



# Tailoring surface charge distribution of carbon dots through heteroatoms for enhanced visible-light photocatalytic activity



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## ABSTRACT

We have developed a facile and effective method to prepare chlorine and phosphorus-functionalized carbon dots (CDs) and investigated what the roles of these heteroatoms are played in carbon dot properties. Our researches suggested that Cl and P elements incorporated in superficial carbon atoms could tailor charge distribution on the surface of CDs, facilitating more effective photogenerated charge separation. Therefore, Cl and P-functionalized CDs show much higher photocatalytic activities than Cl and P-free CDs and commercial TiO<sub>2</sub>. This work gains an insight into how to effectively tune the photogenerated charge behaviors of CDs to achieve excellent properties.

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## 1. Introduction

Carbon dots (CDs) have been garnered much research attention because of their unique advantages [1,2]. Not only can they be prepared inexpensively and on a large scale, but also offer excellent photophysical properties without incurring the burden of intrinsic toxicity or elemental scarcity [1]. Therefore, CDs are promising substitutes for the present semiconductor quantum dots with heavy metals [3]. It is increasingly hot that CDs are used for photocatalysis as an additive of the popular photocatalyst, such as TiO<sub>2</sub>, Ag<sub>3</sub>PO<sub>4</sub> and C<sub>3</sub>N<sub>4</sub> [2,4–7]. The roles of CDs played in the nano-composites harvest visible light and facilitate the excited electron transfer along their interfaces, allowing charge separation and stabilization, thus generating longer-lived holes on the surface [2,4]. This is mainly ascribed to unique photoinduced electron transfer (ET) property of CDs [8]. Due to the origin of carbon dot photoluminescence (PL) from radiative recombination of surface-confined electrons and holes that are generated probably by charge separation in CDs [3,9–12], both electron donors and acceptors can apparently scavenge these surface-confined holes and electrons, respectively, to result in their fluorescence quenching of the CDs. Accordingly, CDs could act as electron reservoir and this

capacity should depend on surface states of CDs since they are closely associated with surface energy traps induced by quantum confinement effects [6,9]. However, it remains unclear till now what kinds of surface states are responsible for enhanced this capacity of electron reservoir.

To utilize energy harvested from sunlight efficiently to promote photochemical reaction, we must understand and explore the operation of surface states for improving the transfer of excitation energy in CDs. This would allow the design of surface groups or surface compositions of CDs that can direct, sort and respond to excitation energy [10,12–14]. Typically, oxygen is one of main compositions in CDs and its content ranges from 5 to 50% depending on the synthetic route [2]. These O-containing groups in CDs not only create the surface electronic states, but also they are generally interacted with the heteroatoms introduced to modulate surface energy traps of CDs [11,12,15,16]. The –OH group likely makes for surface trap stabilization while the C=O group could facilitate the transfer of excitation energy [16–18]. The same function with C=O group has also been observed from chlorine-containing group [19,20]. Because of high electronic affinity of the N atom, the main roles of amino groups are played in promoting radiative recombination of electrons and holes trapped on the surface of CDs [21]. Moreover, it was demonstrated that this amine-induced surface states could be reinforced dramatically by the co-doped sulfur atoms, leading to higher recombination efficiency

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and the reduction of recombination ways [22–24]. As compared with nitrogen, the phosphorus atom has a larger atomic radius and higher donor ability. Although the P-doped CDs and P,N co-doped CDs were also synthesized by phosphoric acid as P source and applied in bioimaging [25–27], the function of P and other heteroatoms in CDs remains confusing as the photocatalyst. In this work, we firstly prepared Cl- and P-functionalized CDs (Cl,P-CDs) by a facile approach and found the effects of Cl- and P-groups on photoinduced charge transfer and separation in CDs, inducing the enhanced photocatalytic activities.

## 2. Experimental section

Typically, 400 mg phosphorus pentachloride was slowly added in 20 mL ethylene glycol in a glass vial under strong agitation using a bath sonicator at room temperature. Then the obtained mixture was transferred to a poly(tetrafluoroethylene)-lined autoclave (50 mL) and heated 200 °C for 5 h (Fig. S1). The dark brown suspension containing Cl,P-CDs was obtained after naturally cooling to room temperature. This brown solution was neutralized by the addition of NaOH and was then dialyzed to remove the excess salts and reagents. The solid powders of Cl,P-CDs were obtained by freeze drying for the measurement of photocatalytic activity. The other experimental measurements and material characterizations can be seen in [Supporting Information](#).

## 3. Results and discussion

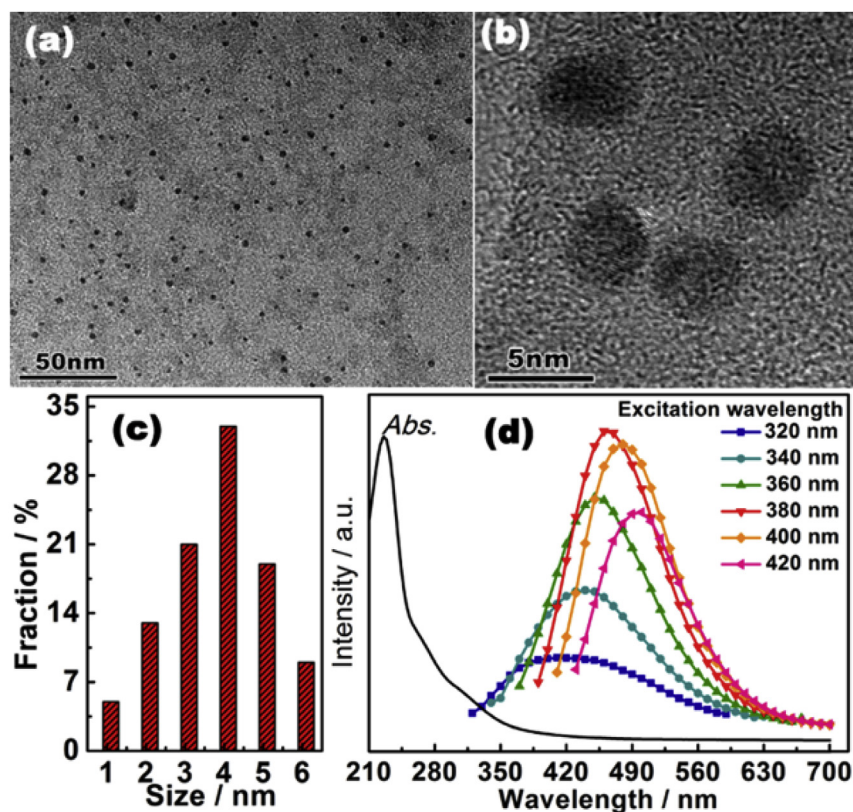
### 3.1. Structure, size and optical properties

To investigate the intrinsic crystal structure of Cl,P-CDs,

transmission electron microscopy (TEM) was performed. TEM image shows that Cl,P-CDs are dispersed uniformly on TEM grid (Fig. 1a) and assume a round shape with diameters ranging from 1 to 6 nm (Fig. 1c). The high-resolution TEM (HRTEM) observation in Fig. 1b reveals the low crystallinity of the Cl,P-CDs. The incomplete crystallization structure are commonly observed in Cl,P-CDs. Fig. 1d presents the UV–vis absorption and PL spectra of the Cl,P-CDs. Analogous to previous reports, Cl,P-CDs typically show strong optical absorption in the UV region, with a tail extending out into the visible range. The peak at about 220 nm is ascribed to  $\pi-\pi^*$  transition of aromatic C=C bonds; the shoulder at about 310 nm is assigned to  $n-\pi^*$  transition of C=O bonds [19]. The Cl,P-CDs exhibit excitation-dependent PL behaviors, which are common in fluorescent carbon nanomaterials [2]. They have optimal excitation and emission wavelength at 380 nm and 470 nm, respectively. The radiative recombination of surface-confined electron and hole is an increasingly adopted emission mechanism for CDs [3,12]. Structure defects at the surface could offer a platform for confining excitation energy [3,28], whereas energy gaps variation of the surface energy traps should be closely associated with the surface chemistry [7,12,28]. As a result, multi-PL emission sites are generated with the changes of surface characteristics and they could be responsible for excitation-dependent PL behaviors of Cl,P-CDs.

### 3.2. Compositions

The elemental analysis by energy dispersive X-ray (EDX) spectroscopy shows that the Cl,P-CDs are composed of C 82.36 wt%, O 11.75 wt%, Cl 2.11 wt% and P 3.78 wt% (Fig. 2a), in which the observed Cu element is from the TEM copper grid. To further investigate the elemental compositions and Cl, P bonding modes in



**Fig. 1.** TEM (a) and HRTEM (b) images of Cl,P-CDs, size distribution (c) and UV–vis absorption and PL spectra (d) of Cl,P-CDs excited at the different wavelength. (A color version of this figure can be viewed online.)

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