Arrays of TiO$_2$ nanorods embedded with fluorine doped carbon nitride quantum dots (CNFQDs) for visible light driven water splitting

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ABSTRACT

Graphenic semiconductors such as carbon nitride are attracting increasing attention as photocatalysts due to their chemical stability, visible light absorption and excellent electronic properties. The photocatalytic activity of nanostructured TiO$_2$ catalysts is constrained by the wide bandgap and concomitant low visible light responsivity of TiO$_2$. In this context we present the formation of new fluorine doped carbon nitride quantum dots (CNFQDs) by solid state reaction and the subsequent examination of their heterojunctions with TiO$_2$ for photoelectrochemical water splitting. Arrays of rutile phase TiO$_2$ nanorods embedded with CNFQDs were synthesized by a simple *in situ* hydrothermal approach and the resulting nanomaterials were found to exhibit strong visible light absorption. The energetics at the heterojunction were favorable for efficient electron transfer from CNFQDs to TiO$_2$ under visible light irradiation and transfer of holes to the aqueous electrolyte. CNFQD-sensitized TiO$_2$ nanorods exhibited a strong photoelectrochemical response up to 500 nm. Reuse experiments confirmed robustness and long term stability of the sample without exhausting the catalytic performance. The present work demonstrates a new pathway to sensitize TiO$_2$ to visible photons by the *in situ* formation of embedded heterojunctions with fluorine doped carbon nitride quantum dots.

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1. Introduction

The energy crisis due to depletion of fossil fuel reserves and alarming environmental pollution has triggered research to search for alternative, clean and sustainable energy resources [1,2]. Photoelectrochemical water splitting to produce hydrogen using visible light and applied bias has wide potential to solve these problems due to the high free energy content of H$_2$ ($\Delta G = +237$ kJ mol^{-1}), a nearly inexhaustible supply of resources *ie:* water and sunlight, and the generation of water as the sole by-product following combustion [3—5]. Due to energy constraints, water splitting requires a photocatalyst which can reduce the activation energy barrier by supplying electrons and holes to reduce hydrogen and oxidize water. In search of the ideal visible light active photocatalyst, numerous semiconductor materials have been explored but most of them suffer from one or more debilitating drawbacks such as a lack of visible light absorption, a lack of photostability or a low catalytic quantum efficiency [6].

In recent years, carbon quantum dots (CQDs) which are sp^2 and sp^3 hybridized graphitic or turbostratic quasispherical carbon nanoparticles have proven to be excellent electronic materials for photocatalysis, catalysis, sensing and OLEDs due to facile synthesis, small band gap, intense photoluminescence (following surface passivation), and size and surface tunability of optoelectronic properties [7]. Carbon nitride quantum dots (CNQDs), nitrogen rich descendents of the carbon nitride frame work composed of a tris-*s*-triazine skeleton, are gaining popularity over CQDs due to their higher chemical and photostability, easy synthesis and brighter fluorescence [8—11]. Doping with heteroatoms (N, S, O *etc*) and surface functionalization can further improve the fluorescence intensity, carrier lifetime, and photocatalytic behavior of CNQDs [12]. For instance, Lu et al. prepared S and O co-doped CNQDs using thiourea and citric acid which exhibited excellent performance for mercury detection and cell imaging [13]. Interestingly fluorine doping in carbon nitride can distort the symmetry of some

conjugated domains, in turn altering the band gap and band edge positions to improve photocatalytic performance [14]. Wang et al. demonstrated the synthesis of F doped carbon nitride quantum dots (F−C_3N_4) of size range 1.5—2.0 nm by fragmentation of bulk sheets in ethylene glycol under ultrasonication treatment which exhibited excellent PL quantum yields (39.03%) [15].

TiO_2 is the most studied semiconductor photocatalyst due to its high catalytic activity, non-toxic nature, chemical and photo-corrosion resistance, and wide abundance. However, TiO_2's wide band gap and less reductive conduction band constitute the key obstacles limiting performance [16]. Doping or decorating TiO_2 with noble metals (Au, Ag, Ru, Pd, Cu, Pt, CuPt, *etc*) [17−21], doping with non-metals (C, N, S, F, *etc*) [22−26], sensitization with various molecular complexes (Ru, Ir, Pt, Re complexes) [27−29], composite formation with low band gap semiconductors [30,31], and defect creation [32,33] have been employed to increase visible light absorption, enhance charge separation and lengthen the carrier life-time. Yet, the quantum efficiencies of TiO_2-based photocatalysts for visible photons remain too low, preventing the scale-up of the technology [34] [7,35,36]. Photoelectrochemical cells in which the photoanode is a sintered film of colloidal nanoparticles suffer from significant transport and recombination losses due to the random-walk nature of charge migration in such films [37]. One dimensional structures such as vertically oriented arrays of monocrystalline TiO_2 nanorods offer continuous vectorial percolation pathways and improved charge transport owing to a more ordered structural and crystalline feature [38−46], which motivated us to use TiO_2 nanowires as scaffolds for CNQDs.

Due to their lower band gap and aromatic π-conjugated framework, carbon nitride quantum dots can play the dual role of 1) photosensitizer − i.e. can donate electron to another system after absorption of light and 2) electron sink - can uptake electrons from another system to facilitate charge separation. To exploit this behavior, CNQD-decorated semiconductors photocatalysts have been reported. Pan et al. [47] and Su et al. [48] prepared CNQD-decorated TiO_2 nanotubes for enhanced activity for dye photo-degradation. In another report Su et al. formed TiO_2 nanotube arrays (TNTAs) decorated with ultrasmall CNQDs which then showed a three fold increase in photocurrent compared to the TNTAs alone, in photoelectrochemical water splitting experiments [49]. Although the photocatalytic performance increased upon decoration of CNQDs on TNTAs nanostructures, severe leaching of the CNQDs from the semiconductor surface and the resulting photocorrosion limits their practical usability. *In situ* growth of semiconductor materials in the presence of quantum dot sensitizers can lead to the formation of embedded nanostructures possessing enhanced robustness and reusability while maintaining similar photoactivity [50−52]. For example, *in situ* synthesized C_3N_4-CdS nanocomposite prepared by precipitation−deposition method showed excellent activity for the degradation of 4-aminobenzoic acid [53]. Similarly graphitic-C_3N_4 nanosheet hybridized N-doped TiO_2 nanofibers synthesized by an *in situ* approach afforded increased H_2 production and degradation [54]. Inspired by these studies, we synthesized fluorine doped carbon nitride quantum dots (CNFQDs) embedded in TiO_2 nanorods (CNF:TNR) by the *in situ* growth of TiO_2 nanorods in the presence of CNFQDs. The synthesized CNF:TNR photocatalyst materials exhibited excellent photoelectrochemical performance, robustness and reusability.

2. Results and discussion

2.1. Morphology, structure and composition of CNF:TNR nanocomposites

The fluorescent fluorine doped carbon nitride quantum dots (CNFQDs) were prepared by modifying a procedure previous reported for the synthesis of carbon nitride quantum dots [55]. The CNFQDs were synthesized by the solid state reaction of urea and citric acid (which serve as sources for the formation of the carbon nitride skeleton) and ammonium fluoride (which provides the fluorine dopant) at 200 °C in a Teflon autoclave (Fig. 1a). The *in situ* synthesis of CNFQDs embedded TiO_2 nanorods (CNF:TNR) was performed by hydrothermal treatment of titanium (IV) butoxide in the presence of acetic acid, HCl and an aqueous suspension of CNFQDs at 200 °C, and a schematic illustration of this *in situ* process is shown in Fig. 1b.

The obtained CNFQDs exhibited a bright blue fluorescence under UV light as seen in the Inset of Fig. 2a. The PL spectra (Fig. 2a) illustrate the excitation dependent emission behavior of prepared CNFQDs wherein the emission peaks are red shifted from 417 nm to 422 nm as the excitation wavelength is changed from 370 nm to 390 nm, in line with previous reports on carbon nitride quantum dots [15,56,57]. The average particle size of the CNFQDs was found to be 7 nm as determined from dynamic light scattering (DLS) (Fig. S1) and the associated average zeta potential (surface charge) was calculated to be −21.3 mV (Fig. S2), which is attributed to amine and carboxylate groups on the surface of the quantum dots [55]. Various CNF:TNR samples were prepared by maintaining reaction times of 2, 4, 6 and 8 h, and are denoted by CNF:TNR-2h, CNF:TNR-4h, CNF:TNR-6h and CNF:TNR-8h respectively. During hydrothermal growth of TiO_2 nanorods (TNRs), the fluorinated carbon nitride quantum dots get partially embedded in the nanorods. The embedding of the CNFQDs in the nanorods was inferred from Raman, infrared and photoelectron spectra (shown and analyzed later) as well as from the leaching characteristics of the samples. CNFQDs are very soluble in KOH and surface adsorbed carbon nitride quantum dots are known to leach out during KOH treatment; however *in situ* CNF:TNR samples did not show the slightest leaching even after repeated cycling in KOH. We attribute the embedding of the quantum dots in the TNR framework to the interaction of the active surface groups on the CNFQDs with the exposed facets of growing rutile crystallites. The embedded nature of the quantum dots provides robustness and stability to the CNFQDs/TNR composite, and also enables the absorption of visible light. Due to the entrapment of CNFQDs in the TNR structure, the color of the samples turns to dark brown as seen in Fig. 2b with the deepest color obtained for a reaction time of 2 h. However no significant change in color was observed upon increasing reaction time (Fig. 2b). CNF:TNR samples hydrothermally grown on FTO for reaction times longer than *ca* 12 h delaminated from the underlying FTO coated glass substrate.

The morphologies and size parameters of TNRs and CNF:TNR samples were determined using a field emission scanning electron microscope (FESEM). The FESEM top view of bare TNR samples grown after 2 h hydrothermal treatment exhibits evenly distributed TiO_2 nanorods on FTO substrate with blunt ends (Fig. 3a and c) while the cross sections indicate a mean nanorod length of ~1.0 μm and a near identical thickness throughout (Fig. 3e). The top view of the CNF:TNR-4h sample in SEM images show multidirectional well distributed nanorod clusters having slightly pointed ends (Fig. 3b and d). The change in morphological character to unsymmetrical pointed nanorods occurs due to the intercalation of CNFQDs in the rutile crystal structure during the growth process which disturbs the TNR growth pattern. The average length of CNF:TNR-4h nanorods was found to be ~1.0 μm (Fig. 3f).

The SEM images of the CNF:TNR-2h, CNF:TNR-6h and CNF:TNR-8h samples also reveal similar morphological geometry while the average length was found to be ~0.75 μm, 1.4 μm and 1.5 μm respectively (Fig. S5). The SEM elemental mapping of CNF:TNR-4h sample indicates the carbon to be evenly distributed in the