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Nitrogen-doped luminescent carbon nanodots for optimal photo-generation of hydroxyl radicals and visible-light expanded photo-catalysis

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ABSTRACT

Luminescent carbon nanodots (CNDs) have been obtained by hydrothermal processing of ascorbic acid (AA) and ethanolamine (EN). The resulting N-doped carbon nanostructures exhibit interesting and tunable emission capabilities with a dual behavior as down-converters and more importantly, as up-converting quantum dots. Herein, we also evaluate the optical response of these CNDs to selectively generate highly reactive oxidative hydroxyls (•OH) upon irradiation with different light-emitting diodes (LEDs) in the visible–NIR range. Finally, the role of the N-doped CNDs as nano-sensitizers to maximize the solar light harvesting and expand the photo-catalytic response of a commonly used UV-active catalyst such as TiO_2 was successfully tested in the degradation of an organo-chlorinated compound under visible light.

1. Introduction

Research on photo-luminescent semiconducting nanomaterials, generally defined as quantum dots (QDs), has attracted a vast interest and experienced rapid development in the last decades, due to their promising and diverse potential applications in optoelectronics and bio/nano-technology. Most recently, the interest of QDs is also focusing on the development of novel carbon-based materials with narrow size distributions below 10 nm, that maintain an analogous and tunable wavelength-dependent optical response associated to quantum confinement and surface state emissions [1–8]. These carbon-based nanoparticles represent a new type of fluorescent nanomaterials that include fluorescent carbon nanotubes (CNTs), graphene quantum dots (GQDs), nanodiamonds and carbon nanodots (CNDs). The latter family of carbon nanoparticles is generally formed by less ordered structures with a different ratio of carbon backbone and surface groups depending on the preparation method (generally a bottom-up approach that includes a variety of polymerization and carbonization processes of small organic molecules depending on the synthesis conditions) [2]. Nowadays, CNDs are attracting a strong interest as a valid alternative to conventional quantum dots due to their lower fabrication costs, lower intrinsic toxicity and greater availability. Furthermore, CNDs exhibit superior versatility for surface chemical modification and great stability in multiple solvents, including the aqueous media for potential bio-applications [9–15].

Remarkably, some CNDs have recently shown unique capabilities as up-converting nanomaterials being able to sequentially absorb two or more longer wavelength photons that are emitted as shorter wavelength (and more energetic) photons [16–18]. This nonlinear optical response, traditionally observed in certain organic dyes or in inorganic lanthanide nanocrystals, has widened the potential application of CNDs in biologically related processes as biomarkers [10,19,20], biosensors [21] or Photodynamic Therapy (PDT) agents working in the NIR window where minimal background signal and deeper tissue penetration are ensured [2]. Furthermore, the potential use of CNDs as sensitizers of photo-catalytic supports [22–26] (typically TiO_2) has been also recently explored as alternative to direct carbon-doping or carbon coating of TiO_2 [27–34].

In the present work, we describe the successful synthesis of CNDs obtained after a hydrothermal heating process of ascorbic acid (AA) and ethanolamine (EN). These CNDs have been characterized and have shown appealing up-converting properties, most probably induced by the presence of N atoms doping the generated carbon nanoparticles. Furthermore, we have indirectly confirmed the up-converting capabilities of the CNDs after their assembly on commercial anatase

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supports and their irradiation with different broad spectrum illumination sources. Interestingly, an improved generation of hydroxyl radicals and an expanded photo-catalytic response towards the degradation of 2,4-dichlorophenol (a persistent organo-chlorinated pesticide) have been observed in the visible–NIR range.

2. Materials and methods

2.1. Chemicals

L-Ascorbic acid (AA), ethanolamine (EN), anatase TiO_2, terephthalic acid (TA) and 2,4-dichlorophenol (2,4-DCP) were purchased from Sigma-Aldrich (analytical grade) and used without further purification.

2.2. Synthesis of carbon nanodots and assembly on TiO_2 supports

CNDs were synthesized by hydrothermal processing of AA and EN. A 1:3 molar ratio solution of both organic precursors (1 M) was mixed and magnetically stirred in a beaker for 10 min. Later on, the solution was transferred into a Teflon-lined stainless–steel autoclave and heated at 250 °C for 4 h (Fig. 1). The resulting suspension was cooled down to room temperature, centrifuged and filtered through a 0.10 μm PTFE membrane (WhatmanTH) to remove larger aggregates. The resulting brownish yellow suspension contained the carbon nanodots and was labeled as AAEN and stored at 8 °C. An aliquot of the AAEN CNDs (2 mL; 1.5 mg L^{-1}) was further assembled into an anatase (TiO_2) support (0.5 g in 2.5 mL of deionized water) using a slow temperature evaporation ramp at 65 °C for 90 min in a vacuum oven (Fig. 1). The synthesis of the nanoparticles has been carried out using the platform for Production of Biomaterials and Nanoparticles of the NANBIOSIS ICTS.

2.3. Characterization techniques

Fluorescence measurements were performed using a LS55 Fluorescence Spectrometer (PerkinElmer) equipped with a xenon arc lamp as the light source and a quartz cell (10 × 10 mm). The CND spectra were acquired in a UV–visible–NIR spectrophotometer (V-67, Jasco Company) with a quartz cell of 1 cm light path. The morphologies and particle size distributions were determined by transmission electron microscopy (TEM) (FEI Tecnai T20 and F30, operated at 200–300 kV, respectively). To prepare the samples, the nanoparticle suspensions were diluted with water prior to casting on a holey carbon TEM grid. The functionalization of the CND surface was analyzed by Fourier transform infrared (FTIR) spectroscopy (Bruker Vertex 70 FTIR spectrometer) and X-ray photoelectron spectroscopy (XPS) with an Axis Ultra DLD (Kratos Tech.). A monochromatic Al Kα source (1486.6 eV) was employed with multiple runs at 12 kV, 10 mA and pass energy of 20 eV was used. The binding energies were calibrated to the internal C1s (284.3 eV) standard. Analyses of the peaks were performed with CasaXPS software, using a weighted sum of Lorentzian and Gaussian component curves after Shirley background subtraction. Raman analysis was carried out with the aid of a Laser Raman WiTec-Alpha 300 spectrometer using an Ar^+ ion laser exciting at 532 nm. The Raman light was collected in a backscattering geometry. The instrument was calibrated against the Stokes Raman signal of pure Si at 520 cm^{-1} using a silicon wafer crystal plane surface. Background subtraction was carried out with a second order polynomial fitted with the least squares method.

2.4. LED-assisted generation and detection of hydroxyl radicals

The generation of hydroxyl radicals (•OH) under the irradiation of selective wavelengths was carried out in the presence of three different light-emitting diodes (LEDs) (LED ENGIN, LZ4 models) at 532 nm (green LED), 740 nm (red LED) and a combination of 450 nm and 550 nm (white LED), respectively. Terephthalic acid (TA) was used as an indirect fluorescent probe that selectively reacts with hydroxyl radicals [23,35]. In a typical experiment, 0.6 mg of catalyst was dispersed in the probe solution containing TA (3 mL, 5 mM) and deposited in a cuvette with 1 cm path length. Prior to irradiation with LEDs, the suspensions were magnetically stirred in the dark for 30 min. Different aliquots were taken after selected irradiation time intervals and analyzed by fluorescence spectroscopy without retrieval of the catalyst.

2.5. Photo-catalytic experiments

The photo-catalytic capabilities of the CND–TiO_2 nanohybrids were evaluated by degradation of 2,4-DCP under visible light irradiation with a Xe lamp (cutoff filter for λ <420 nm). In a typical experiment, 20 mg of the CND–TiO_2 nanohybrids (0.5% wt. CNDs as determined by TGA) was suspended in an aqueous solution containing 2,4-dichlorophenol (2,4-DCP, 100 mL, 25 mM) and stirred overnight in dark conditions to ensure the establishment of adsorption/desorption equilibrium between 2,4-DCP and the photo-catalyst before irradiation. Multiple aliquots were progressively taken and analyzed at different irradiation times with the aid of an ultra performance liquid chromatograph

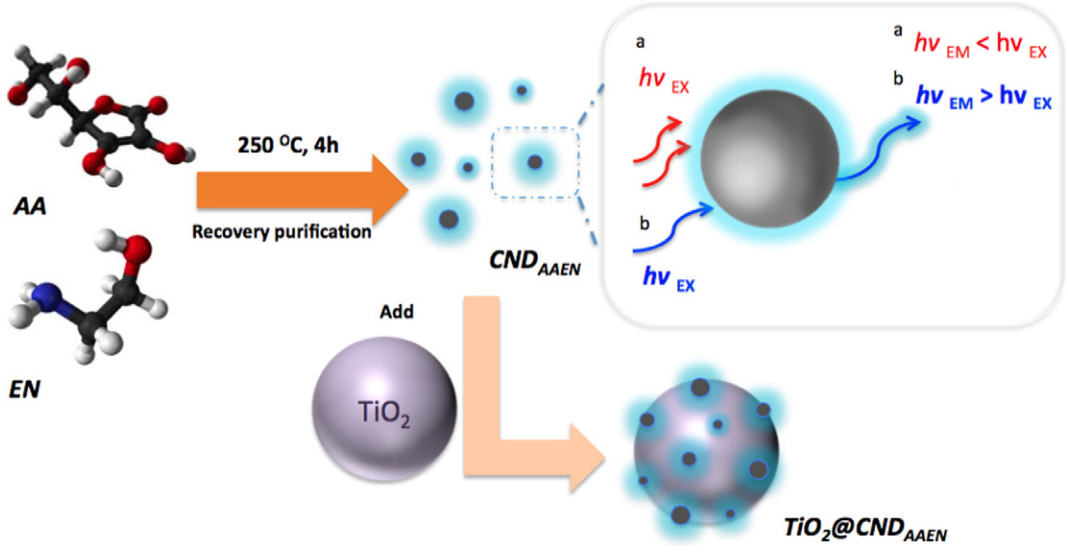

Fig. 1. Scheme of the hydrothermal processing of carbon nanodots with down-conversion (a) and up-conversion (b) properties and their assembly on TiO_2 supports.