Novel Synthesis of Carbon Dots and 2D materials for optical and electrochemical applications

Thesis submitted by

Dipayan Roy

Synopsis

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To mitigate the energy crisis and environmental hazards by anthropogenic activities in modern world, highly durable and cost-effective nanotechnology must be developed. Electrochemical based nanotechnology and nanosensors provide efficient clean energy and environmentally friendly technologies for energy conversion, energy storage and sustainable development. In the energy storage system, water electrolysis involves oxygen and hydrogen evolution, providing energy storage in fuel cell economy. Fuel cells are commercial energy sources to produce electricity by chemical reactions at cathode and anode through oxygen reduction and hydrogen oxidation respectively. In recent times, energy storage technologies like capacitors, and batteries have attracted the scientific community for the development of smart devices. Considerable theoretical and experimental investigation is necessary to understand the catalytic mechanism for highly efficient and durable smart devices for commercial applications. In this regard, size and morphology dependent nanomaterials facilitate various chemical, optical sensor and electrochemical properties due to quantum confinement effect, surface plasmon resonance, high surface to volume ratio, packing fraction, chemical stability, mechanical strength and various catalytic sites. However, selective materials structure and band alignment for various sensing, energy conversion, energy storage applications, and correlation with device is essential to enhance the efficiency of the interfacial mechanism. The catalytic mechanism and reaction rate by nanomaterials is modified with particle size, surface area, preferred morphology, surface optimization, vacancies, defects, doping, functionalization, coating, and the formation of binary and ternary composites. Several research groups have implemented multiple synthetic parameters to improve energy-based applications. Two-dimensional (2D) materials have unique properties due to multiple band gap, layer thickness, porosity, surface area, edge active sites. Therefore, such efficacy can be achieved by suitable material design using diverse synthetic protocols. Indeed, the optical, electronic, and structural properties of 2D materials with reaction mechanisms in the domain of energy and sensing application require more fundamental insight. Carbon based materials like graphene, carbon nanotubes have emerged as potential applications in electric devices, drug delivery but lower mass production as well as understanding of the defect formation and its functions are still unexplored. Besides, till now, transition metal dichalcogenides (TMDs) can serve as an electrode material where most of the TMDs are theoretically predicted. Secondly, it is difficult to enhance the conductivity of the basal plane of TMDs and rigorous synthetic techniques have been modulated using epitaxial growth, chemical vapour deposition (CVD), ion intercalation, exfoliation and high temperature annealing. Owing to developing better electrode and sensing material, synthetic procedures and internal mechanisms must be paid more attention. Aiming this, quantum dots and 2D material based heterostructure have been synthesized by controlling reaction parameters, additives, defects, porosity, surface area, and band alignment. The surface reactivity, surface area and porosity of graphene are enhanced with nitrogen functionalization by incorporating a reducing agent imidazole, a biomolecule under ambient temperature. The pyridinic, graphitic, pyrrolic and amine type functionalization on graphene (NrGO-90) increases defect density, defect length and interlayer distance, confirmed with different experimental protocols like Raman spectroscopy, X-ray diffraction (XRD) analysis. NrGO-90 exhibits four electron transfer processes for oxygen reduction reaction (ORR) in fuel cells. It is noticed, that at higher temperatures, the pyridinic and amine nitrogen are converted to graphitic nitrogen (for NrGO-400) as well as change in mesoporous nature, layer stacking and low defect density shrinks the ORR kinetics and capacitive performances. Theoretical analysis suggests favorable negative free energy pathways during ORR pathways at pyridinic and amine sites and validates our experimental analysis. The stand-alone ORR performances of NrGO-90 and NrGO-400 are determined from overpotential, onset potential Tafel slope, half wave potential, limiting current density and rate constant. The porous interlayer space and surface active sites for NrGO-90 also boost specific and volumetric capacitance of 287.5 F/g at 1 A/g current density and 880 mF/cm^2 at a scan rate of 2 mV/s respectively. Such dual efficacy of NrGO is covered with conventional reduced graphene oxide (catalytic inactive for ORR) and other metals with 2D porous heterostructures. A similar observation has been manifested for hexagonal boron nitride (hBN) which is catalytically inactive for electrochemical performances due to insulating in nature. A new strategy has been demonstrated by incorporating boron vacancy (~7%) on hBN basal plane which can enhance the conductivity for ORR reaction. Looking ahead, the hBN and MoS_2 heterostructure (HBPS) enhances the B-OH bond polarity due to charge transfer between two heterostructures. The long time ultrasonication stimulates to removal B-OH group and facilitates boron vacancy upto ~28%. Control over the change in geometry of hBN sheet due to vacancy also lowers the band gap and enhances electrochemical active surface area (ESCA). The vacancy sites are favourable adsorbent of oxygen which is reduced to four OH^- ions and follows the ORR kinetics with four electron transfer process. Notably, theoretical analysis suggests boron vacancy mediated hBN sheet and hBN and MoS_2 heterostructure without boron vacancy follows two electron transfer processes and promotes hydrogen peroxide formation as a major product instead of OH^- ions. Regarding applications in water splitting and hydrogen evolution reaction (HER), platinum related noble metals and 2D heterostructures have been widely investigated whereas high cost, low durability and complex catalytic mechanisms need to be optimized. To reduce the basal plane inactivity of TMDs like MoS_2, interlayer spacing and surface functionalization are necessary for facile charge transfer process. The catalytic limitation of MoS_2 has been overcome by formation of MoS_2-MoO_3 heterostructures with oxygen vacancies. The in-situ preparation of MoS_2-MoO_3 has multiple Mo oxidation states ($Mo^{4+/5+/6+}$) due to oxygen vacancies. The metal $Mo^{5+/6+}$ states are active sites for alkaline HER, ferrocyanide, and para nitrophenol (PNP) reduction. A series of experiments containing Mo^{4+} state (MoS_2 nanosheet, MoS_2 quantum dots, sulphur vacancy induced MoS_2) has been employed to compare the benchmark multiple activities of MoS_2-MoO_3. However, the $Mo^{5+/6+}$ states are inactive for acidic HER catalysis while adsorbed hydrogen spillover from oxygen (MoO_3) to sulphur site (1T MoS_2) triggers the acidic HER kinetics with lower overpotential at 114 mV/decade. The superior acidic and alkaline HER of MoS_2-MoO_3 is determined in terms of lower overpotential, charge transfer resistance, Tafel slope and higher turnover frequency (TOF), ESCA. The surface sites are masked via integration with masking agent to correlate the activities of binding sites obtained from experimental as well as theoretical validation. The resulting synergistic performances can be employed as a hydrogen storage device for commercial applications. Upcoming challenges are to establish the sensing dynamics of environmental pollutants by low dimensional materials like quantum dots using optical based spectroscopy. The size and functional group dependent carbon/graphene quantum dots (CQD) show broadband excitation and emission which is deconvoluted with four/five individual peaks. The involvement of the surface functionalized groups (OH, epoxy, COOH, COO^-, NH_2) turns the CQD surface to negative zeta potential. The sensing with toxic pollutant Hg^{2+} involves ground state and excited state quenching via sp^2 carbon at basal plane, $(COO^-)_2$-Hg^{2+}, NH_2-Hg^{2+} complex formation. The recovery of deconvoluted emission and excitation spectra are carried out with ethylene diamine tetraacetic acid (EDTA) at different Hg^{2+} concentrations. The higher energy peak (π-π^*) has lower

recovery percentage in terms of FWHM, peak intensity and area. Whether, the peak originates from n-π* transitions (COOH, COO^-, NH_2) shows comparatively higher recovery than core state transitions. After recovery, positive surface changes to negative due to complexation of Hg^{2+} with EDTA. The study reveals the sensing mechanism and optical properties of CQD are mainly governed by surface states rather than core states.

Keywords: NrGO, ORR, capacitance, hBN, DFT, Boron Vacancy, Tafel slope, Electron transfer, Band gap, MoS_2–MoO_3, oxygen vacancy, PNP reduction, band engineering, HER, hydrogen spillover, Nitrogen doped carbon quantum dots, photoluminescence, PL signals, Hg^{2+}, PL recovery

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Signature of the supervisor

Dipayan Roy (07.11.2023)

Signature of the Candidate

Dr. Sourav Sarkar
~~Director~~
Associate Professor
School of Materials Science & Nanotechnology
Jadavpur University
Kolkata - 700032