ABSTRACT

Unique optical, physicochemical, and surface properties of atomically thin two-dimensional (2D) materials provide enormous opportunities for environmental remediation, clean energy conversion, and storage. Those properties are further tuned by using dopants. Due to their distinct electronic configuration and optoelectronics properties, the rare earth elements and compounds act as proficient dopants in combination with 2D materials.

In this work, 2D-graphitic carbon nitride nanosheet (2D-g-C_3N_4) is synthesized through a single-step liquid phase alcoholic exfoliation of bulk-g-C_3N_4 to use as a catalyst for synergistic decontamination of organic pollutants (methylene blue (MB), bromophenol blue (BB), and ampicillin (AMP)), solar light driven self-cleaning of methyl orange (MO) stain, and electrocatalytic oxygen evolution reaction (OER). The catalytic preeminence of the 2D-g-C_3N_4 over the bulk one is observed from the defect engineering viewpoint. These defect intensifications are examined through diffraction, spectroscopy, microscopy, and specific surface area measurement. Photo and electrocatalytic performances of 2D-g-C_3N_4 are also compared with the pristine bulk-g-C_3N_4. The catalytic processes are also illustrated in terms of reaction kinetics and stability.

Lanthanum (La^{3+}), cerium (Ce^{3+}), and gadolinium (Gd^{3+}) trivalent ions are decorated on 2D-g-C_3N_4 through an easily scalable chemisorption process at optimized conditions (solution pH, process temperatures, and contact times). This functionalization results in defects formation, lattice strain, morphology variation, surface area intensification, and band gap reduction. The experimental observations are further validated with the help of density functional theory (DFT) based first-principles calculations. La^{3+}-2D-g-C_3N_4 is utilized for low-concentration ciprofloxacin remediation under UV light irradiation, and the reaction intermediates are determined through liquid chromatographic-mass spectroscopy (LC-MS) and high-performance liquid chromatography (HPLC) studies. Characterization studies of the reused photocatalyst confirm photocatalytic stability. Localized point defect-induced Ce^{3+}-2D-g-C_3N_4 catalyst is utilized for methylene blue (MB) decontamination under visible mercury light (λ>420 nm) and sunlight (intensity of~212 K lux). Experimental FTIR spectra of Ce^{3+}-2D-g-C_3N_4 are further validated with IR spectra of the DFT study. For Gd^{3+}-2D-g-C_3N_4, the highest activation energy (24.17 kJ mol^{-1}) is elucidated for Gd^{3+} chemisorption that correlates with the strong interaction energy of -34.14 eV obtained from DFT. Modified band gap energy (2.81 to 1.83 eV), highest I_D/I_G ratio (0.72 to 1.05), and the highest specific surface area (69.12 to 109.6 m^2/g) make Gd^{3+}-2D-g-C_3N_4 most efficient compared to La^{3+}-2D-g-C_3N_4, Ce^{3+}-2D-g-C_3N_4, and pristine 2D-g-C_3N_4. The magnetic catalyst shows 98 % remediation efficiency for ultrasound (US) assisted photodegradation of methyl orange (MO). Gd^{3+}-2D-g-C_3N_4 is further utilized for electrocatalytic oxygen reduction reaction (ORR) and solid-state supercapacitor applications. Further, 2D-g-C_3N_4 is modified with gadolinium-2-methylimidazole (Gd-2-mim) as metal-organic framework (MOF) (Gd-2-mim/2D-g-C_3N_4) through heterostructure formation for bifunctional electrocatalytic OER and ORR capability. A stable nanoporous morphology and enhanced specific surface area of Gd-2-mim/2D-g-C_3N_4 provide improved electrocatalytic active sites by exhibiting the highest onset potential (0.85 V) and lowest charge transfer resistance (R_{ct} = 96.2 Ω) for ORR and lowest overpotential (59 mV @10 mA cm^{-2}) for OER among all the synthesized catalysts. A plausible bifunctional mechanism is also portrayed based on the electrocatalytic reaction kinetics. Post characterizations assure the electrocatalytic stability of Gd-2-mim/2D-g-C_3N_4. The catalyst is capable of effectively substituting the state-of-the-art electrocatalysts Pt/C and RuO_2 for ORR and OER, respectively.

Keywords: 2D-g-C_3N_4; Rare earths; Metal organic framework (MOF); Chemisorption; Defect Engineering; Density functional theory (DFT); Photodegradation; Electrocatalysis; Supercapacitor; OER and ORR