

Azafullerene-like Nanosized Clusters

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ABSTRACT Carbon nitride materials have extraordinary potential in various applications, including catalysts, filled-particles, and superhard materials. Carbon nitride nanoclusters have been prepared under mild solvothermal conditions by a reaction between 1,3,5-trichlorotriazine and sodium azide in toluene. The bulk material formed has a C₃N₄ composition and consists of spheres with diameters ranging from ~1 nm to 4 μm. Nanometer-sized clusters of C₃N₄ stoichiometry have been isolated on surfaces by sublimation or simple physicochemical methods. The clusters have then been characterized by atomic force microscopy and X-ray photoelectron spectroscopy. The laser desorption ionization mass spectra show peaks assignable to the C₁₂N₁₆, C₂₁N₂₈, and C₃₃N₄₄ molecules which could correspond to cage structures with 4, 7, and 11 units of the C₃N₄ subunit, respectively. The structure and stability of these new nitrogen-rich carbon nitride nanocages has been investigated using density functional theory calculations.

KEYWORDS: azafullerene-like · carbon nitrides · nanomaterials · AFM · XPS · DFT

The study of carbon based nanomaterials has attracted considerable attention since the discovery of fullerenes¹ and carbon nanotubes.² Their chemical synthesis, functionalization, and important physical and chemical properties have been the focus of most studies of the production of new functional materials.³ Other studies have suggested that closely related “hybrid” materials, derived from partial replacement of some carbon atoms by nitrogen, boron, silicon, etc. could also present extremely attractive properties.⁴ In particular, the theoretical predictions of superhard, crystalline, diamond-like carbon nitride materials (β-C₃N₄)^{5,6} have led recent studies focusing on the preparation of these materials.⁷ However, the formation of these superhard 3D materials has not been yet achieved. Most of the *ca.* 1000 studies reported to date have therefore led to the production of bulk carbon nitrides with mainly layered, graphitic-like structures rather than single-phase crystalline C₃N₄ materials.^{8–14} A detailed review of this issue has recently been published.¹⁵ Carbon nitride materials have shown several poten-

tial applications as metal-free catalysts in Friedel–Craft reactions,^{16,17} as a reactant for metal nitride nanoparticle synthesis,¹⁸ and as a photocatalyst for hydrogen production.¹⁹ Very recently a first report on postfunctionalization of as-synthesized carbon nitride solids by simple protonation, the controllable and reversible protonation of a nanostructures solid, g-C₃N₄, has been reported.²⁰ Protonation not only provides better dispersion and a high surface area but also improved performances of the material. Despite the interesting predictions of their physical properties, few works have reported the formation of nanoscale carbon nitride solid nanotubes,^{21–23} nanospheres,^{24–28} and nano-onions.²⁹ In fact, the closed structures reported to date have diameters of between 5 and 20 nm and can be considered nanomaterials rather than molecules. The formation of morphologies other than 2D graphitic-like structures is probably hampered by the greater stability of this structure.

The main challenge in the synthesis of carbon nitride nanostructures is that small carbon nitride clusters are thermodynamically less stable than graphite and nitrogen molecules. However, mild synthetic methods, such as solvothermal synthesis, are able to produce these materials when the appropriate starting reactants are selected.⁷ In a recent work, carbon nitride nanostructures were produced using the arc-discharge technique and analyzed by mass spectrometry.³⁰ Here we report a simple procedure for the preparation and isolation of different C₃N₄ nanocages with diameters of around 1 nm.

RESULTS AND DISCUSSION

Nitrogen-rich carbon nitrides (C_{3n}N_{4n}) were prepared under mild conditions by reacting 1,3,5-trichlorotriazine with sodium azide

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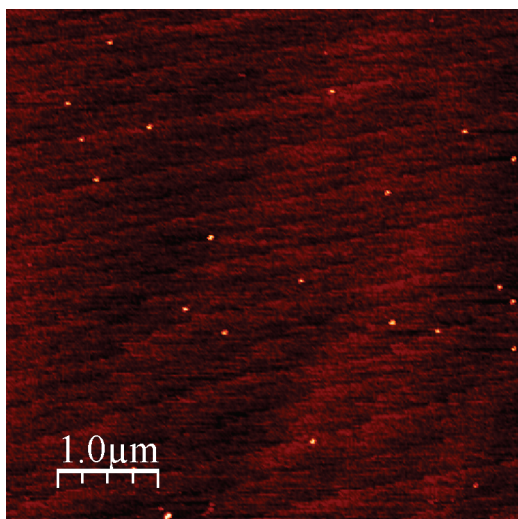


Figure 1. AFM topography image on mica of the adsorbed material separated from the C_3N_4 bulk by sublimation.

in a Teflon-lined stainless reactor at 230 °C and a maximum pressure of ~ 1.2 bar, for 20 h. X-ray photoelectron spectroscopy (XPS) analysis of a compacted pellet of the resulting brown solid obtained showed that the N(1s) core level peak can be resolved in two components. The main component at 399.1 eV is assignable to sp^2 -bonded nitrogen atoms of pyridine origin. The second component, at 400.88 eV, can be assigned to sp^3 -hybridized nitrogen atoms bound to three carbon atoms.^{31,32} The 3:1 ratio, N(sp^2):N(sp^3), observed between the areas of the two nitrogen components is consistent with the C_3N_4 expected composition. The C(1s) peak shows two components: a small one at 284.8 eV which can be assigned to standard *ex-situ* C contamination and the main one at 287.9 eV assignable to C in nitride compounds (Figure S3). The ratio between the intensities of the C/N peaks is 0.78, which is very consistent with a C_3N_4 stoichiometry. Other experimental complementary techniques reinforce the chemical characterization of this material (see Supporting Information). Morphological characterization of the bulk C_3N_4 material by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images reveals (Figure S4) that most of the C_3N_4 bulk material consists of spheres with diameters ranging between a few nanometers and 4 μm .

Despite previous papers already describing spherical morphologies with C_3N_4 composition,^{24–28} closed structures of carbon nitrides with a diameter of less than 5 nm have never been reported. However, the inhomogeneous distribution

in sizes found in our synthesis suggests that smaller spheres could also be present in this material. To confirm such a possibility, we explored two different separation methods based on (i) sublimation and (ii) sonication–centrifugation.

In the first, we sublimated the C_3N_4 bulk material in a high vacuum chamber ($P \approx 10^{-7}$ mbar) at $T \approx 400$ °C in front of a mica surface. Atomic force microscope (AFM) images show uniform nanoparticles deposited on this surface with a height distribution in the 1.0–2.0 nm range (Figure 1). Similar results are observed in the deposition of the toluene suspension obtained by sonication (2 h, 680 W) and centrifugation (10000 rpm, 30 min) of the bulk material (Figure S5). The height of the nanoparticles absorbed by this procedure is consistent with those isolated by sublimation, within the bounds of statistical error. However, the former method enabled morphological characterization by TEM of the solid separated by sonication–centrifugation, confirming the presence of particles as small as *ca.* 1.5 nm (Figure 2). The sonication–centrifugation process gave nanocages (range 1.0–2.0 nm) with a yield close to 18% (see Methods). We performed XPS spectroscopy in order to obtain information on the chemical composition of the carbon nitride nanocages. The XPS data are very similar to those obtained in the bulk material (Figure 3), therefore confirming their composition. The IR spectrum shows the features expected of a typical carbon nitride material (Supporting Information and Figure S6). Sublimation on a gold surface from the bulk material, at different sublimation times (10 and 60 min) and under different adsorption conditions, was also carried out (*ex-situ* and *in situ*; see the Supporting Information for additional data). The XPS analysis unambiguously shows that the deposited material is carbon nitride. Nitrogen and carbon peaks show components at the same binding energies as those observed in the bulk carbon nitride material. However, the carbon peak shows a new component at 289.9 eV. This can be as-

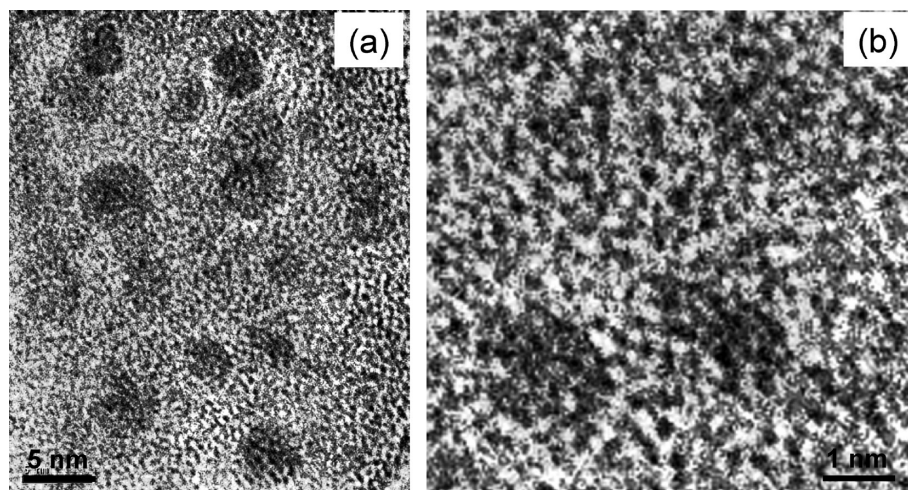


Figure 2. TEM image of carbon nitride nanoparticles with size ranging from *ca.* 1.5 to 4.5 nm (a) and zoomed showing some particles with size close to 1 nm (b).

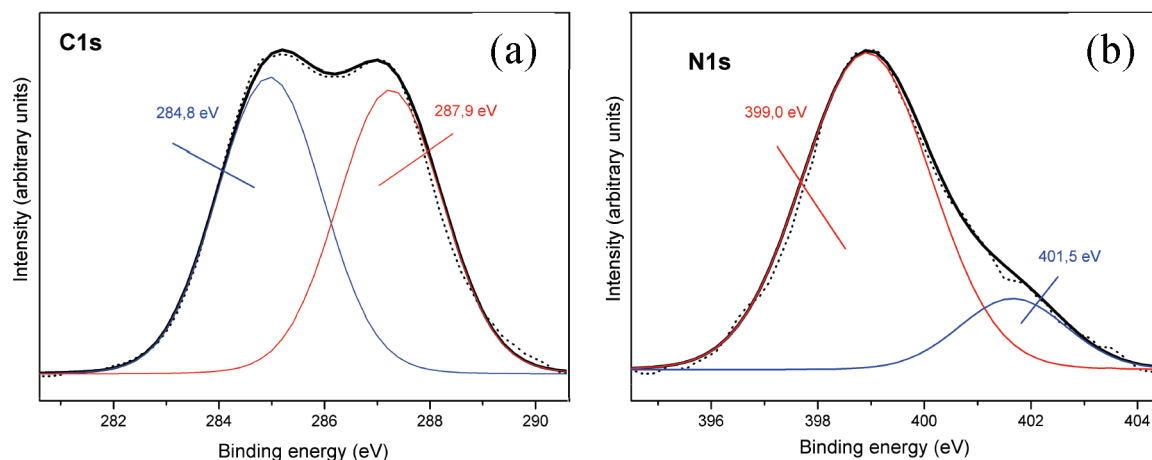


Figure 3. XPS spectrum of the C_3N_4 nanocages isolated by sublimation–centrifugation procedure in the C(1s) (a) and N(1s) (b) regions.

signed to the interaction between the π orbital of the carbons of the triazine rings and the gold surface.³³

Mass spectrometry provided further characterization of the material. The best results were obtained by laser desorption ionization (LDI) in a reflectron time-of-flight (TOF) apparatus. These experimental conditions, like those used in thermal sublimation, favor the observation of small clusters. Typical mass spectra (Figure 4) show characteristic peaks at 368, 644, and 1012 amu, assigned to the ions of $C_{12}N_{16}$, $C_{21}N_{28}$, and $C_{33}N_{44}$ (4, 7, and 11 units of C_3N_4 , respectively). No evidence of any other possible closed structures of $(C_3N_4)_n$ was found under various experimental conditions. In the same mass range of the spectra, a prominent peak was observed at 566 amu ($C_{18}N_{25}$). This probably originated from the fragmentation of $C_{21}N_{28}$ in which a C_3N_3 unit was lost. Other peaks at lower masses that cannot be attributed to closed structures are assigned to fragment ions [C_6N_{10} (212 amu), C_6N_9 (198 amu), C_6N_8 (184 amu), C_6N_7 (170 amu), C_3N_6 (120 amu), C_3N_4 (92 amu), C_3N_3 (78

amu), C_5N (74 amu), CN_2 (40 amu), C_2N (38 amu), and C_2 (24 amu)]. This experiment therefore suggests that the particles isolated on surfaces by sublimation with a height of around 1 nm are probably molecules associated with mass peaks detected by laser desorption ionization mass spectra.

Density functional theory (DFT) calculations were performed using the SIESTA method^{34,35} in order to consider possible structures for the peaks observed in the mass spectra (see Supporting Information). The structures obtained for the neutral clusters were also relaxed with a positive unit charge. All the clusters kept the same structure, showing that they are suitable candidates for the ion peaks observed in the laser desorption mass spectra. To further check the stability of the resulting structures, they were annealed using *ab initio* molecular dynamics³⁶ up to a temperature similar to that anticipated in the laser-desorption experiments (~ 700 K). Their evolution was then monitored at that temperature for up to 5 ps. Some of the structures underwent substantial changes and bond breaking during the heating or the subsequent simulation, but no fragmentation was observed. Figure 5 shows our proposed cluster structures for the observed mass peaks. $C_{33}N_{44}$ (1012 amu) was found to have a formation energy of 0.49 eV/atom and an atom–atom diameter and height of 1.04 and 0.75 nm, respectively. Some of its bonds began to break after 0.3 ps molecular dynamics at ~ 700 K. Two tube-like structures are proposed for $C_{18}N_{25}$ (566 amu) and $C_{21}N_{28}$ (644 amu). They have the same diameter of 0.46 nm, roughly the height of the smallest structure observed by AFM (Figure 1). $C_{21}N_{25}$ (0.70 nm) is the shortest structure and results from eliminating one of the benzoic rings from the $C_{21}N_{28}$ tube (0.81 nm). Their formation energies are similar—0.61 and 0.66 eV/atom—and both suffered bond breaking when heated in molecular dynamics annealing to ~ 350 and ~ 500 K, respectively.

Another cluster, $C_{18}N_{26}$ (580 amu), is shown in Figure 5d. Although it does not exactly match the mass peak ob-

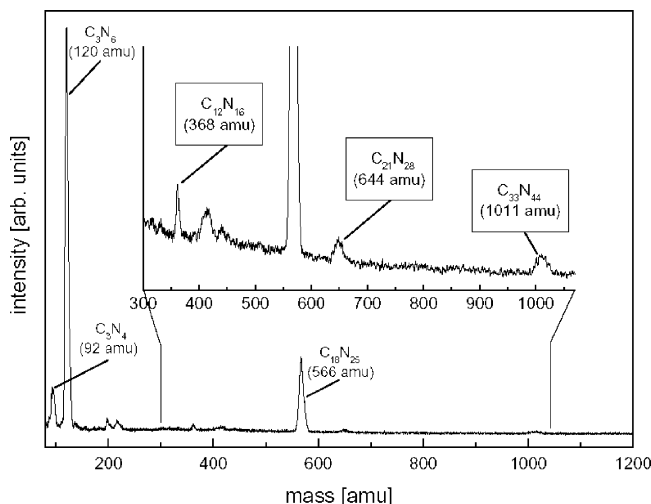


Figure 4. Mass spectrum measured by laser desorption ionization at 355 nm on a reflectron time-of-flight mass spectrometer of a solid sample obtained by sublimation. The insert shows a magnification of the part of the spectrum corresponding to the larger masses.

served at 566 amu ($C_{18}N_{25}$), the difference is close to the TOF resolution. Moreover, it has a very stable structure with a formation energy of 0.52 eV/atom and no signs of bond breaking after a 5 ps simulation at ~ 700 K. It is an oblate spheroid, with a diameter and height of 0.82 and 0.39 nm, respectively. A candidate structure for the observed peak at 368 amu ($C_{12}N_{16}$) is shown in Figure S8. It has a diameter of 0.47 nm. However, that closed structure has a large formation energy of 0.99 eV and it was found to suffer from spontaneous bond breaking (without fragmentation).

AFM images prove the so-called van der Waals diameter of the molecule. For instance, in the case of C_{60} the atom–atom diameter is 0.7 nm while the van der Waals diameter is 1 nm, which is the height observed by AFM. Our cluster sizes should therefore range between 0.8 and 1.4 nm, which are compatible with the sizes observed by AFM.

The calculated formation energies are for graphite and N_2 molecules. As a reference, the formation of the relaxed infinite layer of graphite- C_3N_4 is endothermic by 0.21 eV/atom. Its structure is locally corrugated but globally flat. The formation energies of C_3N_4 clusters are even more positive, as anticipated from curvature effects, so that all of them are only local energy minima. Theoretical structures and properties in heterofullerenes have been reported.^{37,38} Bigger cages³⁹ and nongraphite- C_3N_4 structure⁴⁰ have also been studied.

To conclude, we successfully synthesized and isolated nitrogen-rich carbon nitride molecules by soft

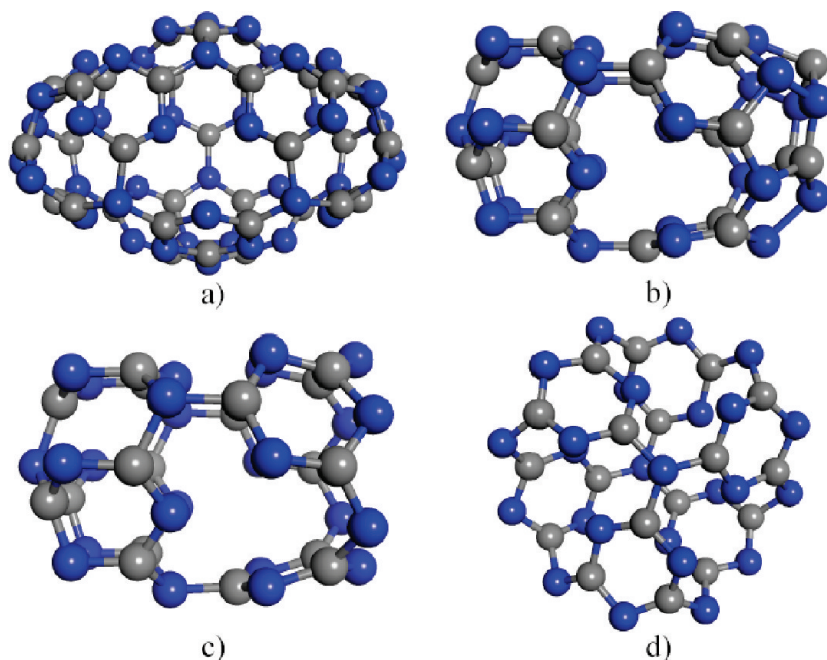


Figure 5. Proposed graphite- C_3N_4 cage-like structures for the peaks observed in mass spectra: (a) $C_{33}N_{44r}$, (b) $C_{21}N_{28r}$, (c) $C_{18}N_{25r}$, (d) $C_{18}N_{26r}$.

solvothermal methods of around 1 nm. The azafullerene-like molecules isolated on surfaces were morphologically characterized by means of AFM and TEM and chemically characterized by XPS. DFT studies suggest cage structures for the new molecules detected by mass spectrometry. Since we have been able to detect as well as isolate several nanometer-sized carbon nitrides of C_3N_4 stoichiometry, a rich chemistry can probably be developed around these systems. Solubilization experiments by selective oxidation aimed at large-scale isolation and/or synthesis are currently under way.

METHODS

The chemicals and solvents were purchased from commercial suppliers (Aldrich and Fluka) and used without further purification. The elemental analyses were performed in a Perkin-Elmer 240-B microanalyzer. The thermo decomposition gravimetric analyses were performed in a Perkin-Elmer Thermal Analyzer. The Fourier transform infrared (FTIR) spectra were recorded on a FT-IR Bruker IFS60v spectrophotometer (operating in a vacuum).

The X-ray photoelectron spectroscopy (XPS) analysis of the nitride samples were carried out in an ultra-high-vacuum (UHV) chamber equipped with a hemispherical electron analyzer, using a Mg $K\alpha$ X-ray source (1253.6 eV). The base pressure in the UHV chamber was 10^{-9} mbar, and the experiments were carried out at room temperature. The O(1s), C(1s), N(1s), and Au(4f) Core level peaks were recorded using a pass energy of 20 eV. Binding energies were calibrated against the binding energy of the C 1s peak at 285.0 eV for the nitrides pellet and against Au (4f_{7/2}) peak at 84.0 eV for the gold surface samples. The fine fine-shape of the core levels was fitted by using a Shirley-type background and a convolution of Gaussian/Lorentzian functions.

LDI spectra were performed on the samples using the third harmonic of a Nd:YAG laser (355 nm), with a pulse width of 8 ns and a repetition rate of 10 Hz on a reflectron TOF mass spectrometer. The sample was inserted into the vacuum chamber of the

mass spectrometer by means of a routable solid probe. The tip of the solid probe was placed between the repeller and extractor electric plates of the TOF spectrometer. The sample surface was parallel to the TOF direction and perpendicular to the laser beam direction. A CW electric field of 300 V/cm was applied to extract the ions formed, perpendicularly toward the reflectron plates. Typical voltages in the reflectron plates were 4500 and 3000 V. The total flight length from the interaction region to the microchannel plate (MCP) detector was 2 m. Laser radiation at 355 nm with energy of about 30 μ J/pulse was focused on the sample using a 25 cm focal length lens. The performance of the instrument and mass calibration was checked by performing LDI on the fullerene (C_{60}) samples. For the carbon nitrides, several experimental conditions (laser power and beam focusing, extraction and reflectron voltages) were tested to optimize the measured spectra. The measured TOF spectra of the carbon nitrides were converted into mass spectra by an internal calibration.

AFM images were acquired in dynamic mode using a Nanotec Electronica system operating at room temperature in ambient air conditions. For AFM measurements, Olympus cantilevers were used with a nominal force constant of 0.75 N/m. The images were processed using WSxM. The surfaces used for AFM were Moscovita mica (E.M.S Co.), highly ordered pyrolytic graphite (NTI Europe Co.), and gold deposited on glass (10 nm thickness; Arrendee Co.). To obtain reproducible results, very flat sub-

strates were used with precisely controlled chemical functionalities, freshly prepared just before the chemical deposition. Muscovite mica and highly oriented pyrolytic graphite were cleaved with adhesive tape. The gold surfaces (Precious Metal Coated Substrates, Arranged) were dipped in a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1) mixture for 10 min. The surfaces were then immersed in 5 mL of water and sonicated (680 W) for 5 min. Finally, the surfaces were heated with a flame for 1 min in order to obtain a reconstructed Au(111) surface.

The morphology and microstructure of the prepared material were analyzed by SEM (JEOL JM6400) equipped with a 40 Kv microprobe and TEM (JEOL JEM-4000 EX 400 kV and JEM 2000 EX 200 Kv). The substrates used for SEM and TEM microscopy were copper discs and grids of copper 200 mesh with support of carbon (E.M.S Co.), respectively. For SEM measures, the solid material was directly deposited onto the discs. The TEM samples were prepared by suspending 0.001 g of the bulk material in 5 mL of acetone. The suspension was then stirred for 10 min and the grid immersed for 10 s in the suspension and then dried in air. The TEM 200 kV samples were prepared by a deposition of 40 μL on the grid of a suspension of 0.05 g of the C_3N_4 bulk material in 5 mL of toluene.

Synthesis. A 45 mL Teflon-lined stainless reactor was loaded with 1.0 g (5.4 mmol) of $\text{C}_3\text{N}_3\text{Cl}_3$ (1,3,5-trichlorotriazine), 1.5 g (23.1 mmol) NaN_3 (sodium azide) and 30 mL of dried toluene and then sealed. The solids were well-ground before hand in an Agatha mortar. The manipulations were performed in a glovebox with flowing argon. The reactor was heated at 220 °C and a pressure of 1–1.2 bar for 20 h and then allowed to cool naturally at room temperature. The brown solid obtained was filtered off and washed with toluene (4×50 mL) and with boiling water (10×50 mL). The solid was then dried under a vacuum (10^{-2} mbar) at 80 °C for 10 h to give 0.13 g (17.8% yield based on $\text{C}_3\text{N}_3\text{Cl}_3$). Calcd (exptl) for $\text{C}_3\text{N}_4 \times 1.4\text{H}_2\text{O}$: C, 30.7 (29.4); N, 47.8 (48.8); H, 2.4 (2.6).

Details of the Separation of C_3N_4 Nanocages by Sonication—Centrifugation. A 5 mg portion of the $\text{C}_3\text{N}_4 \times 1.4 \text{H}_2\text{O}$ bulk sample was suspended in 5 mL of water and sonicated for 2 h at 680 W. The suspension was then centrifuged at 10000 rpm for 30 min. The solvent of the resulting supernatant was eliminated under vacuum to produce 10 mg of a brown-yellow solid (17.8% yield).

Computational Details. The SIESTA method was used in all the DFT calculations. Exchange and correlation were treated using the generalized gradient approximation³¹ (GGA). A basic set of double- ζ atomic orbitals was used, including polarization orbitals. The range of the orbitals was set by an energy shift 1 of 20 meV. A cutoff of 250 Ry was used for the real-space integration grid. The initial cage-like geometries were produced by connecting C_3N_3 aromatic rings through triply coordinated nitrogen atoms. The topologies of initial candidate structures were generated by hand, using a Polydron construction model to impose the triple coordination of both subunits. These structures were relaxed by a conjugate gradient minimization of the total energy, until all the residual atomic forces were below 0.03 eV/Å. To check that the final geometries were local energy minima, they were relaxed again after random maximum atomic displacements of 0.1 Å. The dynamic simulations at 700 K were performed using mixed-force first-principles molecular dynamics³⁶ with a time step of 1 fs and force corrections applied every 5 fs.

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Supporting Information Available: Description of experimental procedures and data, as well as figures showing TEM and AFM images and IR and XPS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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