

Photoluminescent Carbogenic Dots

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Photoluminescent carbogenic nanoparticles (or “carbon” dots) represent an exciting new class of oxygen-containing carbonaceous emitters that adds another dimension to the versatile properties of carbon-based materials. Carbon dots are discrete nanoparticles of near spherical geometry with sizes below 10 nm, and they inherently fluoresce in the visible upon light excitation. Their isotropic shape along with their ultrafine dimensions and ease of synthesis provide a new platform for nanocarbon emitters as an alternative to fullerenes or carbon nanotubes.¹

The carbon dots may be classified as dispersed or supported. Dispersed carbon dots comprised of surface functionalized nanoparticles have been obtained either by physical means^{2–5} (e.g., laser ablation of graphite, electrochemical soaking of carbon nanotubes, or vapor deposition of soot) and subsequent chemical treatment (e.g., oxidation and functionalization, i.e., a multistep process) or more recently through thermal oxidation of suitable molecular precursors (i.e., a one-step process).⁶ This latter chemical approach is quite attractive because (i) it directly leads to oxygen-containing functionalized carbon dots with precisely engineered surface properties and (ii) by careful selection of the carbon source and surface modifier a better control of size, shape, and physical properties is possible.⁶ For instance, surface functionalized carbogenic nanoparticles were previ-

ously synthesized in a one-step thermal oxidation using different citrate salts, where the citrate unit served as the source of carbon while a compensating organic ammonium provided the covalently attached surface modifier. We refer to these particles as carbogenic because of their oxygen content. Depending on the counterion of the citrate salt, organophilic or hydrophilic derivatives could be derived. Examples of supported dots include carbon-based nanoparticles entrapped in sol–gel derived silica. They are produced via carbonization of preloaded organic precursors.⁷

Here we report the chemical synthesis and photoluminescence properties of new dispersed as well as supported carbogenic dots. Specifically, we first demonstrate new ionically charged carbon dots by extending the citrate method⁶ we described previously. Second, we describe the synthesis of supported carbon dots using thermal oxidation of an appropriately ion-exchanged NaY zeolite. The second method results in near spherical carbogenic nanoparticles grafted onto the external surfaces of the zeolite, the latter retaining its structural integrity and exchange properties. As such, these hybrids combine the unique properties of zeolites with the photoluminescence of the supported carbon dots thus presenting a simple and inexpensive alternative to zeolite–carbon nanotube hybrid emitters.⁸ In addition, since the host is based on a functional microporous solid, the present system is entirely different than the previously reported photoluminescent carbon/silica composites.⁷

Briefly (see more experimental details in Supporting Information), the precursor to the dispersed carbon dots is obtained by protonating the amine groups of sodium 11-amino-undecanoate [$\text{H}_2\text{N}-(\text{CH}_2)_{10}\text{COO}^-\text{Na}^+$] with citric acid [$\text{HOOCCH}_2\text{-C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$] to form the corresponding ammonium carboxylate salt ($-\text{NH}_3^+\text{OOC}-$). The molecular precursor incorporates both functionalities of the resulting carbon dots: the citrate provides the source for the carbonaceous core while the amino carboxylate serves as the surface modifier of the nanoparticles. Thermal oxidation of the citrate salt at 300 °C in air results in ionically modified carbogenic nanoparticles with a nominal composition $(\text{C}_{3.3}\text{O}_3\text{H}_4)\text{HN}(\text{CH}_2)_{10}\text{COONa}$. The amide linkages ($-\text{NHCO}-$) from the thermal dehydration of $-\text{NH}_3^+\text{OOC}-$ tether the undecanoate corona covalently to the surface of the citrate-derived carbogenic core.⁶ The nanoparticles, henceforth denoted as C-SALT, exhibit a high concentration of pending carboxylate groups with sodium counterions balancing their charge (Scheme 1). These features offer the resulting nanoparticles ionic character and hence dispersability in water producing stable, deep brown colloidal sols (Scheme 1). C-SALT precipitates in acidic pH but reversibly redisperses in an alkaline environment. Ion-exchange with cationic species (multivalent inorganic ions, dyes, surfactants, and polyelectrolytes) instantly leads to a precipitate. Characteristically, exchange of Na^+ for cetyltrimethylammo-

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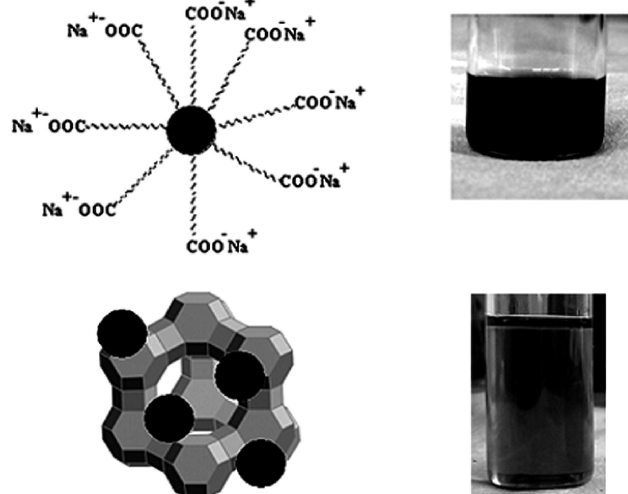
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Scheme 1. Representative Schematics of the Carbogenic Dots^a



^a The pictures on the right depict in grayscale a colloidal dispersion of C-SALT in water and an ultrafine suspension of surface-treated C-ZEO in toluene.

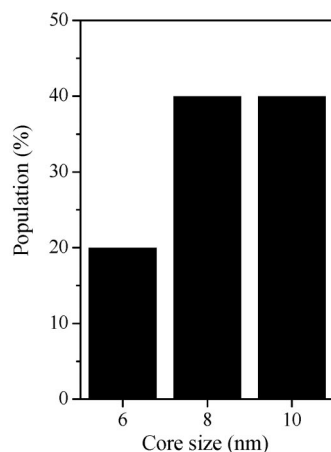
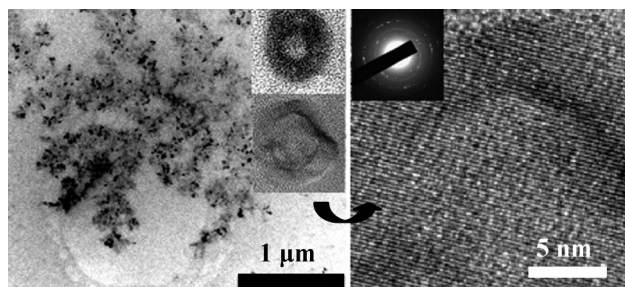


Figure 1. Top: TEM (left) and HR-TEM (right) images for C-SALT. The corresponding insets show individual core-shell dots and the SAED pattern of the crystalline core. The HR-TEM image comes from the analysis of the inset particle shown with the arrow. Bottom: core size histogram for C-SALT.

nium [C₁₆H₃₃N(CH₃)₃⁺] results in an organophilic derivative that is dispersible in tetrahydrofuran.

TEM imaging of C-SALT illustrates near spherical nanoparticles with a core-shell structure (Figure 1). The light interior is evidently the carbogenic core while the surrounding ionic shell exhibits the darker contrast. The total size of the dots ranges from 10 to 20 nm while that of the cores is

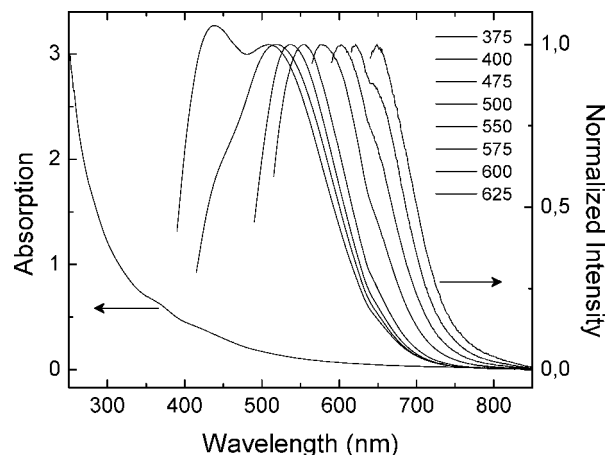


Figure 2. Absorption and normalized fluorescence spectra of C-SALT in water at different excitation wavelengths.

between 5 and 10 nm. Generally, the citrate method leads to core sizes less than 10 nm with a rather inhomogeneous size distribution⁶ (Figure 1). The core is crystalline consisting of parallel crystal planes³ as demonstrated by HR-TEM analysis and the corresponding selected-area electron diffraction (SAED) pattern (Figure 1). The lattice spacing of 3.8 Å calculated from HR-TEM is consistent with the (002) lattice spacing of carbon-based materials with turbostratic disorder⁹ and agrees well with the XRD pattern of C-SALT, which shows a weak reflection centered at $d_{002} = 4$ Å (Figure S1 in Supporting Information). Attempts to obtain Raman spectra were unsuccessful due to the high fluorescence of the nanoparticles. On the basis of these results, we suggest that the cores consist of carbonized intermediates with a highly defected structure of coexisting aromatic and aliphatic regions, similar to graphite oxide¹⁰ or the interrelated carbogenic networks of lignite, coal, and humic substances.¹¹ Regarding the shell around the core, FT-IR spectroscopy (Figure S1, Supporting Information) shows strong absorptions from the tethered undecanoate ligand (–CH₂–, 2850–3000 cm^{–1} and 1350–1470 cm^{–1}; –COO[–], 1640 and 1560 cm^{–1}) as well as a sharp peak at 1700 cm^{–1} characteristic of amide linkages.⁶

The absorption and emission spectra of a C-SALT solution in water (Figure 2) are comparable to those previously reported for carbogenic dots.^{2–6} The emission band maximum shifts to longer wavelengths as the excitation wavelength increases across the whole visible range suggesting a superposition of different types of fluorescent species (e.g., condensed polyaromatic systems). The fluorescence quantum yield measured against an aqueous solution of quinine sulfate and an ethanol solution of anthracene ($\lambda_{\text{exc}} = 340$ nm) is about 3%. The photoluminescent behavior of C-SALT is still an open question, given the complexity of the system. It has been previously suggested that the tethered modifier stabilizes the surface of the carbon-based nanoparticles helping to generate energy traps that emit light when stimulated.² These

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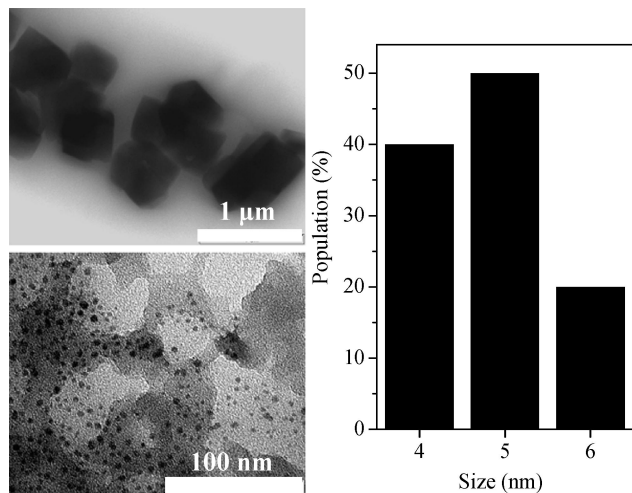


Figure 3. Left: TEM micrographs of C-ZEO (top) and of the carbonogenic nanoparticles obtained after HF etching (bottom). Right: size histogram for the carbonogenic nanoparticles.

energy traps may actually involve free electrons (radicals), based on previous EPR studies.⁶ Besides this mechanism, the pyrolytic formation of several different polyaromatic fluorophores within the carbonogenic core may also explain this optical behavior.^{5,12} For instance, lignite, coal, and humic substances are also known to fluoresce in a wavelength-dependent manner due to the presence of intrinsic polyaromatic fluorophores of different type.¹² A detailed optical study is currently underway.

In the case of the supported dots, thereafter denoted as C-ZEO, NaY zeolite was chosen as the solid host to support the carbonogenic nanoparticles (Scheme 1). The synthesis consists of first ion-exchanging NaY zeolite with 2,4-diaminophenol dihydrochloride followed by thermal oxidation at 300 °C in air, that is, well above the decomposition temperature of the zeolite-hosted organic species (see experimental details in Supporting Information). The exchange takes place mostly near the external surfaces of the zeolitic crystallites and proceeds little within the host structure due to the difficulty of the big cations in accessing the zeolite channels. Accordingly, oxidation results in nanoparticles residing mostly at the external surface of the zeolite matrix. C-ZEO contains 10% (w/w) carbonogenic particles with an average composition $C_{3.3}H_{1.7}NO_{1.1}$ and exhibits the structural and ion-exchange properties of the pristine zeolite as evidenced by XRD and FT-IR measurements (Figure S2 in Supporting Information).¹³

Direct TEM imaging of C-ZEO shows submicrometer zeolite particles, which because of their size and contrast obscure the carbonogenic nanoparticles that might be present (Figure 3). Nevertheless, etching C-ZEO with hydrofluoric acid removes most of the zeolite matrix¹⁴ and enables imaging of the carbonogenic nanoparticles as near spherical entities with a size in the range of 4–6 nm (Figure 3). The carbonogenic nature of the nanoparticles was confirmed by

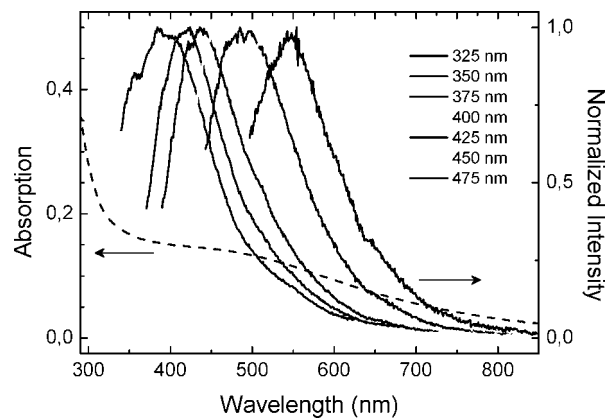


Figure 4. Absorption (dashed line) and normalized emission spectra of the surface-treated C-ZEO in toluene at different excitation wavelengths (solid lines).

XRD and FT-IR (Figure S3 in Supporting Information). More specifically, the XRD pattern displays a sharp, low intensity reflection centered at $d_{002} = 3.3 \text{ \AA}$ that is very close to the graphite 002 lattice spacing,^{3,14} whereas the FT-IR spectrum shows weak, broad absorptions between 1000 and 1700 cm^{-1} (C=C, C=N, C=O, and C—O) due to mild thermal oxidation.¹⁵ Similar bands are also observed for graphite oxide as well as oxidized carbon soot, although more intense due to severe chemical oxidation.^{5,10}

Ion-exchange at the external surface of C-ZEO with the bulk PEGylated ammonium $(CH_3)(C_{18}H_{37})N^+(CH_2CH_2O)_mH-(CH_2CH_2O)_nH$ (Akzo-Nobel, Ethoquad 18/25, $m + n = 15$) leads to a stable, pink-brownish toluene suspension of the supported carbonogenic particles (Scheme 1). Both the absorption and the emission spectra of the surface-treated C-ZEO in toluene exhibit similar luminescent behavior as the dispersed nanoparticles described above (Figure 4). However, the quantum yield measured against an aqueous solution of quinine sulfate and an ethanol solution of anthracene ($\lambda_{exc} = 340 \text{ nm}$) is only about 0.1%.

In summary, we report the chemical synthesis and photoluminescence properties of a new series of dispersed or supported carbonogenic nanoparticles. In the first case, ionic nanoparticles are obtained by thermal oxidation of an appropriate citrate salt. In the second, carbonogenic nanoparticles decorate the external surfaces of zeolite crystals and are obtained by thermal oxidation of a preexchanged zeolite host.

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Supporting Information Available: Detailed experimental procedures and instrumentation, XRD and FT-IR profiles of C-SALT, XRD and FT-IR profiles of C-ZEO in comparison with the pristine NaY zeolite, and XRD and FT-IR profiles of the carbonogenic nanoparticles obtained after etching C-ZEO with HF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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