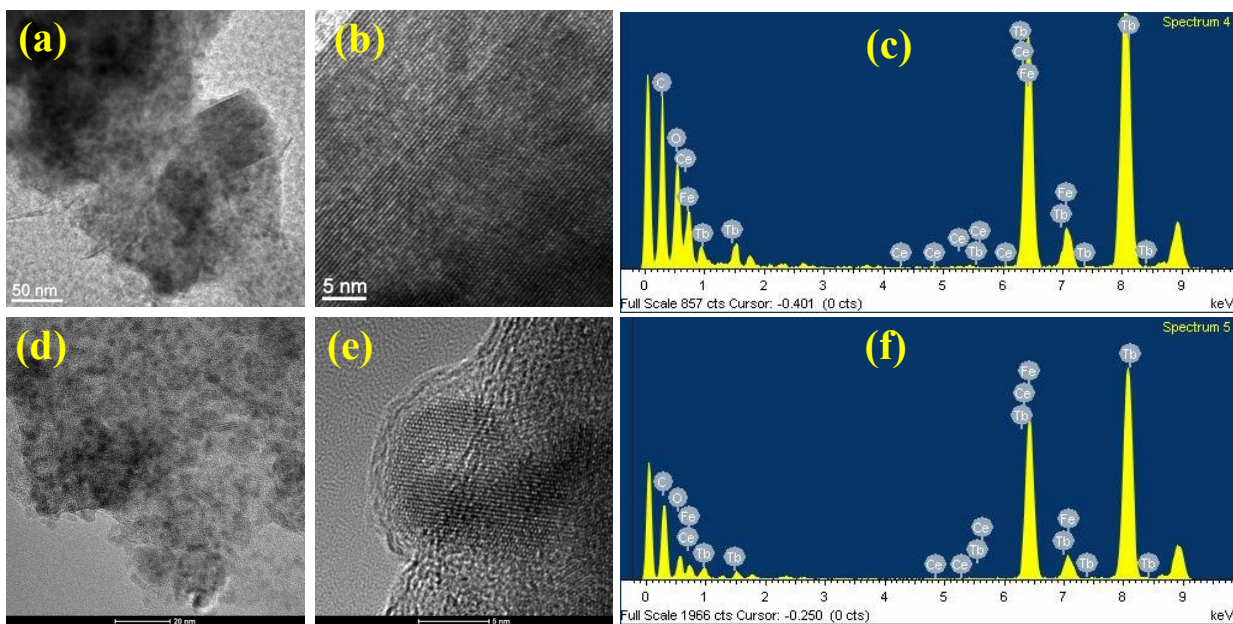


Fig. S3 (a) TEM (50 nm) and (b) HRTEM lattice fringe (5 nm) and (c) EDS data for pure FeCl₃-derived 1Ce-1Tb@G24. (d) TEM (20 nm) and (e) HRTEM lattice fringe (5 nm) and (f) EDS data for IOTs-derived 1Ce-1Tb@G24.

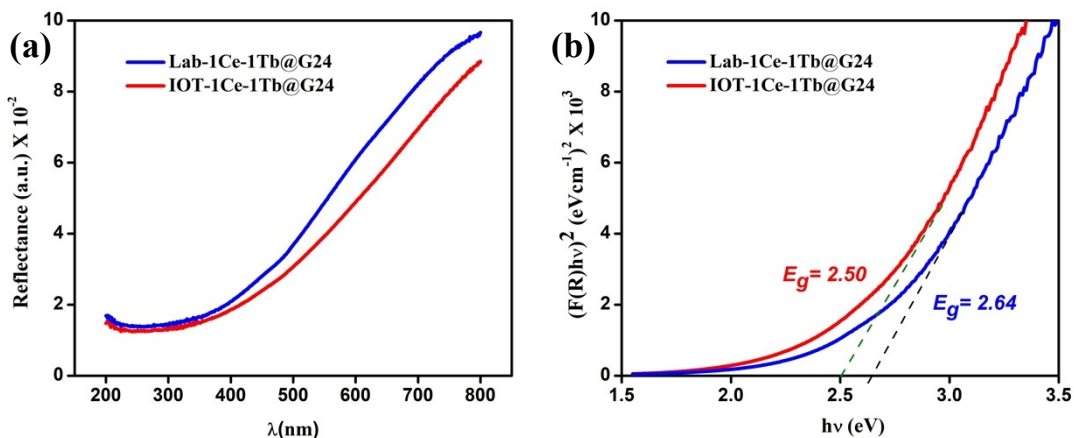


Fig. S4 (a) Diffused reflectance spectra and (b) Band gap (K-M plot) comparison of pure FeCl_3 -derived and IOTs-derived 1Ce-1Tb@G24 samples.

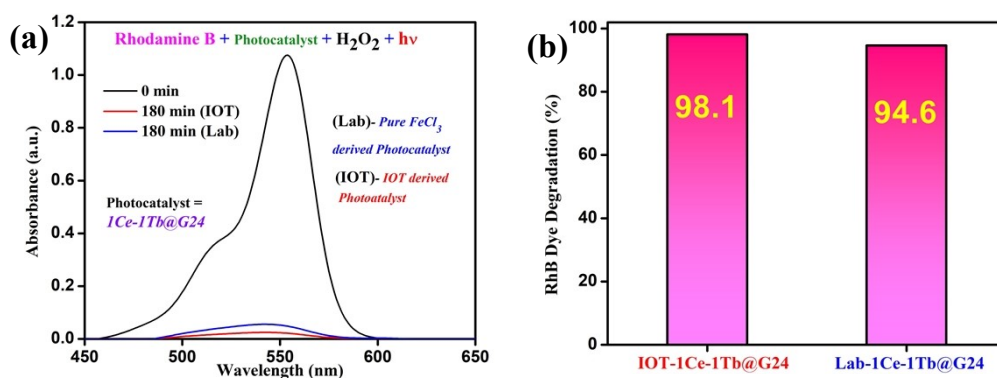


Fig. S5 (a) Absorbance comparison curve for photocatalytic RhB dye removal and (b) percentage dye degradation (Bar diagram) comparison of pure FeCl_3 -derived and IOTs-derived 1Ce-1Tb@G24 samples.

References

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