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Graphene as gas sensors and adsorbents for various dyes, oil spills: A perspective

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Abstract

Graphene-based materials have developed as capable applicants as adsorbents for various dyes. Low costs of production, high surface area, large porosities and large number of modification methods make them excellent materials for sensors, adsorption studies and removal of toxic compounds such as pesticides, dyes, oil spills, antibiotics, etc. from aqueous solutions. In recent years, there have been many structural modifications in the 2-D graphene sheet for synthesizing superior materials such as graphene-metal composites, metal oxide composites, bio-composites, hydrogels, etc. for improving the structural properties and widen its applications. In this review, we have incorporated the examples from both experimental and density functional theory studies (DFT) for adsorption of various dyes and oils spills on pristine and modified graphene sheets.

Keywords: Pristine Graphene, DFT, adsorption, dyes, oil spills

Introduction

The three different carbonaceous materials, activated carbon, graphene oxide, and multi-walled carbon nanotubes. These were modified by nitric acid by oxidation and used as adsorbents for the removal of the methylene blue dye from aqueous solution. The adsorption capabilities of methylene blue onto activated carbon, graphene oxide, and multi-walled carbon nanotubes were 270.27, 243.90 and 188.68 mg g⁻¹, respectively, which follow the order of activated carbon > graphene oxide > multi-walled carbon nanotubes.

Graphene, a 2D nanosurface has large surface area, high electrical conductivity, thermal stability, high mechanical strength, high elasticity with tunable band gap, quantum Hall effect and ambipolar electric field effect. Because of these tremendous properties of graphene, it is mainly used for storage of gaseous molecules, as a gas sensor, as a biosensor in photonic devices in fuel cells removal of harmful components presents in water and so on. Sensors are sophisticated devices, which are used for the sensitive detection and quantitative determination of specific molecules present in the environment. The molecules usually affect the physical, electrical and optical properties of the substrate, and the detector signal is based on these changes. The desirable properties of an excellent gas sensor are high sensitivity, robustness, good regeneration capacity and a large range of applications at low cost. In the past few decades, developments have been made to make ultrasensitive gas sensors for the effective sensing of toxic chemical species like hazardous gaseous molecules (NO_x, HF, HCHO, H₂S, CO, NH₃, SO₂, O₃, and hydrocarbons) and volatile organic compounds (VOCs) which are used as solvents in many chemical reactions, for effective environmental monitoring, medical diagnosis, manufacturing of industrial goods and in the military. Solid-state gas sensors are extensively employed for sensing toxic gases because of their high sensitivity, low cost, miniature size and high adsorbing power. However, achieving a level of sensitivity up to only a single gas molecule has been beyond the reach of the solid-state devices currently in use. This may be due to the fluctuations related to the thermal motion of charges and defects, which lead to intrinsic noise. Nanosurfaces behave as sensitive gas sensors because of their large surface area and high electrical conductivity.

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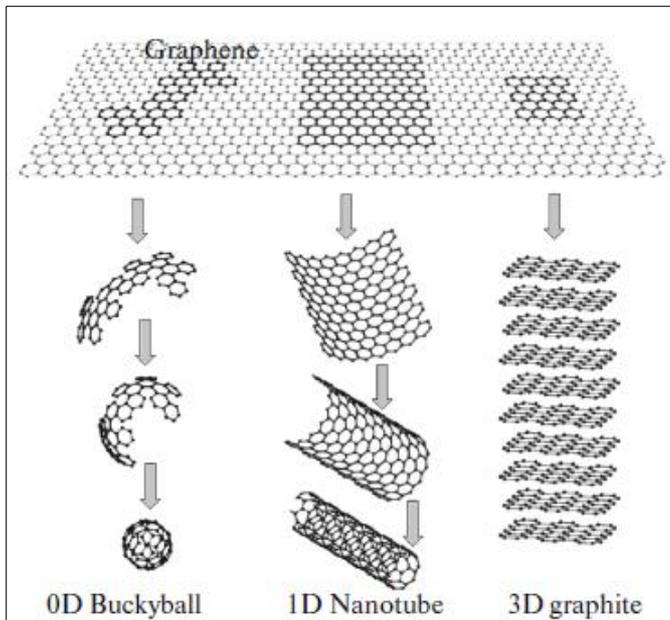


Fig 1: Graphene: mother of all graphitic forms

Applications of Graphene

Dyes

Li *et al.* (2012) ^[1] reported three different carbonaceous materials, activated carbon, graphene oxide, and multi-walled carbon nanotubes. These were modified by nitric acid by oxidation and used as adsorbents for the removal of the methylene blue dye from aqueous solution. The adsorption capabilities of methylene blue onto activated carbon, graphene oxide, and multi-walled carbon nanotubes were 270.27, 243.90 and 188.68 mg g⁻¹, respectively, which follow the order of activated carbon > graphene oxide > multi-walled carbon nanotubes. In batch adsorption experiments, the effect of solution pH range from 2.0 to 9.0 were studied, which showed that the removal efficiencies of activated carbon and graphene oxide are very high and reach 98.0–99.6% and 94.8–98.8%, respectively. The adsorption data could be represented by the Langmuir isotherm model. The kinetics studies showed that the experimental data could be well fitted by the pseudo second order rate equation. The adsorption of methylene blue onto carbonaceous materials was due not only to the large surface area but also to π - π electron donor-acceptor interactions and electrostatic interactions between the positively charged dye ions and negatively charged adsorbents. Xu *et al.* (2013) ^[1] reported that by a facile solvothermal reaction of graphene oxide (GO) and ZnO in an ethanol-water solvent, the composites of reduced graphene oxide/ ZnO (RGO/ ZnO) with different particles size of ZnO were prepared. Fan *et al.* (2012) reported that the magnetic cyclodextrin–chitosan/ graphene oxide materials were used as adsorbents for dye removal. The resulting composite combined features of magnetic cyclodextrin–chitosan and graphene oxide; therefore, they exhibited extraordinary removal capacity and fast adsorption rates for methylene blue dye removal in water. This was due to the high surface area of graphene oxide, hydrophobicity of β -cyclodextrin, and the abundant amino and hydroxyl functional groups of chitosan. Also, the adsorbent could be easily and efficiently regenerated for reuse without any compromise of the adsorption capacity. The adsorption kinetics, isotherms and thermodynamics were studied in detail. The adsorption followed pseudo-second-order kinetics. The equilibrium data were studied using the Langmuir isotherm model. It was found that the adsorption

process was spontaneous and endothermic in nature. Due to its adsorption capacity, easy, handy operation, rapid extraction, and regeneration, it is being considered as a new, efficient and sustainable way towards highly-efficient dye pollutant removal in water and wastewater treatment. Dong *et al.* (2014) prepared poly-dopamine surface-functionalized graphene oxide composites and used them to study the adsorptive property of dyes and heavy metal ions. It was done using controlled self-polymerization of dopamine via catechol chemistry and then used for effectively decontaminating wastewater. The adsorption capacity was shown to be dependent on the thickness of the poly-dopamine coating, the pH and the temperature of the solution. Due to combination of the poly-dopamine layer and graphene oxide nanosheet, it exhibits an excellent adsorption performance, especially towards Eschenmoser-containing dyes. It was observed that the adsorption process was based on the Eschenmoser salt assisted 1,4-Michael addition reaction between the ortho position of the catechol phenolic hydroxyl group of poly-dopamine and the Eschenmoser groups in the dyes. The adsorption isotherms matched well with the Langmuir isotherm model. The thermodynamic parameters were also calculated, which suggested an exothermic and spontaneous adsorption process. In addition, the combination of the poly-dopamine layer and graphene oxide nanosheet exhibited an improved adsorption capacity for heavy metal ions than pure poly-dopamine and graphene oxide. Song *et al.* (2015) ^[5] prepared graphene based encapsulating magnetic graphene into calcium alginate and used it as an adsorbent for the removal of methylene blue. The adsorption of methylene blue onto the graphene composite was investigated with respect to pH, adsorption time, initial methylene blue concentration and temperature. It was found that the adsorption of methylene blue on graphene composites was independent on pH. In this case, the kinetics data was studied by the pseudo-second-order kinetic model. The adsorption isotherm was studied by the Langmuir isotherm. The values of the activation parameters, such as free energy, enthalpy and entropy indicated that the adsorption was spontaneous, favourable and an endothermic process. Hence, the composite has a great potential to be used as an environmentally friendly and economical adsorbent for the removal of dyes from aqueous solutions. Tao *et al.* (2014) prepared graphene oxide nanosheets at ultralow temperature (–60 °C) by the reduction reaction of tetrachloroethylene and potassium in liquid ammonia solution at atmospheric pressure. It was used as an adsorbent for the adsorption of the organic dye rhodamine B because it showed high specific surface area, high adsorption capacity, and rapid adsorption rate of the organic dye rhodamine B from water. Graphene nanosheets are mainly achieved through π - π stacking and ionic interactions, indicating that they could be used as filtration membrane media for environmental applications. The preparation method may be useful for synthesizing other functionalized graphene oxide composites. Kim and co-workers (2013) synthesized three dimensional reduced graphene oxide based hydrogels by the reduction of graphene oxide using sodium ascorbate. The three dimensional reduced graphene oxide based hydrogels showed a large surface area and a uniform pore size distribution. They were used as adsorbents for the removal of the organic dyes, methylene blue and rhodamine B, from aqueous solutions. The results indicated that the three dimensional based hydrogels show excellent removal capabilities for methylene blue (~100%) and rhodamine B

(~97%) due to adsorption through strong π - π stacking and anion-cation interactions. Ao *et al.* (2013) [1] reported a solvothermal method to prepare a novel magnetic composite adsorbent composed of graphene, multi-walled carbon nanotubes and Fe₃O₄ nanoparticles. It was used as an adsorbent for the dye methylene blue. The results showed that the maximum adsorption capacity of the samples was almost equal to the sum of magnetic graphene and magnetic multi-walled carbon nanotubes. The kinetics was well-described by pseudo-second-order and the isotherm obeyed the Langmuir isotherm. The ternary hybrid prepared in this experiment could be used as a potential adsorbent in the dyeing wastewater treatment for its magnetic separability and good adsorption performance. Feng *et al.* (2015) [8] reported that the reduced graphene oxide nanosheets decorated with TiO₂ nanoparticles were bound to activated carbon fibres, forming three-dimensional macroscopic composites. They were used for the adsorption of the organic dye rhodamine B.

Oil spills

Yang *et al.* (2014) [8] reported the preparation of magnetic graphene foam loaded with magnetite (Fe₃O₄) nanoparticles and its application for the adsorption of oil and organic solvents. The foam with porous and hierarchical structures was prepared by a facile solvothermal method. Because of porous structures and magnetic properties, the graphene foam shows outstanding oil adsorption capacity and stability under cyclic operations. It was found that the adsorption capacity of graphene foam is at least four times higher than those of compact films (either graphene oxide or magnetic reduced graphene oxide film). The adsorption capacity observed in magnetic graphene foam was 27.0 g g⁻¹. Losic *et al.* (2014) synthesized graphene-carbon nanotube aerogels with three dimensional interconnected networks, prepared by heating of aqueous mixtures of graphene oxide and carbon nanotubes with ferrous ions. Carbon nanotubes were merged into the network to increase the robustness and hydrophobicity of aerogels. The three dimensional aerogels showed adsorption performance for the removal of petroleum products, fats and organic solvents, especially under the continuous vacuum regime. The result showed that the method could be successfully used for the efficient and cost-effective oil spill clean-up and water purification. Nanoporous graphene was synthesized by chemical vapour deposition method and used as a nanosorbent (Pourmand *et al.*, 2014) [7]. The authors studied the sorption of two samples of crude oil and also hydrocarbons, which cause environmental pollution especially in water, on to nanoporous graphene. It was found that due to the high pore volume, large specific surface area and small pore size, high sorption capacity was attained. Hong *et al.* (2015) [1] prepared surface modified graphene aerogel from self-assembled graphene oxide aerogels by surface modification. Fluorinated reduced graphene oxide was formed by a one-step solution immersion method. The result showed that the fluorinated reduced graphene oxide aerogel has excellent adsorption capacity and recyclability for various types of oils and organic solvents. Additionally, this approach offers a great feasibility of advanced absorbents for various applications in the fields of environment remediation, energy storage catalyst supports, etc.

Conclusions

From the review of graphene-based study, it has been concluded that the adsorbent properties of graphene can be

exploited for the controlling of different pollutants, which cannot be controlled by different controlling agents. Its special properties will help in control of secondary pollutants which are non-degradable. Graphene and its derivatives can be further modified by use of different synthetic methods for control of various pollutants.

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