Coordination Chemistry Reviews 320-321 (2016) 66–81

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Functionalized carbon nanoparticles: Syntheses and applications in optical bioimaging and energy conversion

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Contents

ARTICLE INFO

Article history:
Received 16 December 2015
Accepted 20 February 2016
Available online 10 March 2016

Keywords:
Functionalized nanoparticles
Carbon dots
Fluorescence
Optical imaging
Charge transfer
Energy conversion

ABSTRACT

Semiconductor quantum dots (QDs) are known for their unique optical properties. In recent years, carbon nanomaterials of surface and/or structural defects have been found to exhibit similar properties after functionalization in various schemes. Among these carbon-based QDs are carbon dots, which are generally defined as small carbon nanoparticles with surface passivation. In fact, carbon dots now represent a rapidly advancing and expanding research field. As measured by the optical properties of carbon dots, the most effective passivation has been the surface functionalization of carbon nanoparticles with organic or polymeric molecules, corresponding to much brighter fluorescence emissions across the visible spectrum and extending into the near-IR. Therefore, carbon dots have been pursued extensively for potential bioimaging and other biomedical applications. The mechanistic framework for carbon dots includes photoinduced redox processes, similar to those found in conventional semiconductor QDs. As a result, carbon dots have also been pursued for their photocatalytic functions. In this article on surface-functionalized carbon nanoparticles or carbon dots, their representative syntheses and demonstrated properties and their potential uses as high-performance yet nontoxic fluorescence probes for bioimaging *in vitro* and *in vivo* are highlighted, so is their serving as potent photocatalysts in energy conversion applications.

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http://dx.doi.org/10.1016/j.ccr.2016.02.017
0010-8545/

1. Introduction

Quantum dots (QDs) were originally defined as semiconductor nanocrystals of physical dimensions smaller than the exciton Bohr radius for the quantum confinement effect. Because of the quantum confinement, there is a predictable dependence of the energy gap on the nanocrystal dimension in QDs, as manifested by the corresponding variations in optical properties [1–3]. More specifically, the systematic changes in the beautiful fluorescence emission colors in semiconductor QDs such as CdSe of different sizes have generated much excitement in the research community, with extensive investigations on a variety of potential applications, especially as superior fluorescence probes for imaging and other biomedical applications [4,5]. In fact, the rationale for the use of QDs over organic dyes is now generally accepted in the literature [4,5]. Similarly bright and colorful fluorescence emissions have been found in other nanomaterials containing no conventional semiconductors, and those fluorescent nanomaterials are often referred to, more phenomenologically perhaps, as QDs as well, despite in most cases the absence of any classical quantum confinement effect. Among more popular and promising recent additions to the loosely defined QD family are carbon-based QDs, including carbon dots (Fig. 1) [6,7], graphene quantum dots [8,9], nanodiamonds [10,11], and "carbon nanotube quantum dots" [12,13]. For most of these QD-resembling carbon nanomaterials, surface functionalization is important or critical as in the case of carbon dots [14]. This is also phenomenologically similar to that in conventional semiconductor QDs, such as the surface capping of CdSe with ZnS for substantial performance improvements, despite the obvious mechanistic differences.

Carbon dots, generally defined as small carbon nanoparticles with various surface passivation schemes (Fig. 1) [6,7], have been leading the recent emergence of various carbon-based QDs, and now represent a rapidly advancing and expanding research field [15–21]. As measured by the optical properties of carbon dots, the most effective passivation scheme has been the surface functionalization of carbon nanoparticles with organic or polymeric molecules, corresponding to much brighter fluorescence emissions across the visible spectrum and extending into the near-IR [22,23]. In fact, fluorescence emissions from "naked" (no deliberate surface passivation) carbon nanoparticles in aqueous or organic suspensions have been reported in the literature, but the quantum yields are generally low to very low [24,25]. It may be argued that the surface passivation effect is provided by the solvent molecules in the suspensions [26]. The same dramatic surface passivation effect resulting in substantially enhanced optical properties has also been reported for graphene quantum dots [27–29]. Since passivation is on defects, improving defect-derived or dominated optical

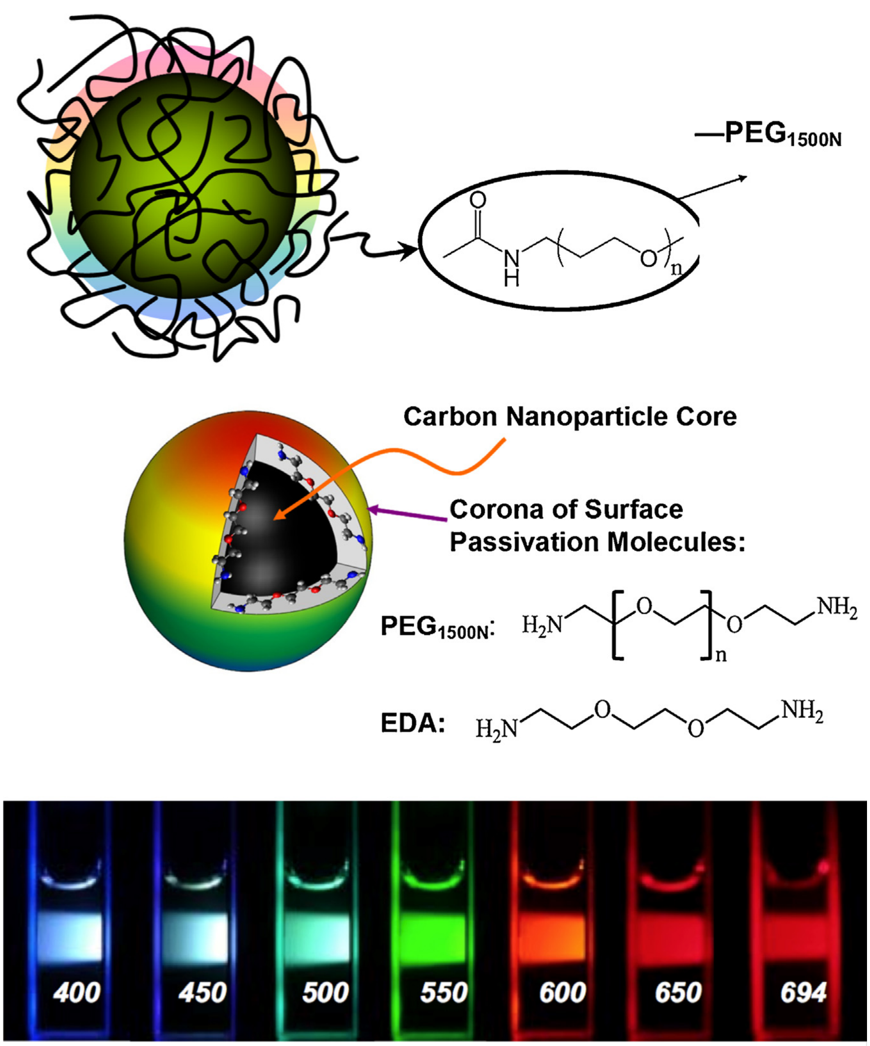

Fig. 1. Upper and middle: Cartoon illustrations used in the literature [22,84] on a carbon dot, generally a small carbon nanoparticle core with attached surface passivation molecules (equivalent to a soft corona). Lower: Fluorescence color variations in carbon dots corresponding to the indicated excitation wavelengths [6]. Reprinted with permission from the cited refs.