

Supplementary Materials

In-situ Synthesis of TiO₂@RGO Nanosheets for Polymers Degradation in a Natural Environment

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1. Synthesis of all the monomers

1.1 Synthesis of 2-(C₄H₈SO₃Na)-2H-benzo[1,2,3]triazole

Benzotriazole (28.6 mmol, 3.4 g) and tetrabutylammonium bromide (460 mg, 1.43 mmol) are dissolved in 140 mL anhydrous DMSO, which is degassed by N₂ for about 5 min. A 16 mL NaOH (14 g) aqueous solution is added via syringe. Then 1,4-butanediol (3500 μL, 66.8 mmol) is added. After stirring for 3 hours at room temperature, the reaction mixture is poured into acetone. Through filtration and washed with acetone, the white precipitate is obtained. The product is purified by chromatography (reversed phase silica gel C-18, 10:1 H₂O:MeOH) to provide the white solid with 41% yield. ¹H NMR (500 MHz, D₂O) δ 7.53 (d, 2H), 7.86 (d, 2H), 4.79 (t, 2H), 2.89 (t, 2H), 2.24 (m, 2H), 1.74 (m, 2H). MS m/z calcd for C₁₀H₁₂N₃SO₃Na: 277 g/mol, found: 254 (C₁₀H₁₂N₃SO₃).

1.2. Synthesis of 4,7-dibromo-2-(C₄H₈SO₃Na)-2H-benzo[1,2,3]triazole

BTN-C₄H₈SO₃Na (0.73 mmol, 0.201 g) and an aqueous HBr solution (33 wt%, 1.3 mL) are added to the flask, and the mixture is stirred for one hour at 100 °C. Cooling the mixture to room temperature, bromine (0.33 g, 0.106 mL) is added. The solution is continued for 12 h at 80 °C. Cooling down to room temperature again, an aqueous solution of NaHCO₃ is added and the reaction is stirred with another 2 hours. The product is purified by chromatography (reversed phase silica gel C-18, 10:1 H₂O:MeOH) to provide the white solid 4 with 83% yield. ¹H NMR (400 MHz, D₂O) δ 7.59 (s, 2H), 4.88 (t, 2H), 2.90 (t, 2H), 2.25 (m, 2H), 1.74 (m, 2H). MS m/z calcd for C₁₀H₁₀Br₂N₃SO₃Na: 435 g/mol, found: 411.7 (C₁₀H₁₀Br₂N₃SO₃).

1.3. Synthesis of 1,2-diamino-3,6-dibromobenzene

NaBH₄ (20 mmol, 0.76 g) was added to the solution of 4,7-dibromo-benzo[1,2,5]thiadiazole (2 mmol, 0.588g) in 20 mL EtOH at 0 °C. After stirring for 1 hour, the reaction was processed overnight. After removing the EtOH, the extraction was conducted with ether and water. The 1,2-diamino-3,6-dibromobenzene could be obtained after drying the organic phase with 80% yield. ¹H NMR (500 MHz, CD₃OD): δ= 6.5 (s, 2H)

1.4. Synthesis of 4,7-dibromo-1,2,3-benzotriazole

The aqueous solution of NaNO₂ (0.15 g, 1.65 mmol, 3 mL) is added to the solution of 1,2-diamino-3,6-dibromobenzene (0.4 g, 1.5 mmol) in CH₃COOH (6 mL). After stirring for 30 min at room temperature, precipitate is filtered and washed with water to afford 4,7-dibromo-1,2,3-benzotriazole (0.38 g) as a pink powder (yield is 85%). ¹H NMR (500 MHz, CD₃OD): δ= 7.56 (s, 2H)

1.5. Synthesis of 4,7-dibromo-2-(6-bromo-hexyl)-2H-benzotriazole

4,7-Dibromo-1,2,3-benzotriazole (1.45 mmol, 0.4 g) and *t*-BuOK (4.1 mmol, 0.46 g) were dissolved in 20 mL MeOH. At 60 °C, 1,6-dibromohexane (14.5 mmol) was added to the solution. After stirring for 5 hours, the MeOH was removed and the residue was extracted with CHCl₃ and water. After concentration, purification by chromatography (CHCl₃:hexane = 1:1 vol) provided BTz-Br (0.37 g) in 59% yield. ¹H NMR (500 MHz, CDCl₃): δ = 7.43 (s, 2H), 4.81 (N-CH₂, 2H), 3.41 (Br-CH₂, 2H), 2.2 (-CH₂-, 2H), 1.84 (-CH₂-, 2H), 1.5 (-CH₂-, 2H), 1.42 (-CH₂-, 2H).

1.6. Synthesis of monomer with ammonium-end side chain

The monomers with bromo-end side chain are stirred in trimethylamine at 60 °C for 2 days. Methanol is added to aid dissolution of ionic species. The volatiles are removed and the ionic-functionalized monomers can be dried over night at low pressure (99% yield). ¹H NMR (500 MHz, CD₃OD) for monomer with ammonium-end side chain 3: δ = 7.51 (s, 2H), 4.9 (N-CH₂-, 2H), 3.42 (N⁺-CH₂-, 2H), 3.12 (-N(CH₃)₃, 9H), 2.24 (-CH₂-, 2H), 1.89 (-CH₂-, 2H), 1.51 (-CH₂-, 2H), 1.29 (-CH₂-, 2H).

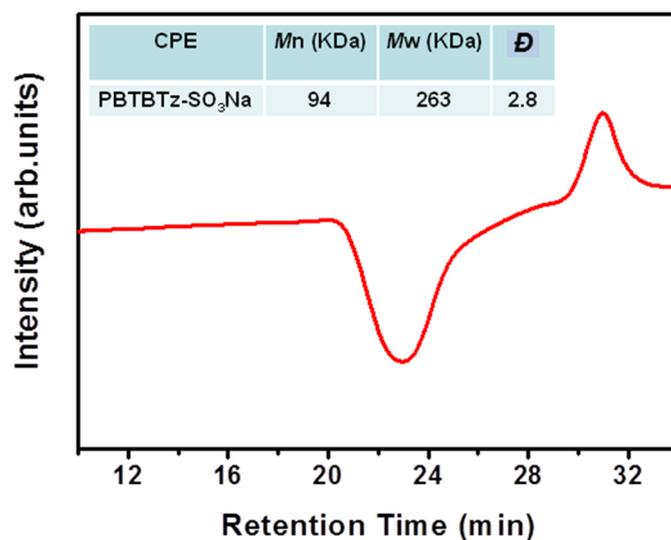
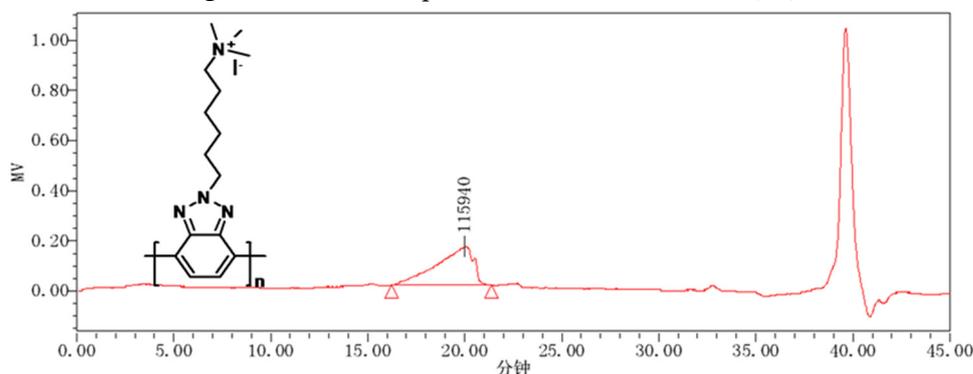


Figure S1. The GPC plots of the PBTBTz-SO₃Na (P3).



GPC 结果

分布名	Mn (道尔顿)	Mw (道尔顿)	MP	Mz (道尔顿)	Mz+1 (道尔顿)	多分散性	MW 标记 1 (道尔顿)	MW 标记 2 (道尔顿)
1	157467	240626	115940	507419	1006844	1.528102		

Figure S2. The GPC plots of the PBTz-TMAI (P2).

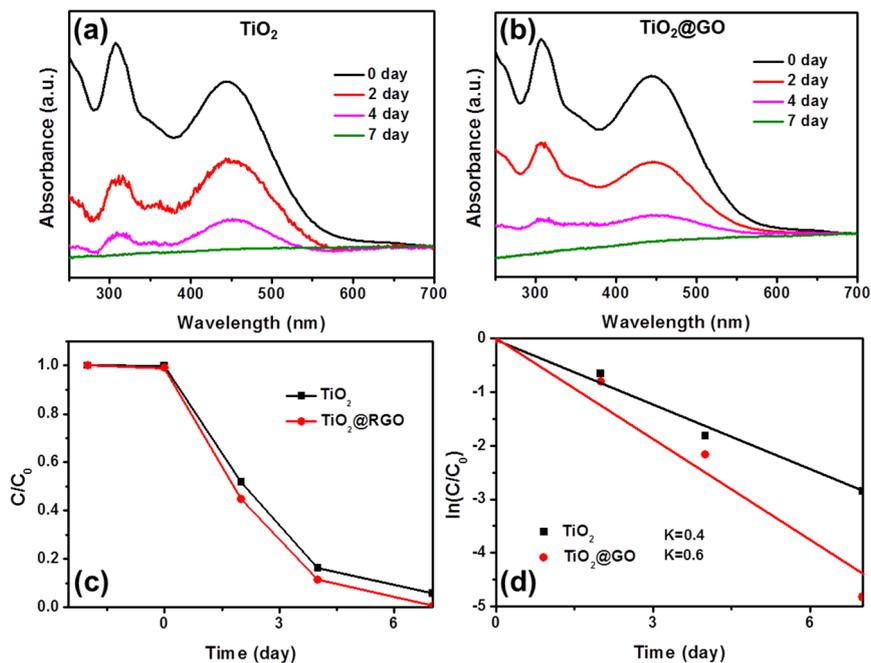


Figure S3. P1 decomposition by (a) TiO_2 and (b) $\text{TiO}_2@GO$ with the illumination under nature light; (c) Comparison of photocatalytic activities of TiO_2 and $\text{TiO}_2@GO$; (d) Dependence of $\ln(C/C_0)$ on time.