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A fluorescent probe based on nitrogen doped graphene quantum dots for turn off sensing of explosive and detrimental water pollutant, TNP in aqueous medium

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ABSTRACT

This paper reports the carbonization assisted green approach for the fabrication of nitrogen doped graphene quantum dots (N-GQDs). The obtained N-GQDs displayed good water dispersibility and stability in the wide pH range. The as synthesized N-GQDs were used as a fluorescent probe for the sensing of explosive 2,4,6-trinitrophenol (TNP) in aqueous medium based on fluorescence resonance energy transfer (FRET), molecular interactions and charge transfer mechanism. The quenching efficiency was found to be linear in proportion to the TNP concentration within the range of 0–16 μM with detection limit (LOD) of 0.92 μM. The presented method was successfully applied to the sensing of TNP in tap and lake water samples with satisfactory results. Thus, N-GQDs were used as a selective, sensitive and turn off fluorescent sensor for the detection of perilous water contaminant i.e. TNP.

1. Introduction

Phenols and their nitro analogues have become a global concern as they have been recognized for their harmful hematotoxic and hepatotoxic effects on the living species. They can implant carcinogenesis and mutagenesis inside the cells of human beings and other living organisms. Nitrophenols are found to be toxic even at a concentration of 150 μg/L [1]. US Environmental Protection Agency has also enlisted various substituted phenolic analogues as "Priority Pollutants" [2]. Nitroaromatic compounds are also a part of "The Bureau of Alcohol, Tobacco, and Firearms (ATF)" list and these are extensively used in military and aviation industries, forensic investigations and manufacturing of fireworks [3,4]. Explosive bombs due to their ease of production and utilization have been widely used by the terrorists, and consequently responsible for human and property loss at an enormous scale [3].

2,4,6-Trinitrophenol (TNP), a nitroaromatic phenolic substance possesses more violent and explosive nature than its another analogues. This compound is extensively used in land mines detection, manufacturing of rocket fuels, dye and pharmaceutical industry [5, 6]. TNP pose serious threats to human life as it causes various health problems such as headache, liver malfunctioning, irritation in skin and eyes, male infertility, anaemia, cancer and cyanosis [6,7]. Through the food chain, when it reaches to the digestive cycle of mammalians, it is metabolized into picramic acid which is ten times more mutagenic than itself [1]. The high aqueous solubility of TNP leads to the poisoning of soil as well as ground water resources and also due to its electron deficient nature, it is resistant to biodegradation. Thus, TNP has been recognized as an environmentally deleterious material due to its explosive and bio toxic nature [7].

A variety of methods have been applied for the determination of explosives such as colorimetric, electrochemical, mass spectrometry, ion mobility spectrometry, surface-enhanced Raman scattering, paper sensors etc. [8–13]. But, these methods require expensive instruments, capable professionals and have poor sensitivity. Fluorescence detection technique has advantages over other detection methods owing to its simplicity, short response time, high sensitivity, cost effectiveness and compatibility in both solid and solution states [7]. Different materials have been reported for the efficient sensing of TNP. Feng et al. reported dual fluorescent sensor for the determination of DNP and TNP using tetraphenylethylene (TPE) Schiff base macrocyclic compound [14]. Ye et al. fabricated a two dimensional Zn(II) based metal organic coordination polymer[Zn(PAM)(en)] and used as a dual probe for the recognition of TNP and Cu(II) [15]. A cross linked inorganic-organic hybrid polymer material, poly(tetraphenylethylene-*co*-cyclotriphosphazene) was developed by Hu et al. and fluorescence quenching was observed with the addition of TNP [16]. Sang et al. synthesized porous covalent organic polymers for the sensitive and selective sensing of TNP [17]. Colorimetric and fluorescent sensor for the recognition of TNP based on N-acylhydrazone receptor was constructed by Peng et al. [8]. (E)-4-

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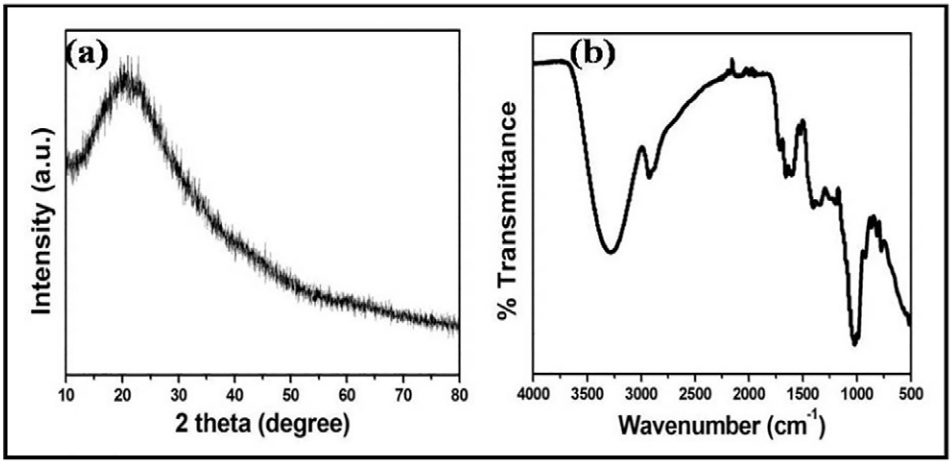

Fig. 1. Typical (a) XRD and (b) FTIR spectrum of the prepared N-GQDs.

(2-(pyridin-4-yl)vinyl)aniline compound was applied by Pan et al. for the recognition of TNP [18]. These probes have been applied in organic solvents, water and organic solvents mixture, and are mostly insoluble in water. These partially aqueous sensing systems are not much beneficial which leads to the development of such fluorescent probes which would be effective for the selective recognition of TNP in aqueous medium.

Graphene quantum dots (GQDs), a new member of the carbon family, are gaining enormous attraction because of their peculiar features like robust chemical stability, less cytotoxicity, marvellous biocompatibility, outstanding water solubility, abundant availability, and resistance to photobleaching [19]. Doping of carbon based nanomaterials with heteroatoms virtually modifies the electronic properties, surface activities and local chemical characteristics of these materials. In particular,

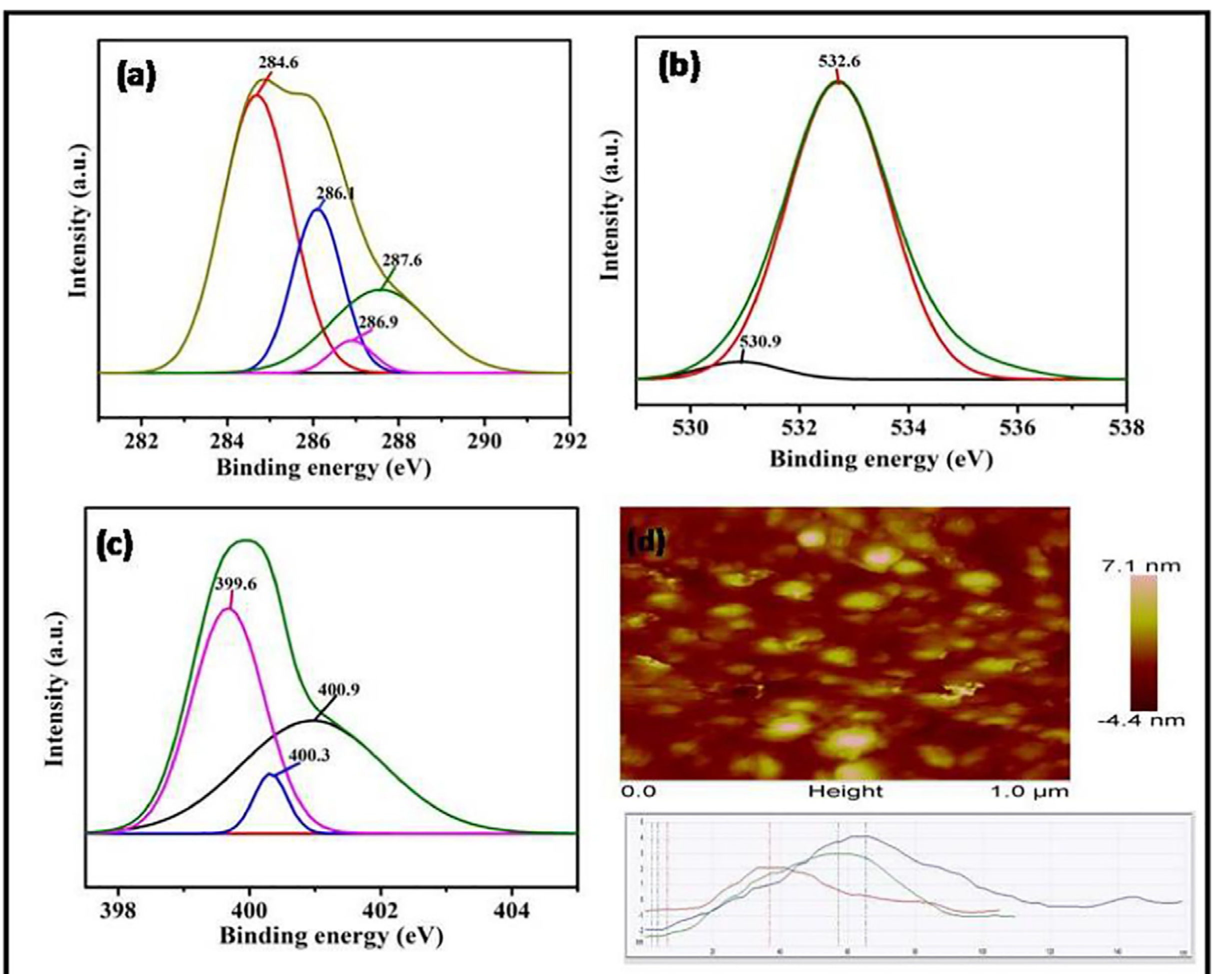

Fig. 2. High resolution XPS spectra of (a) C1s (b) O 1s (c) N 1s (d) AFM image and the height distribution profile of the fabricated N-GQDs.