Direct doping of nanoparticles in glass shows potential for smart applications

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A new and versatile method for integrating light-emitting nanoparticles, without loss of their unique properties, into glass is demonstrated.

Light-emitting upconversion nanocrystals (UPNCs)—tiny particles studded with active lanthanide ions (Ln$^{3+}$)—can convert IR excitation radiation into higher-energy emissions. Improved understanding and manipulation of upconversion properties at the nanoscale has recently fueled the development of new-generation UPNCs.¹ These new-generation nanocrystals emit higher brightness upconversion through the use of high-irradiance excitation (which can unlock the previously inactive emitters).² Alternatively, clustering ytterbium ion (Yb$^{3+}$) sensitizers, in arrays at the sublattice level, are used to promote localized excited states.³ Furthermore, the UPNCs are promising for various applications, including biological sensing, anti-counterfeiting, photon energy management, and volumetric displays. The realization of many of those applications would be particularly helped if the new-generation UPNCs could be incorporated into glass. It remains a challenge, however, to infuse glass with UPNCs that have tailored nanophotonic properties.

The glass ceramic technique is the conventional integration approach for in situ growth of nanocrystals inside a glass.⁴,⁵ In this technique, a glass, which contains precursor ions for the nanocrystals—see Figure 1(a)—is heated above the glass transition temperature to yield the crystal seeds. These seeds then undergo further growth, and thus form nanocrystals across the glass volume: see Figure 1(b). Although this in situ method is promising for certain nanocrystals, it runs into significant chemical and physical disadvantages when dealing with UPNCs. These disadvantages—related to production conditions, solubility restrictions, and post-annealing events—mean that the desired optical properties in hybrid glass are hard to achieve (and they can cause increased light scattering).⁶

To pursue high levels of compositional and structural control over UPNCs in glass, we have thus devised a versatile ‘direct doping’ approach⁶—see Figure 1(c)—as an alternative to the conventional glass ceramic technique. In our direct doping approach, as-synthesized nanoparticles are injected into the molten glass and are then integrated to create a highly controllable hybrid material.⁷,⁸ With this technique, we advantageously combine the flexible selection of glass and sophisticated syntheses of unique nanocrystals. In this way, we can achieve far more control over the composition, concentration, and nanostructure of UPNCs in glass.

In particular, the success of our approach lies in the manipulation of the correct doping temperature and dwell time of the nanocrystals in the glass melt. To thus ensure the survival and even dispersal of UPNCs across the glass, we first determined a suitable glass melting temperature for doping and dispersing ytterbium- and erbium-doped lithium yttrium fluoride (LiYF₄:Yb, Er) nanocrystals. The maximum doping temperature of LiYF₄ is given by its decomposition threshold. In addition, we determined the lower limit of the doping temperature from

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Figure 2. Characterizations of NC-doped tellurium dioxide–zinc oxide–sodium oxide (TZN) glasses. (a) Differential thermal analysis of lithium yttrium fluoride (LiYF₄) NCs, used to determine their decomposition temperature. The blue band represents the doping temperature (T₂) window that is suitable for directly doping the LiYF₄ NCs in a TZN glass melt. Δ: Energy change. T₁: Melting temperature. #: Decomposition threshold. (b) Transmittance spectra of bulk TZN glasses doped with different amounts of LiYF₄ NCs. Er: Erbium. (c) Normalized upconversion spectra of Er³⁺-doped TZN glass, TZN glass doped with 170ppm of LiYF₄ NCs (at three different locations: P1, P2, and P3), and a suspension of LiYF₄ NCs. a.u.: Arbitrary units. (d) A 3D reconstruction of TZN glass doped with 67ppm of LiYF₄ NCs. This is produced by stacking 100 x–y planes (10 × 10μm) of upconversion images, with a depth increment (i.e., between the frames) of 1.5μm. (e) Optical attenuation curves (between 500 and 1300nm) of blank, Er³⁺-doped TZN, and NC-doped TZN glass fibers. Solid curves represent the data, and the range of the standard error is shown by the shaded regions.

We thus used this optimum doping temperature and dwell time as the pre-set conditions to prepare a series of UPNC-doped TZN glasses. We find—that all of these samples exhibit high optical transmittance (very close to the maximum transmission of blank TZN glass). According to Rayleigh–Gans–Mie theory, the negligible amount of light scattering in our glasses to their low-doping concentration (i.e., ≤170ppm w/w), the partial dissolution, and the absence of serious agglomerations of nanocrystals. Furthermore, we obtained almost identical x-ray diffraction patterns and Raman spectra from the blank TZN glass and our UPNC-doped TZN glasses, which suggests that our hybrid glasses retain the original glass network.

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We have also used optical methods to thoroughly inspect our doped glasses. For example, we used the hypersensitivity of Eu³⁺ emissions—Figure 2(c)—to validate the survival of the UPNCs in the glass and to quantify the dissolution fraction of the doped UPNCs as 30–60%. In addition, we used upconversion scanning confocal microscopy—see Figure 2(d)—to produce the first 3D in situ visualization of UPNC dispersion in glass. To obtain this volumetric 3D imagery and thus visualize the spatial distribution of UPNCs in TZN glass, we reconstructed 100 scanned x–y planes. We also acquired the light attenuation spectrum (between 500 and 1300nm) of the samples. We observe a loss of 0.28±0.06dB/m for a UPNC-doped TZN glass fiber. This value is intermediate to the loss from blank TZN (0.35±0.02dB/m) and from an Er³⁺-doped TZN (0.08±0.06dB/m) glass fiber: see Figure 2(e). These loss results indicate that dissolution of the nanocrystals has occurred and the absence of serious nanocrystal agglomerations in the TZN glass fibers.

In summary, we have used our direct doping approach to successfully integrate UPNCs (which have unique properties) in TZN glass fibers. We have thus demonstrated that this new methodology can be used to overcome key obstacles in the conventional glass ceramics technique. We now plan to use core-shell nanoparticles (which are surrounded by an additional robust layer of material) to ensure that the nanoparticles remain intact and are better dispersed within the glass. We will also generalize our direct doping approach so that it can be used to embed other nanoparticles (with interesting photonic, electronic, and magnetic properties) in glass and to thus advance smart glass technology for a wealth of applications, e.g., in biomedical engineering, remote radiation sensing, and 3D volumetric displays.

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