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B, Gd Co-Doped TiO_2 Nanotube Arrays for Efficient Degradation of Gaseous Toluene under Visible Light Irradiation

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Materials and Methods

To obtain the B doped TNA, the procedure was followed, where a certain of H_3BO_3 was added to the electrolyte before the second-step anodization. The as-obtained B doped TNA precursor (B-TNA-1) was then calcined in a tube furnace. This annealed B doped TNA is denoted as B-TNA. To obtain the Gd doped, TNA a certain of Gd $(NO_3)_3$ was added to the electrolyte before the second-step anodization. The as-obtained Gd doped TNA precursor (Gd-TNA-1) was then calcined in a tube furnace. This annealed Gd doped TNA is denoted as Gd-TNA.

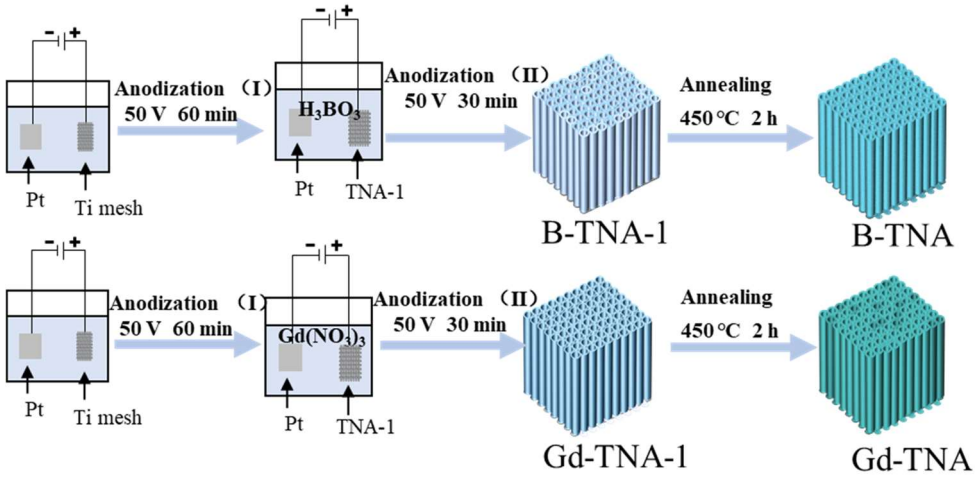

Figure S1. Schematic of the sample preparation of B-TNA and Gd-TNA.

DFT Calculation

Density Functional Theory (DFT) calculations were performed by the Cambridge Series Total Energy Pack (CASTEP) code. Employing ab initio quantum mechanics based on density functional theory (DFT), the plane-wave ultrasoft pseudopotential method was utilized to geometrically optimize both doped and undoped supercells (3×3×1), with the expanded cell structure containing a total of 36 Ti and 72 O atoms. The plane-wave cutoff energy was uniformly set at 400 eV, with a total energy convergence limit of 2×10^{-5} per atom during the self-consistent iteration process. A k-point grid of 3×5×2 was selected for the Brillouin zone, and full geometric optimization was carried out. The generalized gradient approximation (GGA) with the RPBE functional was adopted to calculate formation energy. Formation Energy (E_f) is a physical quantity that describes the stability of a system (such as a crystal, molecule, defect, etc.) relative to its constituent elements or reference states. E_f can be used to evaluate the stability of a system; generally, the lower the formation energy, the more stable the system. For doped systems, the relevant formula for calculating formation energy is as follows:

$$E_f = E_{doped} - E_{perfect} - \sum_i n_i\mu_i + qE_F$$

E_{doped} is the total energy of the system after doping; $E_{perfect}$ is the total energy of the undoped (perfect crystal) system; n_i is the number of dopant atoms of type i; μ_i is the chemical potential of dopant atom i; q is the charge number introduced by doping. E_f is the Fermi energy level.

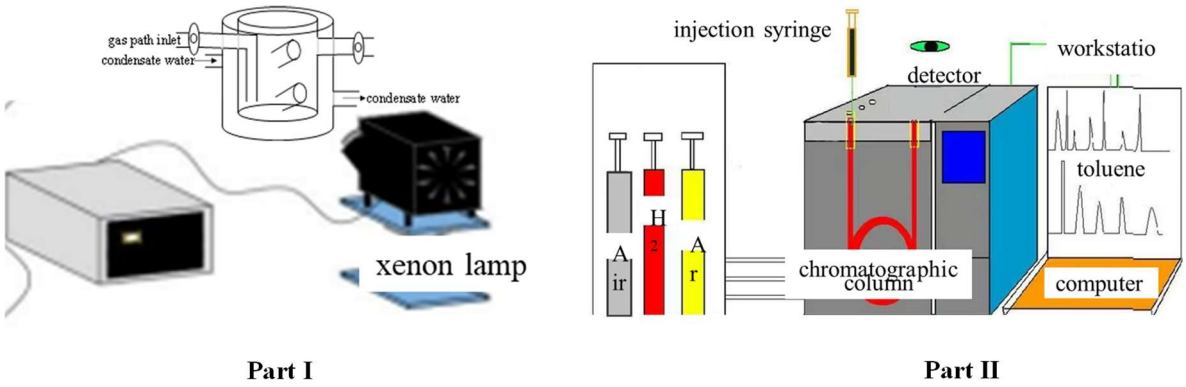

Figure S2. VOCs degradation evaluation system (Part I Lighting system and Part II Test system).

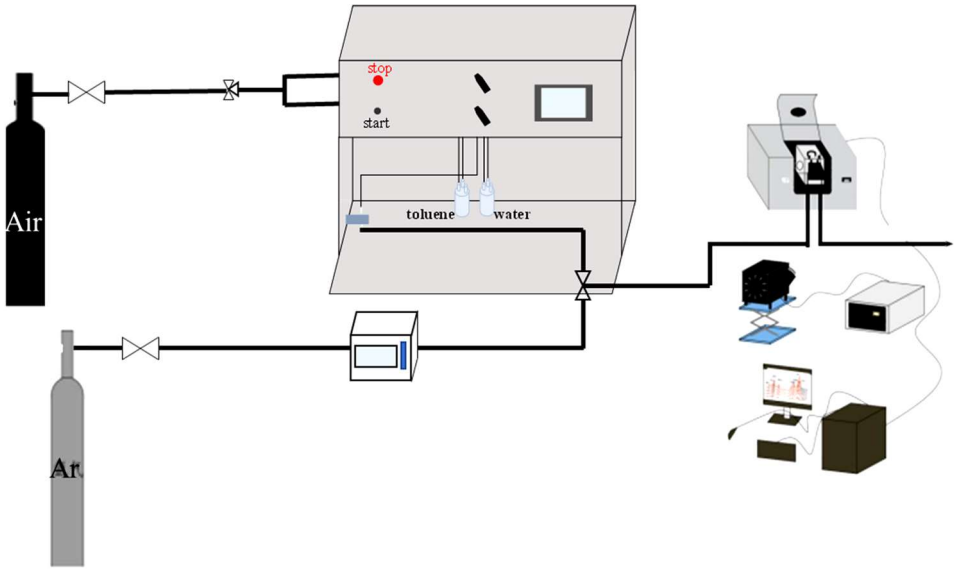

Figure S3. In-situ infrared diffuse reflection device diagram.

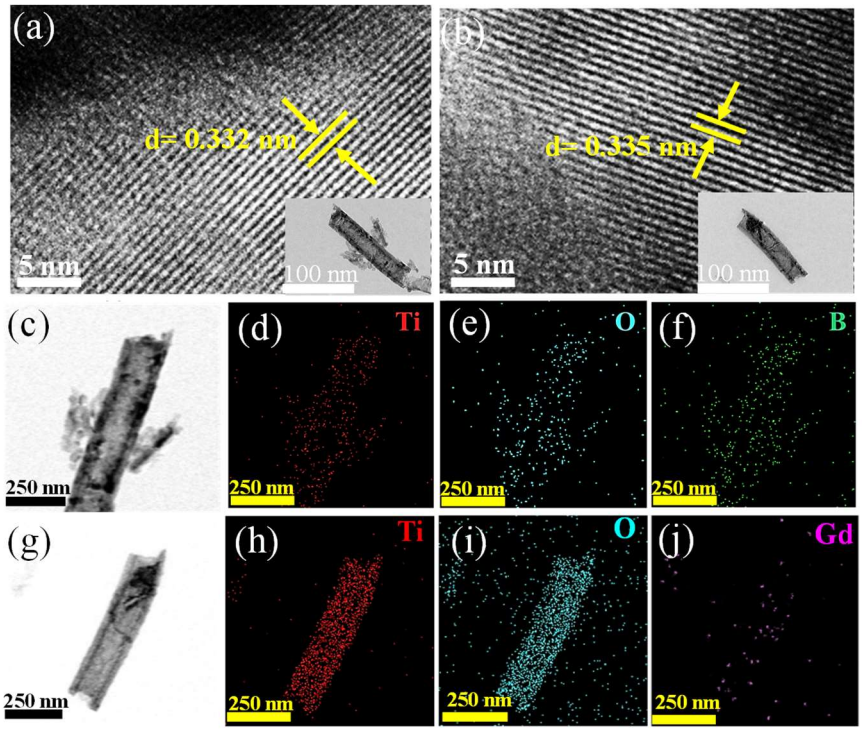

Figure S4. TEM and HR-TEM images for (a) B-TNA, (b) Gd-TNA; (c) TEM image of the B -TNA, and the EDX mapping images of its (d) Ti, (e) O, (f) B atoms; (g) TEM image of the Gd -TNA, and the EDX mapping images of its (h) Ti, (i) O, (j) Gd atoms.

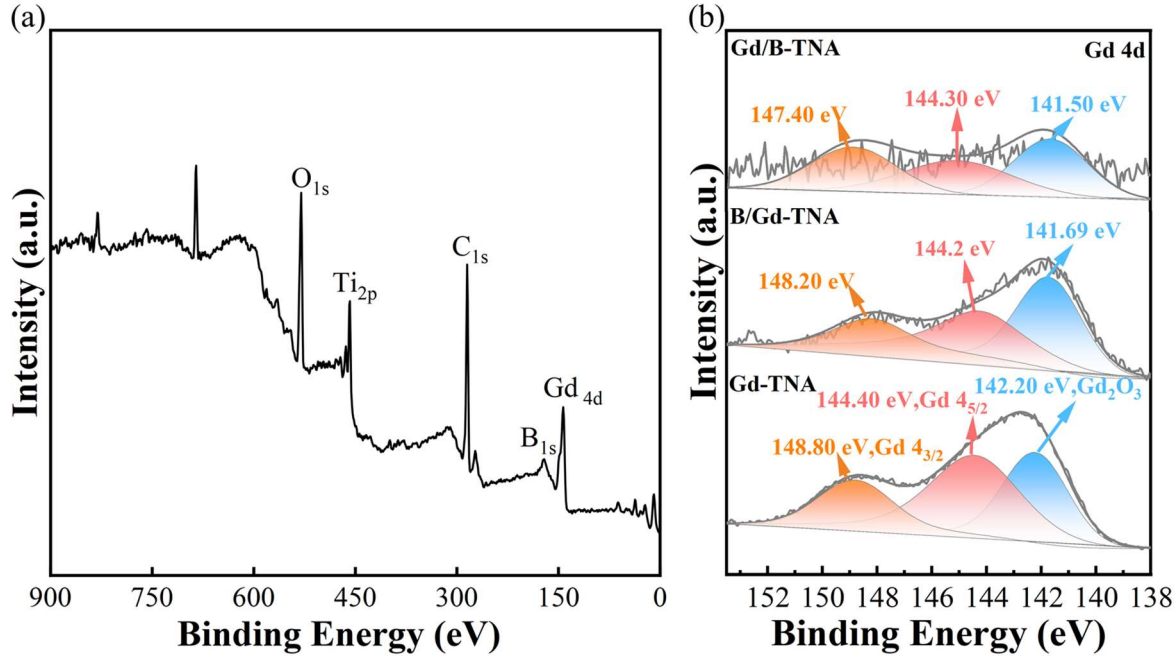

Figure S5. (a) XPS survey of the B/Gd-TNA, (b) Gd 4d XPS spectra of Gd-TNA, B/Gd-TNA, and Gd/B-TNA.

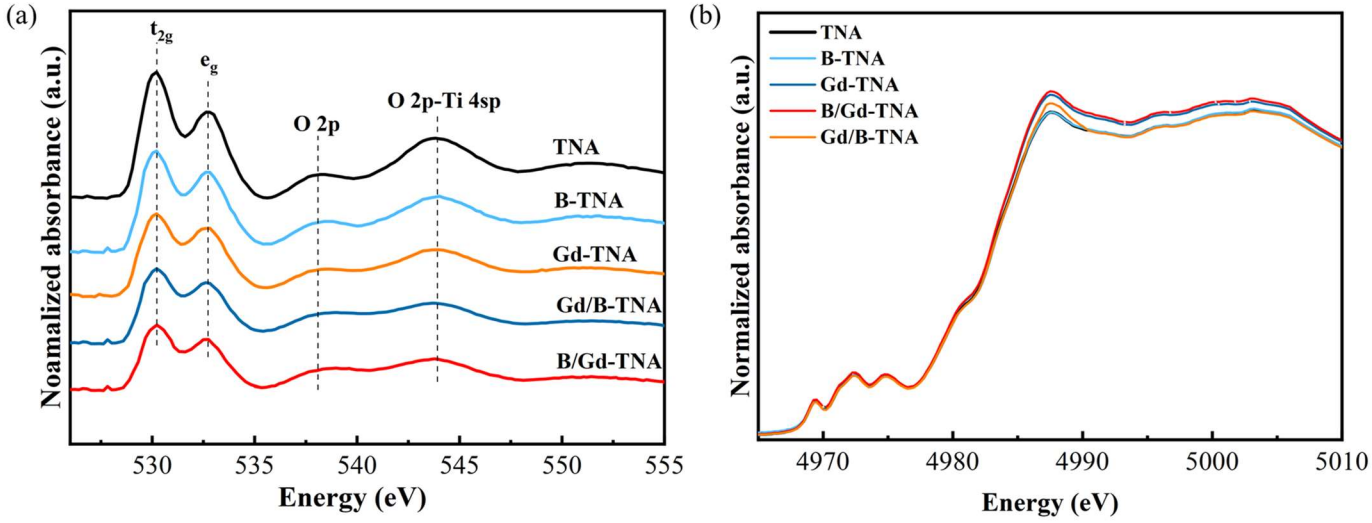

Figure S6. (a) O K-edge and (b) Ti K-edge XANES spectra of the TNA, B-TNA, Gd-TNA, B/Gd-TNA, and Gd/B-TNA.

Table S1. Doping concentration.

	B_x					Gd_x				
x	0.75	1.5	3	6	12	1	2	3	4	5
Electrolyte concentration (mmol/L)	4	6	8	10	12	6	8	10	12	14
EDX (%)	0.6	0.8	1.1	1.4	1.7	0.8	1.2	1.5	1.8	2.3

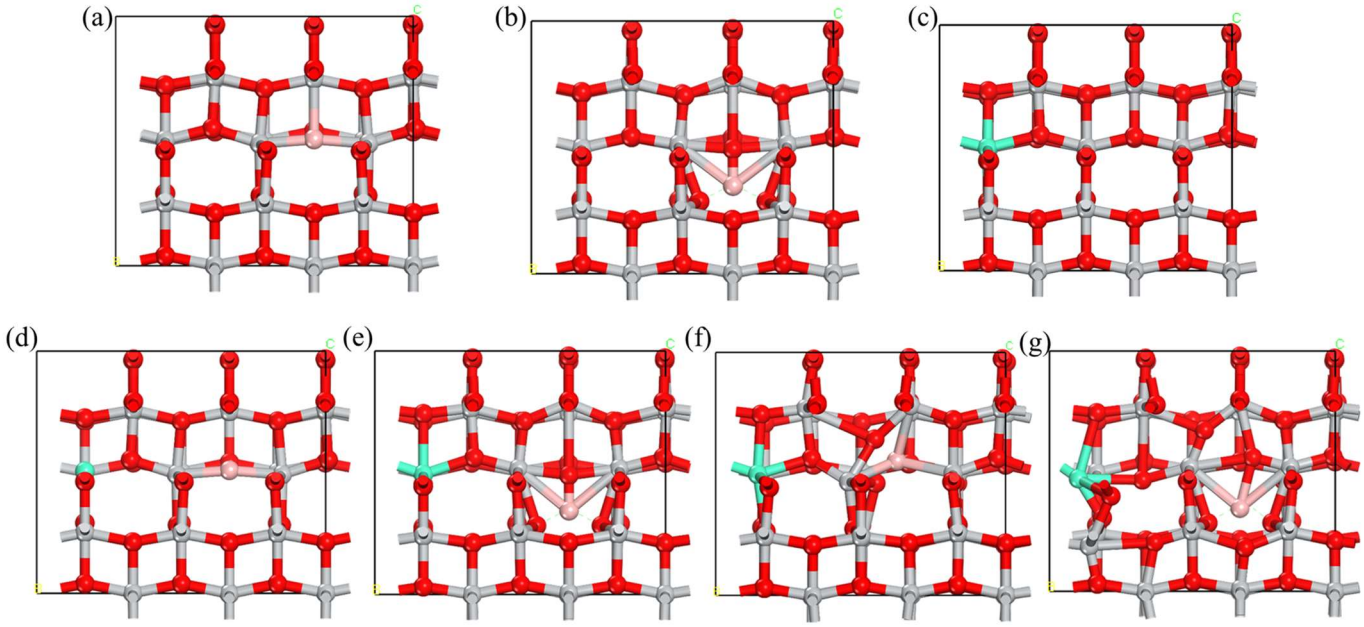

Figure S7. (a) B-TNA (B_s), (b) B-TNA(B_i), (c) Gd-TNA, (d) B/Gd-TNA (B_s), (e) B/Gd-TNA (B_i), (f) Gd/B-TNA (B_s), and (g) Gd/B-TNA (B_i) models (The blue, grey, green and pink spheres depict the Ti, O, Gd and B atoms respectively).

According to the main doping sites of the doping atoms, we employed DFT calculations to analyze the doping sites of B and Gd and the impact of doping atomic sequence on the crystal structure for the B, Gd doped system. The doping sites of B atoms can be classified to replace O atoms (substitutional doping, B_s) and occupy interstitial positions (interstitial doping, B_i), while Gd generally substitutes for Ti atoms [1,2]. As illustrated in Figure S7. From the optimized structures, it is evident that in the co-doping models, the structures with Gd doped first undergo significant lattice distortion, this structural collapse can be observed in the SEM results. The formation energies of different doping models are shown in Table S1. B/Gd-TNA (B_i) has the lowest formation energy, indicating that B/Gd-TNA possesses the most stable structure.

Table S2. Formation Energy (E_f) of doped system.

Doping Models	**B-TNA (B_s)**	**B-TNA (B_i)**	**Gd-TNA**	**B/Gd-TNA (B_s)**	**B/Gd-TNA (B_i)**	**Gd/B-TNA (B_s)**	**Gd/B-TNA (B_i)**
E_f /eV	2.22	2.19	5.23	2.78	6.13	7.98	5.71

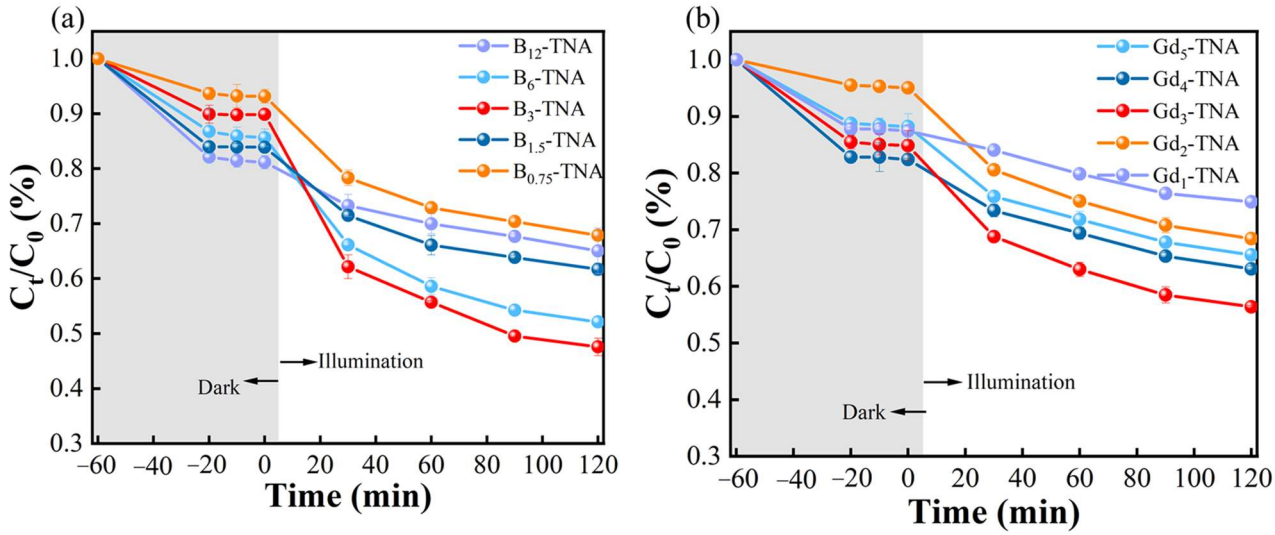

Figure S8. Photocatalytic degradation activity of gaseous toluene (a) B-TNA, and (b) Gd-TNA.

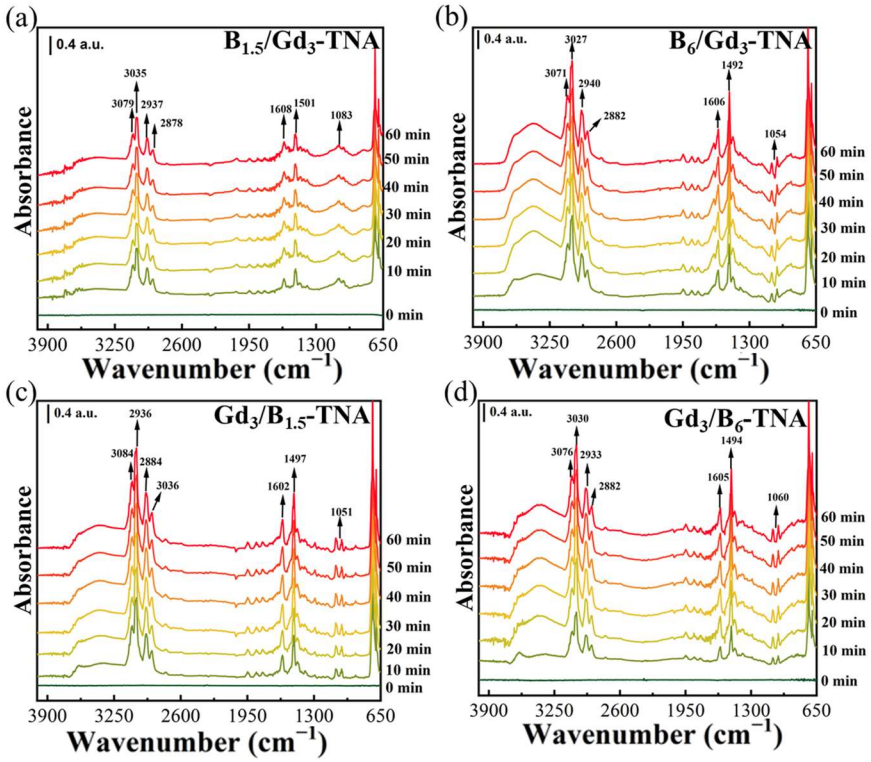

Figure S9. Absorption infrared spectra of toluene over (a) $B_{1.5}/Gd_3$-TNA, (b) B_6/Gd_3-TNA, (c) $Gd_3/B_{1.5}$-TNA, and (d) Gd_3/B_6-TNA.

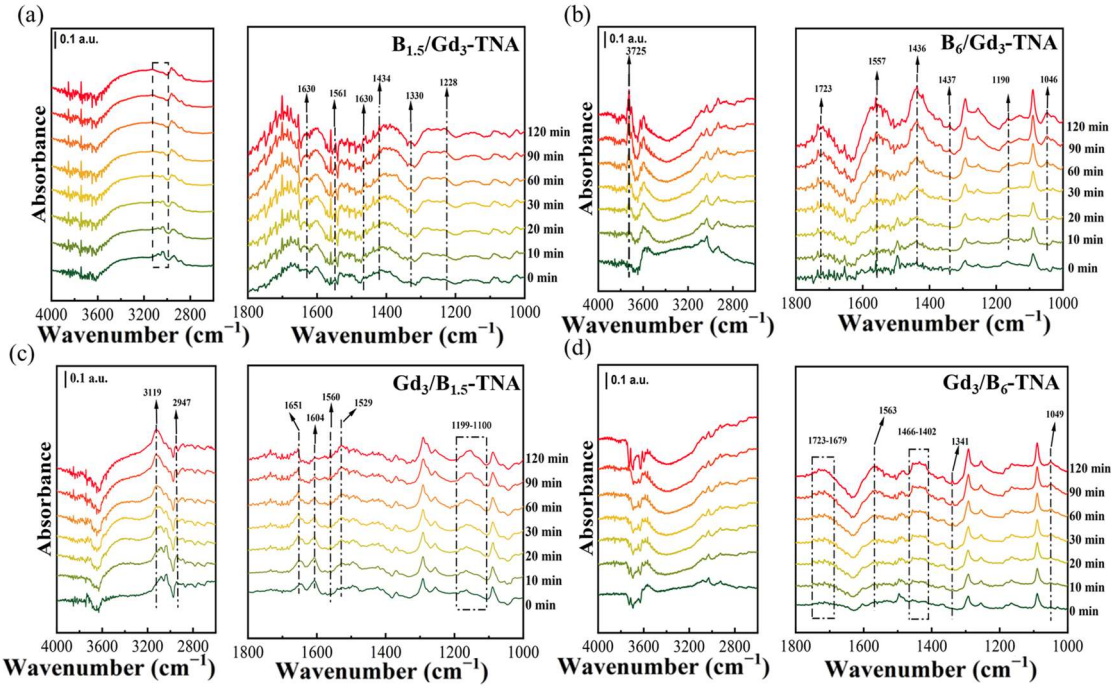

Figure S10. Spectra of catalytic degradation of toluene with (a) $B_{1.5}/Gd_3$-TNA, (b) B_6/Gd_3-TNA, (c) $Gd_3/B_{1.5}$-TNA, and (d) Gd_3/B_6-TNA.

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