Carbon dots in zeolites: A new class of thermally activated delayed fluorescence materials with ultralong lifetimes

Jiancong Liu, Ning Wang, Yue Yu, Yan Yan, Hongyue Zhang, Jiyang Li, Jihong Yu

Thermally activated delayed fluorescence (TADF) materials are inspiring intensive research in optoelectronics. To date, most of the TADF materials are limited to metal-organic complexes and organic molecules with lifetimes of several microseconds/milliseconds that are sensitive to oxygen. We report a general “dots-in-zeolites” strategy to generate high-efficiency TADF materials with ultralong lifetimes. The resultant CDs@zeolite composites exhibit high quantum yields up to 52.14% and ultralong lifetimes up to 350 ms at ambient temperature and atmosphere. This intriguing TADF phenomenon is due to the fact that nanoconfined space of zeolites can efficiently stabilize the triplet excited states of CDs, thus enabling the reverse intersystem crossing process for TADF. Meanwhile, zeolite frameworks can also hinder oxygen quenching to present TADF behavior at air atmosphere. This design concept introduces a new perspective to develop materials with unique TADF performance and various novel delayed fluorescence-based applications.

INTRODUCTION

Materials with long-lived excited states, such as phosphorescence or thermally activated delayed fluorescence (TADF) materials, have aroused considerable interest for their important applications in optoelectronics, photocatalytic reactions, molecular imaging, and security aspects (1–4). In particular, the TADF materials have the ability to harvest triplet excited states for the highly efficient reverse intersystem crossing (RISC) from triplet (T1) to singlet (S1) excited states, thus exhibiting high quantum efficiency and unique optoelectronic properties (5–8). These materials are finding great use in organic light-emitting diodes (OLED) and sensors (9–11). To date, most of the reported TADF materials are based on metal-organic complexes [for example, Cu(I), Ag(I), and Au(I) complexes (12)] and organic molecules [for example, organic donor-acceptor molecules (13, 14) and fullerenes (15)] with lifetimes limited in the range of several microseconds to several milliseconds (16–19). Moreover, most of them display TADF behaviors in the absence of oxygen because oxygen is a strong quencher of the triplet state emission (20). New TADF materials with ultralong lifetimes at ambient conditions are highly desired to promote the multifunctional applications of TADF materials. Because triplet excitons are easily deactivated by nonradiative decay processes derived from the vibration and rotation of emitters and host molecules, energy transfer to other molecules, or triplet-triplet annihilation of emitters, to effectively suppress the nonradiative decay processes is crucial to achieve the long-lived excited states for TADF materials.

In recent years, carbon dots (CDs) as new emerging luminescent nanomaterials have received extensive attraction because of their low toxicity, biocompatibility, photostability, and optoelectronic and photocatalytic properties (21–24). Notably, a new kind of room temperature phosphorescent material has been prepared by incorporating CDs into the matrices of polyvinyl alcohol (25, 26), potash alum (27), and polyurethane (28). The matrices can restrict the intramolecular vibrations and rotations of the functional groups on CDs, thus stabilizing the triplet excited states. Note that the TADF emission with a slow decay lifetime of 676 to 810 ns can be observed in water-soluble CDs from 100 to 250 K in which the frozen solution acts as a rigid matrix to suppress the nonradiative relaxation of CDs and thus promotes the TADF behavior (29). Finding a more suitable host matrix with a strong ability to harvest triplet excited states and generating a new class of CD-based materials having unique TADF properties at ambient conditions would be of great interest. Ordered nanoporous materials with well-confined spaces, especially zeolites with high thermal and chemical stability, are ideal candidates to incorporate functional guests (30–35). Generally, the direct in situ incorporation of photoluminescent materials into inorganic porous materials requires a strong driving force for the assembly of guest luminescent species and host inorganic frameworks (36–38). Fortunately, the hydrothermal or solvothermal synthetic conditions for zeolites are suitable for CDs, in which the organic amines and solvents can provide the raw materials for the formation of CDs (39). Therefore, in situ incorporation of CDs into zeolite crystals under hydrothermal or solvothermal conditions to produce CDs@zeolite composites is highly possible.

Here, a facile and general strategy has been developed to synthesize a new class of CD-based TADF materials with ultralong lifetimes by in situ embedding CDs within a series of zeolitic crystalline matrices under solvothermal/hydrothermal conditions (Fig. 1). The CDs@zeolite composites with high quantum yields (QYs) up to 52.14% and ultralong TADF lifetimes up to 350 ms at ambient temperature and atmosphere have been successfully prepared. By varying the synthetic conditions of zeolites are demonstrated an in situ method to prepare CDs@zeolite TADF materials requiring a strong driving force for the coassembly of guest luminescent species and host inorganic frameworks (36–38). Fortunately, the hydrothermal or solvothermal synthetic conditions for zeolites are suitable for CDs, in which the organic amines and solvents can provide the raw materials for the formation of CDs (39). Therefore, in situ incorporation of CDs into zeolite crystals under hydrothermal or solvothermal conditions to produce CDs@zeolite composites is highly possible.

RESULTS AND DISCUSSION

Synthesis of CDs@zeolite composites

Taking aluminophosphate zeolite AlPO-5 (AFI) as an example, we have demonstrated an in situ method to prepare CDs@zeolite TADF materials...
Fig. 1. Proposed in situ formation process of photoluminescent CDs@AlPO-5 composite. The reaction mixture is composed of inorganic precursors and organic species. Under the solvothermal condition, the formation of CDs is accompanied with the crystallization of zeolite, and the CDs can be in situ embedded and confined in the zeolite matrix during the crystal growth, resulting in photoluminescent CDs@zeolite composite.

Fig. 2. SEM and TEM images and photoluminescence properties of CDs@zeolite composites. (A) Scanning electron microscopy (SEM) image of CDs@AlPO-5 composite (inset, the inorganic framework and the SDA). (B) TEM image of CDs@AlPO-5 composite showing CDs embedded in the inorganic matrix (inset, HRTEM image of a typical CD with a lattice spacing of 0.21 nm). (C) Excitation-emission two-dimensional plot of CDs@AlPO-5 composite. Emission intensity rises with the color changing from blue to green and to red. (D) Fluorescence microscopy images of CDs@AlPO-5 with ultraviolet (UV), blue, and green light excitation. (E to L) The SEM, TEM, HRTEM images, excitation-emission two-dimensional plots, and fluorescence microscopy images with UV, blue, and green light excitation of CDs@2D-AlPO and CDs@MgAPO-5, respectively.
under solvothermal/hydrothermal conditions. The CDs@AlPO-5 composite was solvothermally synthesized by using triethylamine (TEA) as the SDA in the reaction system of Al(O\textsubscript{iPr})\textsubscript{3}-H\textsubscript{3}PO\textsubscript{4}-TEA-HF-triethylene glycol (TEG) at 180°C for 3 days. The as-synthesized CDs@AlPO-5 crystals display hexagonal prism–like morphology (Fig. 2A), and their powder x-ray diffraction (PXRD) pattern reveals the characteristic diffraction peak of the AFI structure (fig. S1A). Liquid chromatography–high-resolution mass spectrometry (LC-HRMS) of the dissolved sample confirms the existence of TEA in the CDs@AlPO-5 composite (fig. S2). The transmission electron microscopy (TEM) image shows that uniform and monodispersed CDs are embedded in the AlPO-5 crystals with an average particle diameter of 3.7 nm (Fig. 2B and fig. S3A). Meanwhile, the CDs with a diameter of about 3.8 nm can also be observed in the synthetic mother liquid of CDs@AlPO-5 (fig. S4, A and B). The high-resolution TEM (HRTEM) image reveals a well-resolved lattice spacing of 0.21 nm, which is close to the (100) facet of graphite (27).

CDs@2D-AlPO composite was synthesized by using 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) as the SDA in the solvothermal synthetic system of Al(O\textsubscript{iPr})\textsubscript{3}-H\textsubscript{3}PO\textsubscript{4}-TTDDA-TEG. Single-crystal XRD analysis reveals that the CDs@2D-AlPO has a layered [A\textsubscript{12}P\textsubscript{3}O\textsubscript{12}H\textsubscript{2}]\textsuperscript{2-} structure, which is isostructural with the framework of aluminophosphate UT-5 synthesized by using cyclohexylammonium as the SDA (40). Protonated TTDDA molecules are located in the layered structure (see Materials and Methods for more details on the synthesis and structure determination; the crystallographic tables, atomic coordinates, PXRD pattern, and structure of CDs@2D-AlPO are provided in tables S1 and S2 and figs. S1B and S5). As shown in Fig. 2E, the CDs@2D-AlPO crystals display plate-like morphology. TEM and HRTEM images show that the CDs with an average diameter of 3.5 nm are embedded in the CDs@2D-AlPO crystals (Fig. 2F and fig. S3B).

By using TTDDA as the SDA, CDs@MgAPO-5 was prepared in the hydrothermal reaction system of Al(O\textsubscript{iPr})\textsubscript{3}-MgHPO\textsubscript{4}-3H\textsubscript{2}O-H\textsubscript{3}PO\textsubscript{4}-TTDDA-H\textsubscript{2}O at 180°C for 3 days. The obtained material has the AFI structure, as confirmed by PXRD study (fig. S1C), and displays polyhedral morphology (Fig. 2I). Well-dispersed CDs with an average particle diameter of 3.4 nm can be clearly observed in the zeolitic crystalline matrix (Fig. 2) and fig. S3C).

These CD-based TADF materials can be successfully prepared by in situ embedding luminescent CDs into zeolites and related open-framework materials in the presence of different organic templates and solvents. The simultaneous formation of CDs and zeolites under the solvothermal/hydrothermal conditions is crucial for the generation of CDs@zeolite composites. In contrast, in the conventional hydrothermal synthesis of AlPO-5 in the system of Al(O\textsubscript{iPr})\textsubscript{3}-H\textsubscript{3}PO\textsubscript{4}-TEA-HF-H\textsubscript{2}O at 180°C, AlPO-5 was crystallized after 3 hours, but no CDs were observed in the mother liquid at the same time. Therefore, the resultant product shows no photoluminescent property.

**Excitation-dependent fluorescence of CDs@zeolite composites**

The as-synthesized CDs@AlPO-5, CDs@2D-AlPO, and CDs@MgAPO-5 composites show the characteristic excitation-dependent fluorescence behavior of CDs (Fig. 2, C, G, and K). The diluted mother liquids of CDs@zeolite also display similar excitation-dependent fluorescence to those of CDs@zeolite composites (fig. S4C). The observed emissions of CDs@zeolite composites can change from blue to green and to red with the prolonging excitation wavelengths (Fig. 2, D, H, and L). Strong deep blue emissions can be observed under a 370-nm excitation with the Commission Internationale de l’Eclairage (CIE) coordinates of (0.17, 0.13), (0.17, 0.14), and (0.17, 0.13) for CDs@AlPO-5, CDs@2D-AlPO,
To understand the origin of TADF behavior, we studied the structure of CDs@AlPO-5 composite by x-ray photoelectron spectroscopy (XPS), UV-visible (UV-vis) absorption spectroscopy, and Fourier transform infrared (FTIR) spectroscopy (fig. S9). On the basis of the XPS analysis, the C–C=C bonds (284.6 eV), C–O=C–N bonds (286.3 eV), C=O/C=N bonds (287.6 eV), and pyridine-like (400.2 eV) and pyrrolic-like N (402.2 eV) atoms can be identified (28). UV-vis absorption spectrum of CDs@AlPO-5 indicates the presence of \( \pi \rightarrow \pi^* \) transition of C=C bonds (263 nm) and \( n \rightarrow \pi^* \) transition of C=O/C=N bonds (350 nm) (25). The FTIR spectrum also shows the presence of C=O/C=N and C=O/C=N bonds (26). The C=O or C=N groups on CDs may facilitate the intrinsic triplet generation through intersystem crossing (43–46). As with CDs@AlPO-5, similar functional groups of CDs can also be found in CDs@2D-AlPO and CDs@MgAPO-5 composites (figs. S10 and S11).

Note that the CDs obtained in diluted mother liquid only show the short-lived fluorescence lifetime (5.1 ns) at room temperature (fig. S12). This suggests that the inorganic frameworks of zeolites play an essential role in stabilizing the long-lived triplet states. In the mother liquid, the excitations of isolated CDs are mainly deactivated through nonradiative routes at room temperature due to the active intramolecular vibrations and rotations. In contrast, the nanosized space in the rigid matrix of zeolites can effectively prevent the nonradiative relaxation by locking the emissive species and inhibiting their intramolecular motions. Note that the size of the CDs is much larger than the micropores in the zeolite structures; the CDs must be confined in the interrupted nanospaces. The interrupted framework of zeolites contains extensive dangling OH groups, which may form complex H-bonding interactions with the surface functional groups of CDs, such as C=N and C=O groups, thus suppressing the nonradiative relaxation of CDs. Meanwhile, the organic SDAs are crucial for the TADF property of CDs@zeolites that can also form H bonds with the functional groups of CDs. When the CDs@AlPO-5 composite was heated at 200°C under vacuum for 5 hours to sublime the organic SDAs, both the TADF lifetime and the QY are decreased. No TADF phenomenon was observed when the composite was vacuum-calcined at 500°C (figs. S13 and S14 and table S4). Therefore, zeolite is not only a desirable host for accommodating CDs to effectively prevent the aggregation of CDs but is also an excellent confinement matrix to harvest triplet excited states.

As for the TADF materials, the energy level is essential for efficient transition and RISC process (\( T_1 \) to \( S_1 \)) stimulated via thermal activities (5, 47). The abovementioned study shows that the as-prepared CDs@zeolite composites have small \( \Delta E_{ST} \) values (0.22 to 0.23 eV), which make it possible for an efficient TADF emission facilitated by the RISC process. The possible mechanism for the formation of these CD-based TADF materials has been proposed in Fig. 4A. Significantly, the CDs@AlPO-5 exhibits ultralong delayed fluorescent lifetime (350 ms), and the delayed fluorescence can be clearly seen by naked eyes. As far as we know, the reported lifetimes of delayed fluorescence are mainly of several microseconds/milliseconds for the TADF materials of metal-organic complexes and organic molecules. The enhanced lifetimes of CDs@zeolite composites may be caused by the highly efficient stabilization of the zeolite framework and organic SDAs to effectively prevent the nonradiative relaxation and result in ultralong TADF behavior. Moreover, the CDs@zeolite TADF composite materials can work in air atmosphere, which is different from most traditional organic TADF materials in which the long-lived decay component would be greatly quenched at the air atmosphere because oxygen is a strong quencher of the triplet state emission. The zeolite matrix is a good oxygen barrier that can effectively hinder the collisions between the functional groups and oxygen molecules.
application as a smart material in dual-mode security protection, it is believed that the CDs@zeolite nanocomposites with long-lived TADF phenomenon can serve as ideal contrast agents for future high-sensitivity bioimaging for efficient avoidance of short-lived background fluorescence. TADF materials with long-lived excited states are also expected to be promising for solar cells because their long-lived excitons are enabled to extend diffusion distances for the efficient generation of free charges, which is a prerequisite for high-performance solar cells (9, 48).

**CONCLUSIONS**

We have successfully demonstrated a facile and general dots-in-zeolites strategy to prepare CD-based TADF materials with ultralong lifetimes by embedding CDs in nanoconfined spaces of zeolitic crystalline matrices. This approach is effective for the in situ incorporation of CDs derived from different organic species into various zeolitic host materials under hydrothermal/solvothermal conditions. The unique TADF property of these materials with ultralong-lived excited states at ambient conditions is benefited from the fact that zeolitic host matrices can effectively stabilize the triplet state by suppressing the nonradiative processes and hindering the oxygen quenching. The as-prepared CDs@zeolite nanocomposites display high QYs and ultralong lifetimes of up to 52.1% and 350 ms, respectively, which affirms their potential applications in security protection and future high-resolution bioimaging application. This method is generally applicable for other luminescent nanomaterials. The considerable flexibility of rational combination of photoluminescent nanodots and a wide range of suitable host matrices with well-confined nanospaces and electrical transport properties (for example, perovskite and TiO2) may facilitate the design of a variety of highly efficient TADF materials for advanced optoelectronic device applications (for example, solar cells and LED). This discovery of a new class of CD-based TADF materials with ultralong lifetimes and high efficiency is developed as a proof of concept, which we believe will promote both fundamental understanding and future practical applications of TADF materials.

**MATERIALS AND METHODS**

**Materials**

All reagents were used without purification. Aluminum isopropoxide (≥98% purity) and TTDDA (97% purity) were obtained from Sigma-Aldrich. H3PO4 (85 weight % (wt %) in water) and hydrogen fluoride (HF; 40 wt % in water) were supplied by the Beijing Chemical Reagent Factory. TEG and MgHPO4·3H2O were obtained from Aladdin Chemical Reagent Co. High-purity water was obtained from Milli-Q purification system. TEA (99% purity) was obtained from Tianjin Fuyu Fine Chemical Co. Ltd.

**Synthesis of CDs@zeolites**

CDs@AlPO-5 was synthesized using TEA as the SDA under solvothermal conditions. In a typical synthesis of CDs@AlPO-5, aluminum isopropoxide was dispersed in a mixture of TEG and H3PO4. Then, TEA and HF were dispersed into the mixture with stirring. A homogeneous gel was formed with an overall molar composition of 1.0 Al2O3:1.3 P2O5:1.6 TEA:1.3 HF:17 TEG. After crystalizing at 180°C for 3 days, the crystalline product was separated, thoroughly washed with distilled water, and dried at room temperature overnight.

CDs@MgAPO-5 and CDs@2D-AlPO were synthesized by using TTDDA as the SDA. In a typical synthesis of CDs@MgAPO-5, aluminum isopropoxide was dispersed in a mixture of water and H3PO4.

Moreover, the as-synthesized CDs@zeolite composites can keep their TADF property for more than half a year at air condition, showing their high stability (fig. S15 and table S5).

**Dual-responsive security protection application**

The advantages of CDs@zeolite TADF materials may open new perspectives for various delayed fluorescence-based applications. Here, we simply demonstrate a promising application of CDs@zeolite composites as a smart material for use in dual-mode security protection, in which traditional photoluminescence acts as one mode of security protection, whereas the visible TADF acts as the other mode with the persistent luminescence after the excitation for the lifetime-encoding feature. As shown in Fig. 4B, the security pattern of a rose is coded with the CDs@2D-AlPO as the flower part and the benzil dye molecule as the leaf and stem parts. Under a 365-nm UV excitation, the flower patterned with CDs@2D-AlPO is blue, and the leaves and stem patterned with benzil dye molecules are green. When switching off the excitation, only the flower represents ultralong delayed fluorescence that can be clearly observed by naked eyes, showing the time-resolved security features.

**Fig. 4. Proposed TADF mechanism of CDs@zeolite composites and dual-responsive security protection application. (A) Left: CDs dispersed in the mother liquid show only the prompt fluorescence (PF) with short-lived lifetime. The triplet state would be quenched by nonradiative processes such as the active intramolecular vibrations (vib) and rotations. Right: The terminal OH groups of the interrupted zeolite framework, along with the occluded organic SDAs may form extensive H bonds with the surface functional groups of CDs to suppress the nonradiative relaxation of CDs derived from intramolecular vibrations and rotations and thus stabilize the triplet excited states. The small ΔE(T) value of the CDs makes it possible for an efficient TADF emission facilitated by the RISC process. P, phosphorescence. (B) The security pattern of a rose is coded with the CDs@2D-AlPO as the flower part and the benzil dye molecule as the leaf and stem parts. Under a 365-nm UV excitation, the flower patterned with CDs@2D-AlPO is blue, and the leaves and stem patterned with benzil dye molecules are green. When switching off the excitation, only the flower represents ultralong delayed fluorescence that can be clearly observed by naked eyes, showing the time-resolved security features.
Then, MgHPO₄·3H₂O and TTDDA were dispersed into the mixture with stirring. A homogeneous gel was formed with an overall molar composition of 1.0 Al₂O₃:0.1 MgO:2.0 P₂O₅:2.1 TTDDA:139 H₂O. After crystallizing at 180°C for 3 days, the crystalline product was separated by washing with distilled water and drying at room temperature overnight. As for the synthesis of CDs@2D-AlPO, aluminum isopropanoxide was dispersed in a mixture of TEG and H₃PO₄. Then, TTDDA was dispersed into the mixture with stirring. A homogeneous gel was formed with an overall molar composition of 1.0 Al₂O₃:1.9 P₂O₅:2.0 TTDDA:18 TEG:3.7 H₂O. After crystallizing at 180°C for 3 days, the plate-like crystalline product was obtained by washing distilled water and drying at room temperature overnight.

The percentages of CDs incorporated in the CDs@zeolite composites were evaluated according to the CHN analysis by comparing the CDs@zeolites with the pure zeolites analog synthesized with the same SDAs. The percentages of CDs calculated on the basis of C content in CDs@AlPO-5 and CDs@2D-AlPO were 0.55 and 0.64 wt %, respectively. However, the percentage of CDs in CDs@MgAPO-5 was difficult to provide because no pure MgAPO-5 could be synthesized by using the same SDA.

### Apparatus and measurements

PXRD data were collected on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5418 Å). The TEM and HRTEM images were taken on an FEI Tecnai G2 S-Twin F20 TEM and FEI Titan G2 60-300 scanning TEM. The infrared absorption spectra were recorded on a Bruker FTIR IFS-66V/S spectrometer in the range of 400 to 4000 cm⁻¹ with KBr pellets. A baseline correction was applied after measurement. UV–vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The XPS measurements were performed using a Thermo ESCALAB 250 spectrometer with monochromatized Al Kα excitation. LC-HRMS was performed on a high-performance liquid chromatography (Agilent 1290) and HRMS (microTOF-Q II, Bruker Daltonics). Thermogravimetric (TG) analysis was performed on a TA Q500 analyzer in air from room temperature to 800°C at 5°C/min. CHN analysis was conducted on a PerkinElmer 2400 elemental analyzer.

### Photoluminescence measurements

Excitation-emission two-dimensional plots, steady-state spectra, and delayed photoluminescence spectra were obtained by using a HORIBA Scientific FluoroMax-4 spectrophluorometer. The fluorescence lifetime spectra were performed with a HORIBA Scientific FluoroMax-4 by using Fluorohub-B fluorescence lifetime system equipped with a photomultiplier tube detector. A nanoLED and a microsecond flash xenon arc lamp were used as the excitation sources. Ludox was used to calculate instrument response factor (IRF). The data were analyzed using DAS6 software using a multiexponential model for lifetime. The average lifetimes (tav) of the measured QY, a tetraphenylethene thin film was used as reference. The measured QY (50.2%) was close to its standard QY of 49.2% (49).

### Supplementary materials

#### REFERENCES AND NOTES


Author contributions: J.Y. supervised and coordinated all aspects of the project. J. Li also coordinated this work. J. Liu carried out synthesis and characterization, interpreted the data, and wrote the paper. N.W. performed the TEM and HRTEM measurements. Y. Yu conducted the dual-mode security protection experiments. Y. Yan solved crystal structures and performed data fitting. H.Z. did part of the experiments and related analyses. J.Y. and J. Li revised the manuscript. All authors discussed and commented on the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: CCDC 1517735 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif). All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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