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Advantages of nitrogen-doped graphene quantum dots as a green sensitizer with ZnO nanorod based photoanodes for solar energy conversion

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ABSTRACT

Graphene quantum dots (GQDs) and nitrogen-doped graphene quantum dots (N-GQDs) have been synthesized by a hydrothermal process. Optical absorption study revealed strong ultraviolet photoabsorption for both GQDs. An additional broad absorption band in the visible region has been observed for N doped GQDs. GQDs and N-GQDs both are highly luminescent and exhibit excitation dependent emission behaviors. Photoelectrochemical properties of GQD and N-GQD sensitized ZnO nanorods have been investigated in details. GQD modified nanorod photoanodes demonstrated superior photoconversion efficiency and incident photon to current conversion efficiency (IPCE) than pristine ZnO nanorods. N-GQD sensitized nanorods exhibited better photoelectrochemical properties than pristine GQD due to higher visible photoabsorption and lower interfacial resistance.

Carbon nanomaterials such as carbon nanotubes, graphene, fullerene, carbon quantum dots (CQDs) and graphene quantum dots (GQDs) have been attracted much attention due to their interesting electrical and optical properties [1–4]. These nanomaterials have potential applications in several optoelectronic devices such as light emitting diodes [2], field effect transistors [3], photodetectors [4], solar cells [5–8], photocatalysis [9], and photoelectrochemical cells [10–12]. Recently, graphene quantum dots (GQDs) have been studied extensively due to their size tunable optical properties similar to semiconductor quantum dots [13]. These zero dimensional carbon nanomaterials are non toxic, environmental friendly, and can be synthesized by low cost chemical process [14]. Doping is a common process to tailor the electronic and optical properties of graphene quantum dots [15]. Several kinds of doping elements like S, N, and B, Si were investigated to modify the properties of GQDs [9,16–18]. Sensitization of GQDs with nanostructured photoanodes is attractive due to their non-toxic nature and strong photoabsorption in UV–visible region depending on their size and doping elements. Sim et al. [10] synthesized N-doped graphene quantum sheets (GQS) as a catalyst with Si nanowire photoanodes for solar-driven hydrogen evolution. N-doped GQS sensitized nanowires showed excellent catalytic activity with applied bias photon to current conversion efficiency 2.29%. Zhang et al. [11] studied N-doped carbon dots (N-CDs) sensitized TiO_2 inverse opals for photoelectrochemical applications. The observed photocurrent density was 2 times than CQD sensitized TiO_2 and 18 times higher than pristine TiO_2 photoanode. Guo et al. [12] have attached GQDs on ZnO nanorods using aminopropyl-triethoxysilane linker molecules and investigated photoelectrochemical properties. The sensitized photoanodes showed open circuit voltage (V_{OC}) ~ 0.15 V and short circuit current (J_{SC}) ~0.064 mA/cm^2. The observed V_{OC} and J_{SC} were 1.8 times and 8 times higher than pristine ZnO, respectively.

In this report, we have grown GQDs and N-doped GQDs using a chemical process. The microstructural, optical absorption and emission properties have been investigated for both quantum dots. The role of GQD and N-GQD as a green sensitizer with ZnO nanorod photoanodes has been explored in details.

Graphene quantum dots (GQDs) and N-doped graphene quantum dots (N-GQDs) were synthesized by a hydrothermal process [19]. The detailed experimental procedure and characterization techniques were presented in supplementary materials. The surface topography of GQDs and N-GQDs was studied using atomic force microscopy (AFM) in tapping mode. Fig. 1 (a) and (b) represents plane view AFM micrographs of GQDs and N-GQDs, deposited on p-Si substrates, respectively. The height distributions of GQDs have been plotted at the inset of Fig. 1(a) and (b). The heights of pristine GQDs and N-doped GQDs are mostly distributed in the range of 0.5–3.5 nm and 0.5–2 nm, respectively. AFM study clearly indicates that, N-GQDs consist of 1–5 monolayers of graphene, whereas GQDs are composed of 1–8 graphene layers [20]. Fig. 1(c) shows the typical TEM micrograph of

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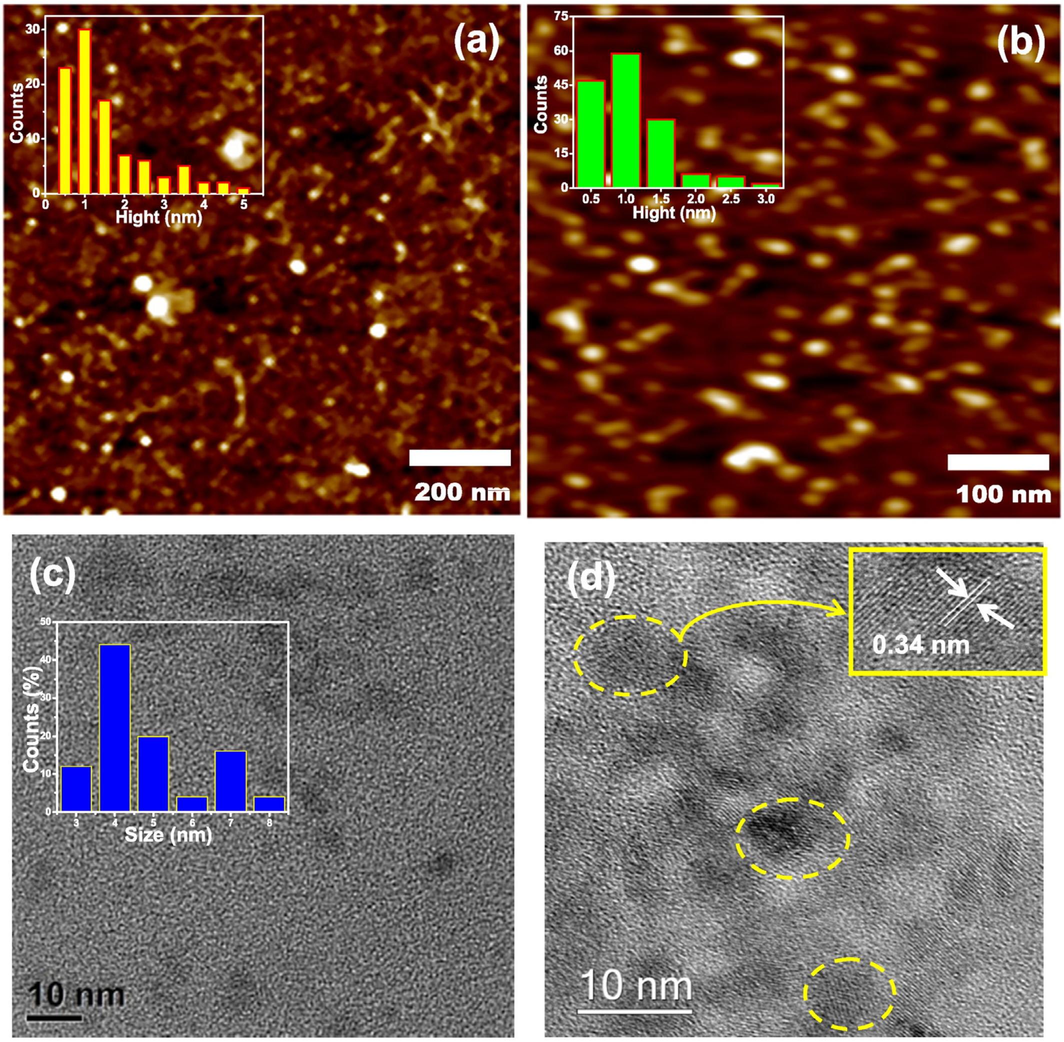

Fig. 1. Atomic force microscopy image of (a) GQDs and (b) N doped GQDs. Height distribution histograms of GQDs and N-GQDs are shown at the inset. (c) Typical TEM micrograph of hydrothermally grown N-GQDs. Size distribution histogram is plotted at the inset. (d) High resolution TEM image of N-GQDs.

N-GQDs of diameter between 3 to 7 nm. The size distribution is plotted at the inset of Fig. 1(c). The high resolution TEM micrograph of N-GQDs is presented in Fig. 1(d). N-GQDs are highly crystalline with interplanar spacing of 0.34 nm, which is similar to the (002) facet of graphitic carbon (Inset of Fig. 1d) [21].

The full range XPS spectra of GQD and N-GQDs are presented in Fig. 2. The dominant binding energy peaks at 283.2 eV and 531.2 eV, are attributed to the presence of C 1s and O 1s electrons, which are the key elements of GQDs. However, N-GQDs showed an extra peak at 399.2 eV, which is ascribed to N1s electrons. The nitrogen atom configurations in GQDs were analyzed by the deconvolution of N 1s peak into three Gaussian parts (inset of Fig. 2). The deconvoluted peaks are located at 398.3 eV, 399.6 eV and 401.5 eV and attributed to Pyridinc, Pyrrolic and Graphitic nitrogen configurations, respectively [22,23]. The optical absorption and emission behaviors of GQDs and N-GQDs were studied after dispersion in aqueous solutions. Fig. 3(a) and (b) represents UV–VIS absorption and emission spectra of GQDs and N-GQDs. The absorption spectrum of GQDs shows two major peaks of wavelength 215 nm and 338 nm. On the other hand, N-GQDs show two dominant peaks located at 238 nm and 334 nm, in addition to a broad absorption band in the range 460 to 500 nm. The origin of such UV absorption peaks at 215–238 nm is attributed to $\pi \rightarrow \pi^*$ transition of CC bonds [9,19,24,25] and at 334–338 nm corresponds to $n \rightarrow \pi^*$ transition of CO bonds [9]. The broad absorption band of N-GQDs observed at 460–500 nm is due to $n \rightarrow \pi^*$ transition of CN

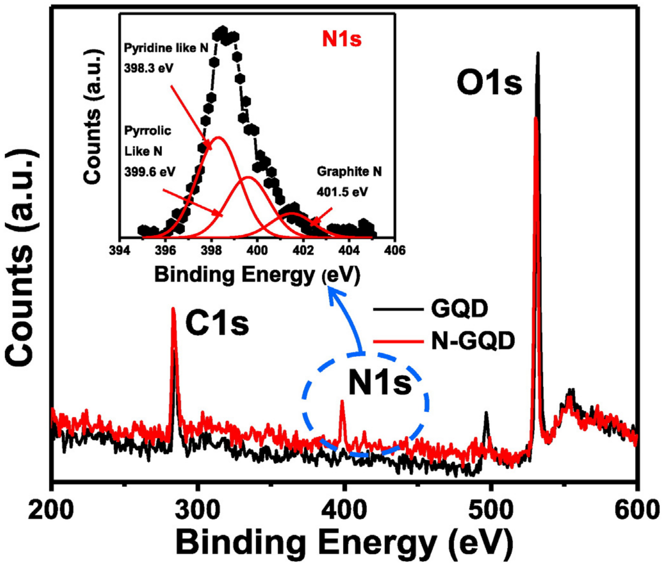

Fig. 2. Full scan XPS spectra of GQDs and N-GQDs. High resolution N1s spectrum of N-GQD is shown at inset.