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Reversible Phase Transfer of Carbon Dots between Organics and Aqueous Solution Triggered by CO₂

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Abstract: Carbon dots (CDs) have attracted increasing attention in applications such as bio-imaging, sensors, catalysis, and drug delivery. However, unlike metallic and semiconductor nanoparticles, the transfer of CDs between polar and non-polar phases is little understood. In this work, a novel class of amine-terminated CDs is developed and their phase transfer behaviour has been investigated. It is found that these CDs can reversibly transfer between aqueous and organic solvents by alternatively bubbling and removal of CO₂ at atmospheric pressure. The mechanism of such CO₂-switched phase transfer involves reversible acid-base reaction of amine-terminated CDs with CO₂ and the reversible formation of hydrophilic ammonium salts. By using the CDs as catalysts, the phase transfer protocol is applied in Knoevenagel reaction for efficient homogeneous reaction, heterogeneous separation, and recycling of the catalysts.

Nanoparticles (NPs) have attracted tremendous attention in many applications such as catalysis,^[1] electronics,^[2] and energy conversion^[3] because of their size- and shape-dependent physical and chemical properties. Usually, some NPs can be well dispersed and used in organics but not in water, while some others can be well dispersed and used in water but not in organic solvents. Thus, transfer of NPs from a polar solvent to a non-polar one (or vice versa) is generally required to maximize the advantages provided by their environments. This makes phase transfer an important aspect in the synthesis, functionalization and application of NPs.^[4]

In this context, a number of excellent works have been reported on the phase transfer of NPs triggered by different stimuli-responses such as ionic strength,^[5] temperature,^[5d,6] pH,^[7] light,^[8] and ligand exchange.^[9] For example, Wang et al.^[5] carried out outstanding work on the transfer of polymer brush-grafted gold NPs from salty water to toluene by altering ionic strength to develop a fundamental understanding of the behavior of inorganic NPs at water-oil interfaces. Zhao et al.^[6a,b,c] reported the transfer of polymer brush-grafted silica NPs between water and oil (ethyl acetate/octane/ionic liquid) driven by temperature, and its application in the development of new phase transfer catalysts. Yang and co-workers^[7a] developed a novel mesoporous silica nanocomposite shuttle, which could reversibly transfer between water and ether (or ethyl acetate) in response to the pH, and be used as a carrier for separation and recycling

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 Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190 (P. R. China) of Pd nanoparticle catalyst. Peng et al.^[8a] proposed a reversible phase transfer approach for α -cyclodextrin-capped gold nanoparticles between aqueous and toluene phases switched by UV and visible light, and the NPs could be applied to catalyze the reduction of 4-nitrophenol. Dorokhin et al.^[9a] demonstrated that in the presence of naphthalene and adamantine derivatives, ferrocene-modified CdSe/ZnS quantum dots could move back and forth between aqueous and chloroform phases by controlling host-guest complexation between ferrocene units and cavity of β -cyclodextrin.

Due to the low-cost, biocompatibility, photostability and facile functionalization, carbon dots (CDs) have emerged as a new class of carbon-based nanomaterials, and widely used in bioimaging, sensors, catalysis, drug delivery and so on.^[10-13] However, to the best of our knowledge, no reversible phase transfer has been reported for CDs to date. Therefore, it is of great significance to develop efficient strategies for the reversible phase transfer of CDs in order to realize the full potential of these NPs.

CO₂ is inexpensive, nontoxic, and easily removable, thus it can serve as a useful trigger for process switching,^[14] but little is known for CO₂-switchable phase transfer of nanoparticles even for metallic and semiconductor nanoparticles. Herein, we developed a novel class of amine-terminated CDs. It was found that these CDs were well dispersed in organic solvents. Interestingly, they could transfer to water by CO₂ bubbling at room temperature and atmospheric pressure. Importantly, they could return to organic phase by removing CO₂ at 60 °C with N₂ bubbling. Thus, the amine-terminated CDs could reversibly transfer between aqueous and organic solvents by alternatively bubbling and removal of CO2. The mechanism of the CO2switchable reversible phase transfer was investigated by the measurements of interfacial tension, water contact angle and ¹³C NMR spectroscopy. Based on the unique phase-transfer behavior of the functionalized CDs, a highly efficient Knoevenagel reaction, product separation and catalyst recycling were achieved where the CDs were used as catalysts.

The amine-terminated CDs were prepared by pyrolysis of the mixture of citric acid and amines in 1-octanol at 180 °C (Scheme 1 and S1), and the detailed procedures were described in the Supporting Information. In order to examine the effect of the structure of amines on the catalytic activity of CDs, the amines used here consisted of primary amine-terminated diamines 1,4diaminobutane (DAB), 1,6-diaminohexane (DAH) and 1,8diaminooctane (DAO), secondary amine-terminated diamines 1ethyl-1,4-diaminobutane (EDAB), 1-ethyl-1,6-diaminohexane (EDAH) and 1-ethyl-1,8-diaminooctane (EDAO), and ternary diamines N,N-diethyl-1,4-diaminobutane amine-terminated (DEDAB), N,N-diethyl-1,6-diaminohexane (DEDAH) and N,Ndiethyl-1,8-diaminooctane (DEDAO). The structure and morphology of the as-prepared CDs were characterized by Ultraviolet-visible (UV-Vis) absorption spectrum, FT-IR spectra, fluorescence (FL) spectra, thermogravimetric analysis (TGA), Xray photoelectron spectroscopy (XPS), and transmission

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electron microscopy (TEM).



Scheme 1. Schematic diagram for the preparation of the primary amine-terminated CDs.

Taking DAB-CD as an example, its UV-Vis absorption peaks appeared at 206, 240 and 301 nm (Figure S1), respectively. The peak at 206 nm might be assigned to π - π * transition of the unsaturated conjugated nanocarbon structure, and the peak at 301 nm could be ascribed to the n- π^* transition of the C=O bond, while the absorption peak at 240 nm would be due to the conjugation between the CD and DAB,^[15-16] which indicates the formation of nitrogen-doped CDs. In the fluorescence spectrum of DAB-CD, the optimal excitation and emission wavelengths at 397 nm and 458 nm were visible (Figure S1), and the CD showed a strong blue fluorescence under the irradiation of UV lamp at 365 nm. Excitation-dependent photoluminescence (PL) behavior was observed for DAB-CD (see Figure S2), which is common in fluorescent carbon materials.^[16] In the FTIR spectrum of DAB-CD, the bending vibration of N-H at 1542 cm⁻¹ and the vibrational absorption band of C=O at 1641 cm⁻¹ (Figure S3) confirmed the formation of amido bond on the surface of the amine-terminated CDs.^[17] Furthermore, TGA was also performed for the amine terminated-CDs (see Figures S4 and S5), and the content of the amine-terminated CDs was given in Table S1.

XPS spectrum confirmed that the surface of DAB-CD was composed of carbon, nitrogen and oxygen elements (Figure 1a). The content of each element was given in Table S1. The fine structure spectrum of C_{1s} exhibited three main peaks at 284.4, 285.2 and 287.7 eV (inset of Figure 1a), which were attributed to graphitic (or aliphatic), nitrous, and oxygenated carbon atoms, respectively.^[15] Based on the data of TGA and XPS, the density of surface amine groups on the resulting carbon dots was calculated, which was in the range from 2.79 to 4.06 mmol/g (Table S1).

It can be seen from TEM images of DAB-CD, well-dispersed spherical nanoparticles with average particle diameter of 5.5 nm were formed (Figure 1b), and most particles had a crystalline structure composed of parallel crystal planes with the lattice spacing of 0.20-0.22 nm (inset of Figure 1b), which are very close to the (100) diffraction planes of graphite.^[16] It was also found that the difference in alkyl chain length of amines had little effect on the structure and morphology of the amine-terminated CDs (see Figures S5-S9). Similar results were also found for secondary amine- and tertiary amine-terminated CDs (Figures S10-S15).

The phase transfer of the amine-terminated CDs was examined in aqueous and 1-octanol phases. Taking DAB-CD as a representative example, it was found that in 1-octanol this CD showed a strong blue fluorescence under the irradiation of UV lamp at 365 nm (Figure 2a). Upon bubbling of CO_2 at room





temperature, they were present almost exclusively in the aqueous phase (Figure 2b). When CO_2 was removed by N_2 bubbling at 60 °C, DAB-CD was returned to 1-octanol phase (Figure 2c). The content of DAB-CD in 1-octanol phase was determined quantitatively by PL spectroscopy (see Figure S16), and it was shown that the mass percent of DAB-CD in 1-octanol phase was 91.5% before bubbling CO₂ (Figure 2d), 6.2% after bubbling CO₂ (Figure 2e), and 90.9% after the removal of CO₂ (Figure 2f), respectively. Therefore, the CO₂-switchable phase transfer of the DAB-CD was reversible. Similar reversible phase transfer process was also observed for secondary amine- and tertiary amine-terminated CDs (Figure S17), and the contents of the amine-terminated CDs in 1-octanol phase increased in the order: primary amine-terminated CDs < secondary amineterminated CDs < tertiary amine-terminated CDs. The possible reason is that the steric hindrance of primary amine on the CDs is relatively small compared with that of other branched chain amines, so its ability to form a hydrogen bond with water is stronger than that of secondary and tertiary amines,^[18] which leads to a higher solubility in water and lower solubility in 1octanol. In addition, it was found that the transfer of the amineterminated CDs from 1-octanol to water phases could also be completed by lowering the aqueous phase pH with aqueous HCI (Figure S18). Importantly, benzene, toluene, dichloromethane and chloroform were also found to be effective organic solvents for the reversible phase transfer (Figures S19-S23).



Figure 2. Photographs of the DAB-CD in 1-octanol and water phases taken under a UV lamp before bubbling CO_2 (a), after bubbling CO_2 (b), and after removal of CO_2 (c). The upper layer in the vials is 1-octanol and the lower layer is water. The PL spectra of DAB-CD in 1-octanol and aqueous phases before bubbling CO_2 (d), after bubbling CO_2 (e), and after removal of CO_2 (f). The black curve is PL spectrum of the DAB-CD in 1-octanol phase and the red curve is PL spectrum in aqueous phases.

To understand the mechanism of phase transfer of the amineterminated CDs between organic and aqueous phases, the

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effect of CO₂ bubbling on the interfacial tension of 1octanol/water was determined in the absence of CDs at 25.0 °C (see Supporting Information). It was shown that the change in interfacial tension caused by bubbling of CO₂ was very small, which was not the driving force for the phase transfer of the CDs from 1-octanol to water. In addition, both temperature and N₂ bubbling were found to have no influence on the phase transfer of the amine-terminated CDs (Figures S24 and S25).

Next, water contact angles of the amine-terminated CDs were measured at 25.0 °C before and after bubbling of CO₂. As an example, the result for the DAB-CD was shown in Figure S26a. It was found that water contact angle of DAB-CD dramatically decreased from 73° to 28° upon bubbling of CO₂, but the value was restored to 72° after CO₂ was removed. Similar trend was observed for the secondary amine- and tertiary amineterminated CDs (Figures S26b and S26c). These data suggest that hydrophilicity of these CDs increased significantly upon exposure to CO₂.^{[7a],[19]} We speculated that the hydrophilicity increase may be ascribed to the acid-base reaction of amines on the surface of CDs with CO₂ and the formation of hydrophilic products in the presence of water.

To confirm this point, ¹³C NMR spectroscopy was used to study the products produced from the acid-base reaction in 1octanol/water biphasic system. As an example, ¹³C NMR spectra of the DAB-CD before and after the reaction with CO2 were shown in Figure 3. A new signal at 160.2 ppm was observed and assigned to HCO3⁻ anion,^[15] which confirms the formation of hydrophilic bicarbonates salts. Furthermore, the new signal at 164.5 ppm could be ascribed to carbonyl group of carbamate.^[14b] Similar results were also found in the ¹³C NMR spectra of the secondary amine-terminated CDs such as EDAB-CD (Figure S27a). For tertiary amine-terminated CDs such as DEDAB-CD, only one new signal was found at 160.2 ppm (Figure S27b), indicating the formation of hydrophilic bicarbonates salts. Thus, for primary amine- and secondary amine-terminated CDs, the ammonium salts were composed of carbamate and bicarbonates salts. However, for tertiary amine-terminated CDs, bicarbonate salt was the only ammonium salt. Therefore, CO2switchable phase transfer mechanism of the amine-terminated CDs involves the acid-base reaction between CO2 and amines of these CDs and the formation of hydrophilic ammonium salts, which resulted in the phase transfer of amine-terminated CDs from organics to aqueous solution.



Figure 3. ^{13}C NMR spectra of DAB-CD before bubbling CO2, after bubbling CO2, and after the removal of CO2

Furthermore, the reversibility of the process was investigated by monitoring ¹³C NMR spectrum of the DAB-CD before and after removal of CO₂. It was shown that the signals at 160.2 and 164.5 ppm disappeared after CO₂ was removed by heating the mixture of DAB-CD-CO₂ at 60 °C for 30min with N₂ bubbling (Figure 3). Moreover, no significant change in fluorescence intensity was observed in 1-octanol within 15 cycles (Figure S28). These results suggest that the reaction between DAB-CD and CO₂ was completely reversible.

Knoevenagel condensation reaction is one of the most important reactions for the C=C bond formation between a C=O group and an activated methylene group, and has been used to synthesize a number of important chemical intermediates, drugs and polymers.^[20] As a proof of concept, our amine-terminated CDs were used in the Knoevenagel reactions to demonstrate the coupling of homogeneous catalysis, heterogeneous separation and recycling of the CD catalysts. As shown in Figure 4, under the catalysis of the CDs, the reaction for the preparation of 2-(4bromobenzylidene)malononitrile proceeded well in 1-octanol at 45 °C, and the product was precipitated from the reaction system and suspended in the organic phase. Then, the CDs could be transferred to water phase upon CO₂ bubbling. After that, the product was filtered out from the organic phase. Once new reactants were added in the organic phase and CO₂ was removed by N₂ bubbling, the same reaction happened again.





As а representative example, the product 2-(4bromobenzylidene)malononitrile produced under the catalysis of DAB-CD was identified by ¹H NMR spectroscopy (see Figure S29), and the yield was 95.2%. After six recycles, its yield still reached to 93.7% (Figure S30). In addition, it was found that the yield for the same reaction catalyzed by different CDs decreased in the order: primary amine CDs (95.2%) > secondary amine CDs (81.1%) > tertiary amine CDs (75.3%). This suggests that the amine-terminated CDs with stronger basicity exhibited higher catalytic activities in Knoevenagel reactions.^[21] To extend the substrate scope, several benzaldehyde derivatives were used to react with malononitrile under the same conditions. Except 4fluorobenzaldehyde, medium (71.5%) to excellent (95.0%) yields were obtained (Table S2, entries 1-6 and 8, and Figures S31-S36). Compared to other carbon nanomaterials,^[22] the amineterminated CDs exhibited superior catalytic activities for the Knoevenagel reaction. The resulting products could be easily separated from the reaction mixture by filtration, and the CDs could be readily recovered and recycled.

In summary, we have prepared a novel class of amineterminated CDs by the pyrolysis of the mixture of citric acid and

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amines. These CDs could reversibly transfer between water and organic solvents by alternatively bubbling and removal of CO_2 at atmospheric pressure. Investigation of ¹³C NMR spectra suggested that reversible acid-base reaction of the amine-terminated CDs with CO_2 and the reversible formation of hydrophilic ammonium salts were the driving force for such a reversible phase transfer. By utilizing the novel property of these CDs, a highly efficient Knoevenagel reaction in organic phase and catalyst separation in aqueous phase were achieved. Additionally, the amine-terminated CDs could be reused for at least six runs without any significant impact on the yield of the products. These findings provide new insight into understanding of the unique phase behavior of CDs, and are expected to motivate their synthesis and applications in different polarities of media.

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Keywords: reversible phase transfer • carbon dots • carbon dioxide • condensation reaction • homogeneous catalysis

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A novel class of amine-terminated CDs was shown to reversibly transfer between aqueous and organic solvents switched by CO₂ at atmospheric pressure, and this unique property was used to demonstrate effective homogeneous catalysis, heterogeneous separation and recycling of the catalysts.

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