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Extraordinary sensitizing effect of co-doped carbon nanodots derived from mate herb: Application to enhanced photocatalytic degradation of chlorinated wastewater compounds under visible light

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ABSTRACT

The present work investigates the role of two types of carbon nanodots (CNDs) as novel sensitizers of TiO_2 to create a visible-light driven photo-catalyst that is not only efficient for solar-driven pollution abatement, but also inexpensive, durable and environmentally-friendly. Two widely available green organic precursors, the Argentinean herb Mate and the Stevia plant have been selected as the carbogenic source to thermally induce the formation of different types of CNDs with different levels of N and P doping and tunable photoluminescence response in the UV–vis-near infrared (NIR) ranges. These CNDs have been successfully assembled with TiO_2 to form heterogeneous photocatalysts that are highly active in the visible-light and NIR- driven photodegradation of 2,4-dichlorophenol (2,4-DCP), a persistent chlorinated organic compound present in numerous pesticide formulations.

1. Introduction

The growing volume of wastes generated by human activities represents one of the most urgent environmental challenges that we face today [1–4]. Persistent and non-biodegradable organics in wastewater are major problems in water management, environmental protection, and water reuse. Traditional treatment methods such as adsorption, coagulation, and secondary biodegradation are often inadequate in treating many of the new, emerging micro-pollutants. They also suffer from high capital and operating costs, and are known to generate undesired secondary pollutants. Advanced oxidation processes (AOPs) [4–9] are capable of efficiently treating a broad range of problematic and refractory organic pollutants in water. The highly reactive radical species and oxidative intermediates (i.e. H_2O_2, $^{\bullet}OH$, $^{\bullet}O_2^{-}$, O_3) provide more complete oxidation and mineralization of the pollutants. Heterogeneous photocatalysis is particularly attractive for wastewater treatment with a clear advantage in terms of cost when the process is solar driven [1,5,8,10–12].

Current research is focused mainly on the optimization of the state-of-the-art solid heterogeneous photocatalysts. These materials are typically semiconductors that can be susceptible to photo-corrosion during long-term operation. Titania photocatalysts are remarkably stable under varied operating conditions and due to their abundance are less expensive than alternative materials [2,3,8]. Nevertheless, TiO_2 having a wide electronic band-gap requires UV irradiation. Moreover, rapid recombination of

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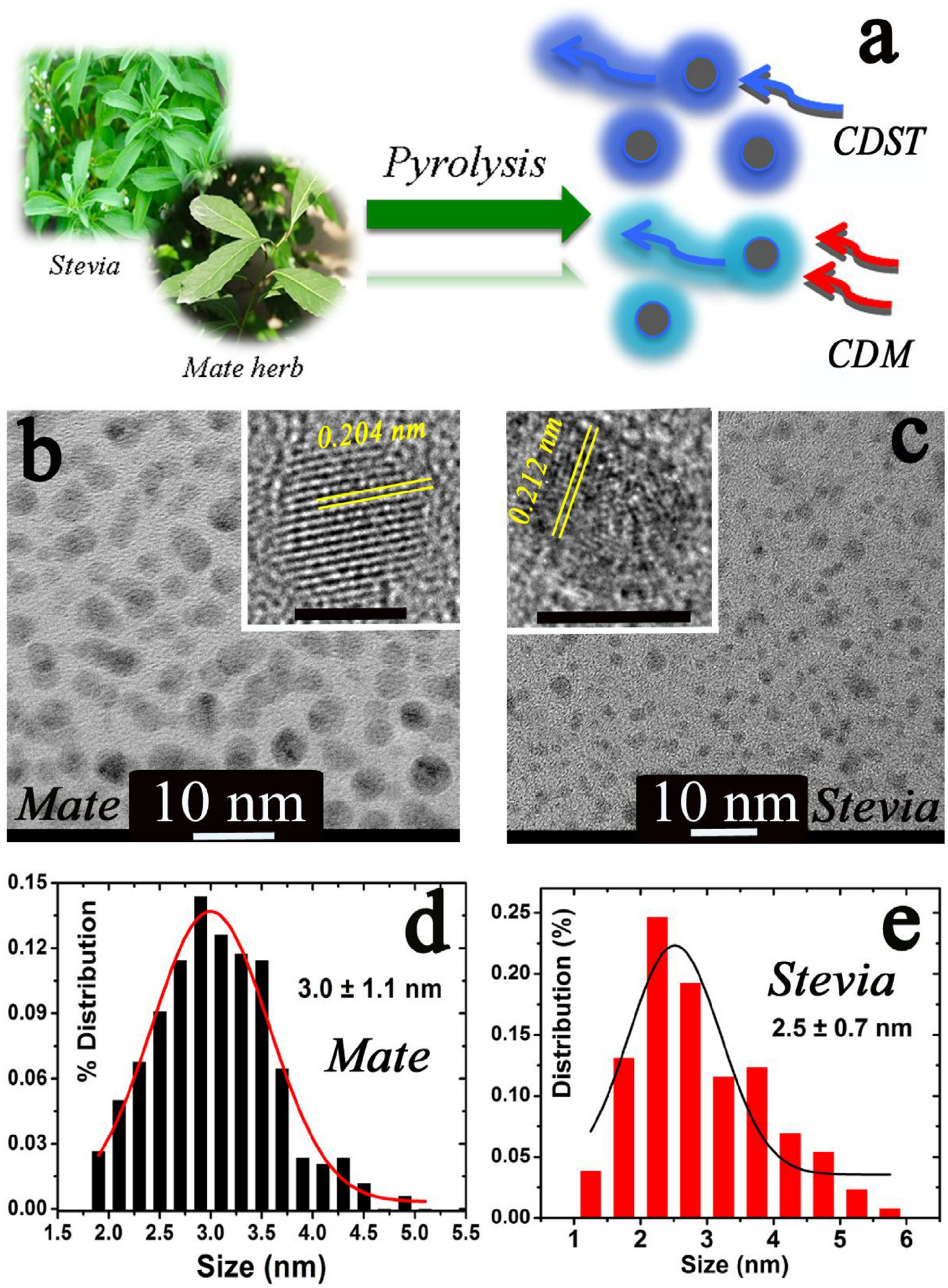

Fig. 1. (a) Scheme of the pyrolysis treatment of Mate and Stevia plant leaves; (b) TEM image of the carbon nanodots retrieved from Mate (inset: HRTEM image of a single CND with (111) orientation corresponding to graphite); (c) TEM image corresponding to the carbon nanodots obtained from the Stevia plant (inset: HRTEM image of a single CND where lattice distances for (020) orientations of graphite are shown); (d) Particle size distribution of the CNDM; (e) Particle size distribution of the CNDST. Scale bars in insets correspond to 3 nm.

the photo-generated electron-hole pair can significantly limit the quantum efficiency. Therefore, narrowing down the band-gap of TiO_2 to increase the visible-light absorption response is an often-used strategy to improve the photocatalyst performance [13,14]. Among the procedures employed are: (i) chemical modifications with light elements such as carbon, nitrogen, boron or sulfur to shift the absorption toward the visible range by creating intermediate energy states that narrow the band gap [13,14]; (ii) addition of plasmonic noble metals that boost absorption in the visible-NIR range due to their surface plasmon resonance (SPR) band [15–21]; (iii) use of sensitizers such as organic dyes and/or narrow band-gap quantum dots that absorb visible light and inject electrons into the conduction band of TiO_2 to suppress the recombination rate of electron-hole pairs as in the case of quantum dot sensitized solar cells (QDSSCs) [22–25].

This work investigates the use of carbon nanodots (CNDs) in TiO_2 to create a visible-light photo-catalyst that not only is efficient for solar-driven pollution abatement, but also inexpensive, durable and environmentally-friendly [26–34]. Carbon nanodots are luminescent nanomaterials characterized by their broad absorption spectra, resistance to photo-bleaching and low toxicity [30,31,33–39]. They are potentially inexhaustible in view of the abundance of raw materials for their production. CNDs may also exhibit an interesting optical behavior as up-converters, thanks to due to size-dependent quantum confinement effects, expanding their potential applicability as sensitizers in the whole solar