

Nanodiamonds Dispersed in Space

The photoluminescence spectra of nanodiamonds in the 520–850 nm matched well with the astronomical observation of extended red emission bands suggesting nanodiamonds are a common component of dust in space.

Diamond in space has been proposed for decades. Early testing of this assumption was made through detecting infrared emission bands from galactic nebulae and circumstellar mediums, and two prominent features at 3.43 and 3.53 μm emitted from the HD 97048 star indicated the presence of interstellar diamonds. However, laboratory tests of terrestrial diamonds over the past years showed no satisfactory matches to the interstellar IR emission bands. In the last two decades, Huan-Cheng Chang (Academia Sinica) and his co-workers studied the IR absorptions of nanodiamonds in various forms including nanocrystal, single-crystal surface and hydrogenated thin film. They observed sharp absorption features at 3.43 and 3.53 μm and assigned them to the CH stretching on C(111) and C(100) facets. This matching of peak positions, band widths and band profiles between the laboratory measurements and the astronomical observations confirmed the existence of nanodiamonds in space.¹

Nanodiamonds are used in many diverse areas of current technological importance, such as micro-abrasion, drug delivery, catalysis, quantum computing, and so on. These applications are based mainly on the electronic and structural properties of the nitrogen-vacancy (NV) centers (defects) within the lattice structures of diamonds. These defects can exist in two different forms: NV⁰ (neutral), and NV⁻ (negatively charged), which can be formed by high energy proton bombardment of diamond nanocrystals, followed by annealing up to 1000 K. Photoexcitation of the nanodiamonds with 532 nm shows a sharp zero phonon line (ZPL) at 638 nm accompanying a broad emission, extending to 900 nm, which arises from the fluorescent centers of NV⁻ defects. Alternatively, the emission by NV⁰ defects appears in the region 550–700 nm with a sharp ZPL at 576 nm when illuminated with light at 170 nm. Compared to the remarkable emission of bulk diamonds in the wavelength region 300–500 nm, there is no emission below 500 nm detected upon far-UV excitation of nanodiamonds. In addition, the quantum yield was determined to surpass 10% when excitation in this region 125–675 nm, which indicates such diamonds are good candidate as carriers of the extended red emission (ERE).

Returning to the astronomical observation, there is a fundamental mystery in astrochemistry and astrophysics, the ERE. The ERE is a broad, unstructured emission band in the wavelength region 500–900 nm, observed in many nebulae and galaxies and although discovered more than 40 years ago, the carrier is still unknown. Proposed carriers include hydrogenated amorphous carbons, polycyclic aromatic hydrocarbons and silicon nanoparticles. The photoluminescence of these proposed carriers all agree well with the ERE, however there is a question regarding their stability in diverse astrophysical environments. Astrophysicists provided a helpful list of conditions to consider when looking for the candidate carrier of the ERE.² Nanodiamonds satisfies all of these conditions. The comparison of the ERE of NGC 7023 with the photoluminescence spectra recorded in the laboratory is shown in Fig. 1.³ The laboratory spectra were synthesized by combining the photoluminescence signals of NV⁰ and NV⁻ with (green curve) and without (red curve) the corrections of the reddening effect. The satisfactory agreement between the astronomical ERE spectrum and the laboratory measurements confirms nanosized diamonds could be a common component of cosmic dust. (Reported by Yu-Jong Wu)

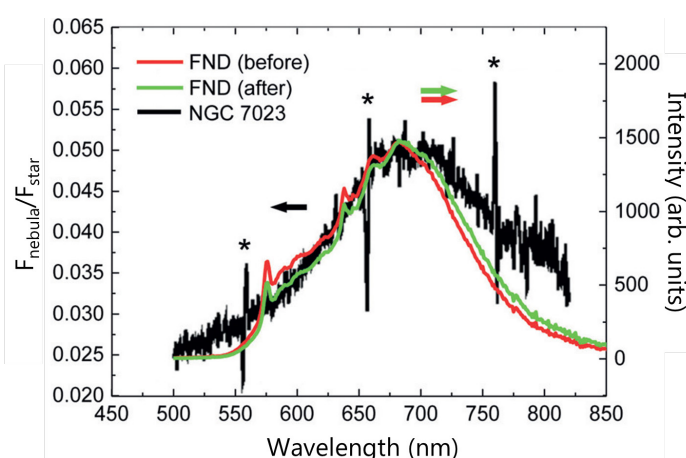


Fig. 1: Comparison of the ERE spectrum and the photoluminescence spectra of nanodiamonds. [Reproduced from Ref. 3]

This report features the work of Bing-Ming Cheng and his co-workers published in *Angew. Chem. Int. Ed.* **56**, 14469 (2017).

TLS 03A1 BM – (HF-CGM) – Photoabsorption/Photoluminescence

- VUV photoluminescence
- Astrophysics, Astrochemistry

References

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Formation of Wannier-Mott Excitons in Solid Carbon Oxide

The spectral shift of the electronic transitions of solid carbon oxide nano-thin film upon change of deposition temperatures results from the formation of the spontelectric field and the presence of Wannier-Mott excitons.

Photoexcitation of insulators and semiconductors may generate electron-hole pairs, rather than free charge carriers. The electron-hole pairs, also called excitons, are attracted to each other by the electrostatic Coulomb force. Now this phenomenon has been found in very diverse materials, including liquids, polymer-fullerene heterojunctions, and inorganic-organic hybrid materials. Excitons may be classified into two major categories based on the properties of the generated excitons in materials. If the generated excitons are entirely located on the same molecule, it is a Frenkel exciton which has a binding

energy in the region 0.1–1 eV. Frenkel excitons are usually found in materials with a small dielectric constant. A Wannier-Mott exciton is the second category of exciton. It is usually found in materials with a large dielectric constant and a low band gap. Yu-Jung Chen (National Central University) and his co-workers¹ reported the presence of the Wannier-Mott exciton in solid CO, which is a material with opposite properties (high band gap and low dielectric constant), by observing the strong temperature dependence of the spontelectric nature of solid CO.

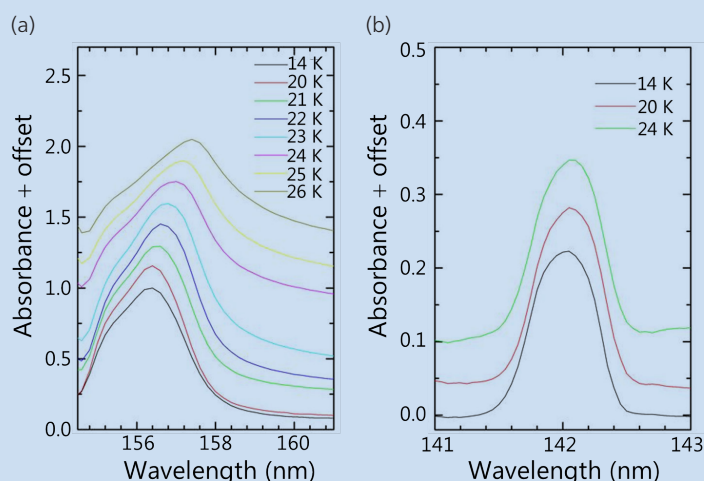


Fig. 1: VUV absorption spectra of (a) solid CO and (b) solid N₂ at various deposition temperatures. [Reproduced from Ref. 1]

The measurements of vacuum ultraviolet (VUV) absorption spectra of various pure molecular icy samples with a thickness in the nanoscale were performed at **TLS 03A1**. These icy samples included CO, N₂O, N₂, and CO₂. The former two species are dipolar and possess a spontelectric behavior, whereas the latter two has no dipole moment and shows no such spontelectric behavior. **Figure 1(a)** shows VUV absorption spectra of solid CO in the (0,0) band of the A ¹Π ← X ¹Σ transition at various deposition temperatures. Spectra of solid N₂ under similar conditions are shown in **Fig. 1(b)** for comparison. A change of a few degrees K in deposition temperature can shift the electronic absorption band of solid CO by several hundred wavenumbers. This observation of band shifts as a function of a deposition temperature results from the spontelectric effect associated with the nature of the molecular disorder. However, this spon-