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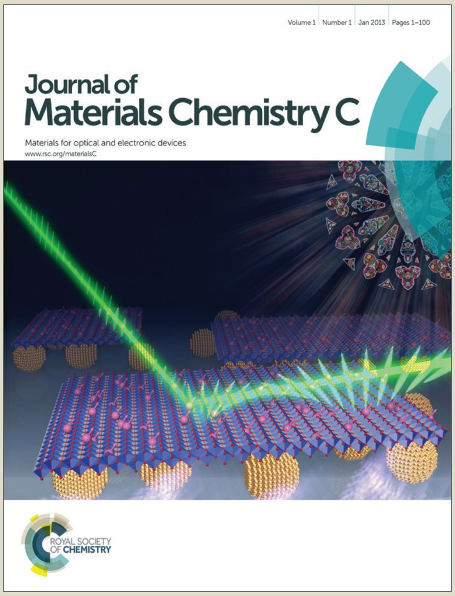

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ARTICLE

Infrared-light induced curing of photosensitive resins through photon up-conversion for novel cost-effective luminescent 3D-printing technology

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Here we explore the ground-breaking photonic approach for infrared-light induced photo-polymerization of organic resins by using photon up-conversion in rare-earth-doped luminescent materials. In particular, we show outstanding high-intense near-infrared to ultraviolet-blue up-conversion emissions from Tm^{3+}-doped K_2YbF_5 crystals, energies of which perfectly match the activation energy of light-sensitive resins that contain photo-initiators for radical polymerisation, widely used in medical surgery, odontology or implants applications, as well as in microstereolithography three-dimensional (3D) printing technology. This innovative technique, in which a cost-effective and low-power continuous wave commercial near-infrared laser diode is used, establishes a significant step forward to the state-of-the-art, by offering lower nominal radiation power and exposure time requirements than those of simultaneous two-photon absorption techniques based on powerful femtosecond lasers. We also present quasi-instantaneous “laser-writing”-like printing of 3D-structures, which exhibit visible luminescence under infrared light, for novel applications in 3D security-ink stamps or fluorescent labels for visual identification of orthodontic adhesives.

Introduction

Recently, there is a tendency to increase the use of advantageous near infrared (NIR) light for different photonic applications through the well-known luminescent process termed up-conversion (UC),[1-2] to induce photo-reactions in light-sensitive resins used in odontology[3] and in microstereolithography 3D-printing technology,[4-9] as recently reported in literature.[10-12] As well as in photoisomerization,[13] photodynamic cancer therapy for photocleavage of photo-responsive groups for drug delivery,[14-16] photocatalysis,[17-19] photopolymerization[10,20] and photolitography[11-12] for biomedical applications among others. Within the framework of this frontier research, special attention has been paid to rare-earth (RE) doped materials, which exhibit high efficiencies in such photon up-conversion of long wavelength (NIR) exciting radiation into high energy emissions (UV-VIS). On the other hand, in the contemporary and revolutionary 3D-printing technologies,[4-5] based on vector microstereolithography (VμSL) and projection microstereolithography (PμSL),[6-9] any microstructure is built, layer by layer, by tracing a light beam focused on the surface of a bath containing a photo-sensitive liquid resin to produce a polymer deposit. It should be emphasized that presently, UV light-sensitive photoinitiators are exclusively used for commercial 3D photolithography.[6] However infrared light, offering convenient benefits such as less photodamage, lower scattering[21] and deeper penetration length[22] than those caused by UV light, emerges as an optimum and cost-effective option for biological media,[23] due to well-known therapeutic windows (i.e. 600-1000 nm), where tissue penetration is higher and direct damaging of cellular components lower, [24] and also for other technical applications. Moreover, the photo-polymerization of composite resin used in odontology applications for dental filling material has practical depth limitations, because of the scattering of irradiated blue visible light. Therefore the use of IR light appears as a clear advantage, since it propagates more deeply into biological tissues due to its longer wavelength.[20]

Thus, combining the NIR to UV photon conversion capability of RE-doped luminescent materials[2,19] and the up-conversion assisted photo-polymerization of photosensitive compounds[10-12,20] really opens a fully unexplored road map for developing an innovating cost-effective 3D printing technology. It should be noticed that there exist only very few pioneering results in this way, recently published, showing the prospects of unprecedented outstanding applications, particularly in odontology[10] and also for the photo patterning of biomaterials such as proteins.[12] Therefore, here we show high-intense NIR to UV-blue up-conversion emissions from hydrothermal Tm^{3+}-doped K_2YbF_5 crystals which have very convenient spectral match with activation wavelength range of commercial photo-

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initiators commonly and extensively used in 3D resin-based printing technology. Consequently our approach is a significant contribution to the state-of-the-art, since involves the achievement of infrared-driven resin curing by up-conversion assisted luminescent process, and also provides lower power requirements and less irradiation time necessary to create printed structures in comparison with some other current procedures, which seem to lead to a practically instantaneous "laser-writing"-like innovative technique. In this context, it should be also emphasized that the use of NIR continuous laser radiation constitute a significant advantage in maintenance costs and ease of maintenance compared with other reported methods based on simultaneous two-photon absorption using powerful femtosecond laser pulses[25,26], which has turned to be somehow inefficient for large-area patterning and time-consuming.[16] Moreover, the proposed approach provides cured polymer 3D assemblies that exhibit visible luminescence under infrared illumination after photo-polymerization process, due to the presence of photon up-converting microcrystals. This peculiarity can be used in security-ink purposes, and also for making orthodontic adhesives visible, which is necessary for their safe and complete removal after orthodontic treatments.[27]

Experimental

Orthorhombic K_2YbF_5 crystals containing Tm^{3+} ions were obtained under hydrothermal conditions. For hydrothermal experiments copper insert lined autoclaves having a volume of about 40 cm^3 were utilized and the inserts were separated by perforated diaphragms into synthesis and crystallization zones. The fluoride crystals were synthesized by a direct temperature-gradient method as a result of the reaction of the aqueous solutions containing 35-40 mol% KF with appropriate oxide mixtures $(1-x)Yb_2O_3$ - xTm_2O_3 at a temperature of about 750 K, a temperature gradient along the reactor body of up to 1 $K{\cdot}cm^{-1}$, and a pressure of about 100 MPa. Under these conditions, spontaneously nucleated crystals from 0.1 to 1.0 mm^3 in size were obtained for 75 h. Synthesized K_2YbF_5 crystals were of long prismatic habit with the width/length ratio being about 1/10, which was caused by the chain structure of K_2YbF_5.[28-29] The purities of the starting materials were higher than 99.99% for rare-earth oxides and 99.9% for KF. The structure type and phase purity of synthesized samples were characterized with conventional powder X-ray diffraction (XRD) technique and powder XRD patterns were obtained by using a Bruker D8 Advance X-Ray powder diffractometer with Cu Kα radiation. Within this research microcrystals of undoped K_2YbF_5 and K_2YbF_5 doped with 0.1 and 0.2 at % Tm^{3+} were synthesized. It should be also noted that observed up-conversion luminescence coming from undoped K_2YbF_5 microcrystals was due to Tm^{3+} trace impurity in a concentration of a few tens ppm as estimated by energy-dispersive X-ray spectroscopy.

Optical absorption spectra of samples were measured with an ultraviolet-visible-infrared (UV-VIS-IR) Perkin-Elmer Lambda 9 spectrophotometer having a resolution of 0.5 nm. Up-conversion measurements were carried out with a 980 nm CW near-infrared laser diode having a power up to 300 mW, focused by using a 4X micro-objective with a focal length of 4.51 mm as well as 0.55 of numerical aperture. The detection of luminescence was realized with a 0.25 monochromator equipped with a photomultiplier. All spectra were collected at room temperature and corrected for instrumental response. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectra (EDS) were taken by using a JEOL JSM-6300 scanning microscope under a working voltage of 20 kV equipped with an electron probe microanalyzer by Oxford Instruments, INCA. Specimens were prepared for an appropriate SEM observation by applying a silver (Ag) coating layer over the samples.

We selected the poly(ethylene glycol) diacrylate (PEGDA) as photo curable organic base resin, containing 1.0 vol % of Irgacure-819® (Ciba Specialty Chemical Inc.) as the UV sensible photo-initiator. Then we added a determined quantity of micrometre-sized up-converting 0.2 at % Tm^{3+}-doped K_2YbF_5 (previously milled in an agata mortar) in a proportion of 100 g/L. In particular we used about 5 mg of up-converting K_2YbF_5 crystal dispersed into 54 mg of the liquid resin solution, that is, approximately a concentration of about 10% in weight, for our printable composition here presented.

A CCD digital camera was used to take different photographs presented in the paper including up-conversion luminescence emitted by the samples. A compromise between exposure time and brightness control was taken into account in order to avoid saturation of the CCD.

Results and discussion

K_2YbF_5 fluoride microcrystals, containing different concentrations of Tm^{3+} ions up to 0.2 at.%, have been synthesized under hydrothermal conditions and characterized by optical spectroscopy. UC emission spectra of K_2YbF_5:Tm^{3+} phosphors obtained under excitation by a 980 nm continuous-wave commercial NIR laser diode are presented in Figure 1. Further details for synthesis conditions of samples and luminescence set-up can be found in the Methods. The most relevant result is the perfect overlap between the high intense UV-blue UC emissions and the absorption spectrum corresponding to the activation range for photo-polymerization of sensitive resins. Accordingly, after suitable energy transfer processes of the 980 nm excitation radiation, effectively absorbed by sensitizing Yb^{3+} ions, very intense UV-blue emissions ascribed to Tm^{3+} electronic transitions in the 290-360 nm spectral range are capable to activate the well-known commercial photo-initiator, named as Irgacure-819® (Ciba Specialty Chemical Inc.), that has been added to the base polymer here utilised, namely poly(ethylene glycol) diacrylate (PEGDA), also commonly used in 3D resin-based printing technology (Fig. S1 and S2 in Supporting Information).

As for luminescence quantum efficiency, we have applied a simple quantitative method for estimating of UC yield, proposed by Suyver *et al*,[30] to determine the number of upconverted photons relative to the total number of NIR excitation photons absorbed by the presented K_2YbF_5: Tm^{3+} phosphor (further details in Fig. S3 in Supporting Information). As a result, we have obtained a value of around 36% for the 0.1 at% Tm^{3+} doped K_2YbF_5 crystal (Fig. 1.), representing in this case the fraction of the total UC photons emitted from the crystal which overlap the absorption range of the UV photo-initiator and therefore contribute to ensuing curing process with high efficiency.

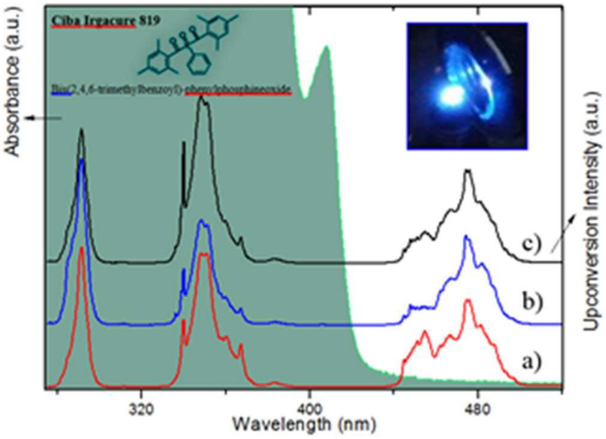

Fig.1. Up-conversion emission spectra of hydrothermal Tm^{3+} doped K_2YbF_5 crystals: (a) undoped, Tm^{3+} trace impurity at a ppm level, (b) 0.1 and (c) 0.2 at% Tm^{3+}, under NIR 300 mW laser diode excitation at 980 nm, overlapping absorption spectrum for UV-sensible photo-initiator Irgacure 819® (Ciba Specialty Chemical Inc.), commonly used in 3D resin-based printing technology. Inset photograph shows the bright blue up-conversion emission of a 0.2 at% Tm^{3+}-doped K_2YbF_5 crystal.

Thus, we have successfully performed several experiments to achieve infrared-induced photosensitive resin curing by up-conversion process for developing novel cost-effective luminescent 3D printing technology. As it can be clearly illustrated in Fig. 2, a commercial 300 mW laser diode at 980 nm is focused with a microscope objective lens over a PEGDA photo-curable resin containing 1 vol% of the UV-sensitive photo-initiator Irgacure-819®. Then a high efficient UV-blue UC Tm^{3+}-doped K_2YbF_5 bulk crystal is placed into this liquid on the focal point of the incident NIR diode laser radiation (inset 1 and 2 in Fig. 2), yielding to the photo-polymerization of the liquid resin, by taking into account the volume of cured resin around the bulk crystal, obtained after 1 minute exposure to NIR focused radiation (inset 3 in Fig. 2). Moreover, the UC emission spectra of a Tm^{3+}-doped K_2YbF_5 crystal have been measured before and after immersion in the photosensitive liquid resin (inset 4 in Fig. 2). The noticeably decrease of the UV emissions located at around 290 and 360 nm clearly indicates the convenient overlap between the UC emissions and the absorption of the UV-sensible photo-initiator added to the resin, which is in fact the responsible of the up-conversion driven curing process. Next, Fig. 3 presents CCD photographs (including a SEM image) of K_2YbF_5 microcrystals before and after photo-polymerization process (i.e, coated by cured resin) induced. It should be clarified that K_2YbF_5 microcrystals remain inalterable after curing process. In other words, we are not modifying the composition neither the consistence of the up-converting microcrystals. We are just using their high intense UV-blue up-converting emissions to induce infrared-light-driven photo-polymerization of the volume of resin around them, as a pure photonic approach to the problem.

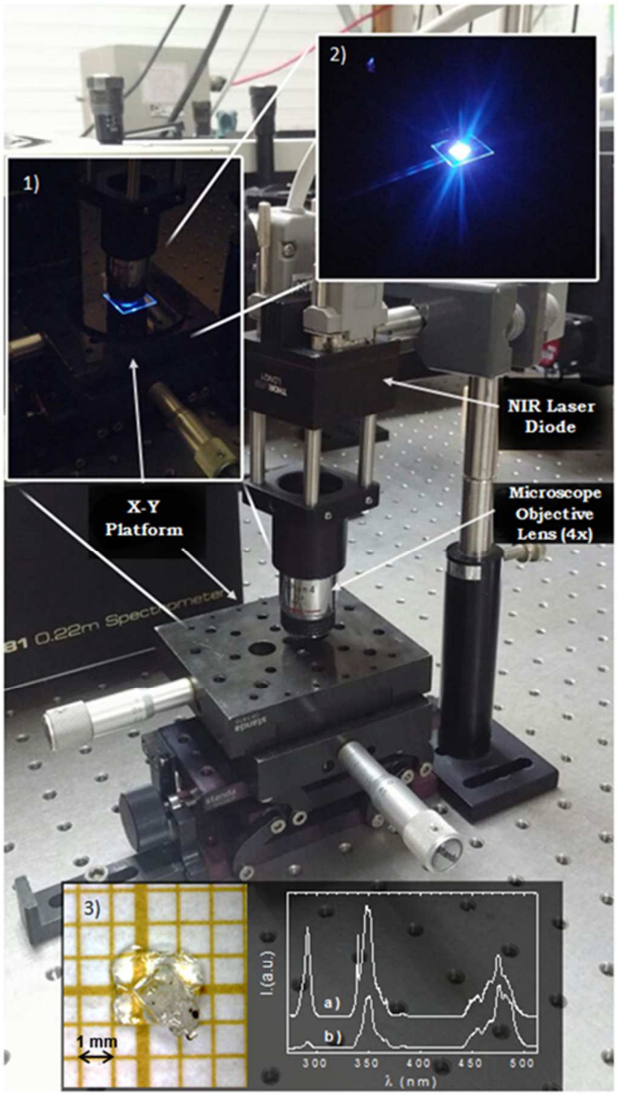

Fig. 2. Experimental set-up for infrared-induced photosensitive resin curing by up-conversion (UC) process for developing novel cost-effective luminescent 3D printing technology. The beam from a commercial 300 mW 980 nm laser diode focused with a microscope objective lens (4x) over a poly(ethylene glycol) diacrylate (PEGDA) resin containing with 1.0 vol% of Irgacure-819®. Inset 1 and 2 show the bright emission from the high efficient UC 0.2 at% Tm^{3+}:K_2YbF_5 bulk crystal, placed on the focal point of the incident NIR radiation. Obtained volume of cured resin around the UC bulk 0.2 at% Tm^{3+}:K_2YbF_5 crystal after NIR-driven photo-polymerization of the liquid resin is presented in inset 3. Inset 4 presents the UC emission of 0.2 at% Tm^{3+} doped K_2YbF_5 collected before (a) and after (b) immersion in the photo-sensitive resin.

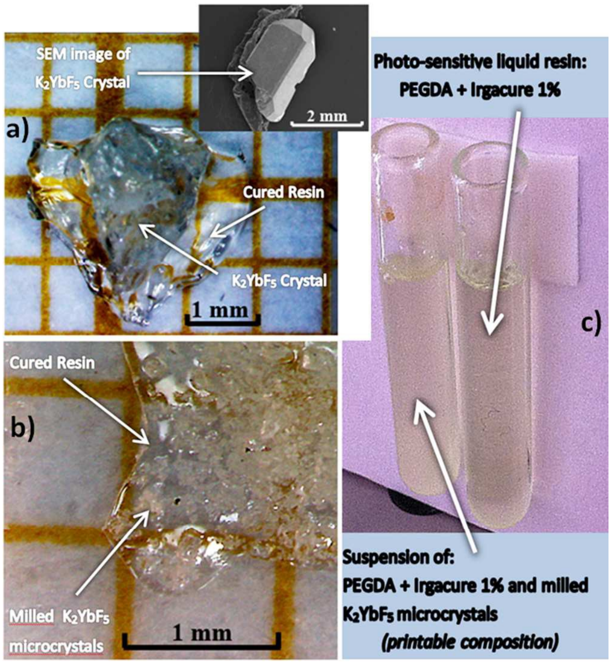

Fig. 3. Photographs of a) a millimeter-sized bulk 0.2 at% Tm^{3+}:K_2YbF_5 crystal coated by cured resin after photo-polymerization process induced by NIR to UV-blue up-conversion emissions (corresponding inset shows a SEM image of a particular K_2YbF_5 crystal); b) powdered micrometer-sized K_2YbF_5 crystals dispersed into a volume of cured resin; and c) vials containing PEGDA liquid resin with the corresponding Irgacure-819® photo-initiator (1% vol) and suspension of this liquid resin solution (PEGDA-Irgacure-819®) with milled K_2YbF_5 microcrystals (printable composition).

Fig. 3c) also presents actual photographs of vials containing PEGDA liquid resin with the corresponding Irgacure-819® photo-initiator (1% vol), and suspension of this liquid resin solution, PEGDA-Irgacure-819® incorporating milled K_2YbF_5 microcrystals, which comprise our printable composition. Similar aspect and viscosity features found for both solutions accounts for the final rheological properties of our printable composition. In particular, the viscosity of the PEGDA photopolymer is 57 cp at 25ºC. We have previously demonstrated (Hernández-Rodríguez et al.[31]) that 3D structures can be printed without any problems with photopolymers containing up to 30-40% of solid content. Similarly, other authors (Adake et al.[32]), have also shown, with analogous materials, that the inclusion of up to 10% of solid content, as it is our case in the present paper, does not seems to affect the relative viscosity of the photopolymer. In fact, we have been even able to use a commercial photopolymer, provided by FORMLABS®, where the typical viscosity is 850-900 cps at 25ºC, 10 times higher than our proposed system.

Our second objective of this research looks into the development of UC-induced printing technique for 3D-structures by using the low-power infrared laser-driven resin curing process. For this purpose a suspension of micrometre-sized up-converting 0.2 at % Tm^{3+}-doped K_2YbF_5 and a liquid PEGDA resin containing 1.0 vol% of UV-sensitive Irgacure-819® has been prepared in a proportion of 100 g/L. Then, the laser diode describes a previously designed pattern, controlled with an X-Y axis micrometer positioner (Fig. 2), even with a continuous moving over the liquid surface (at an estimated speed of 0.3 mm/s) in order to provide local polymerization of the resin. In this particular case, we *have drawn* some resultant printed structures in the form of capital letters, namely ULL (University of La Laguna) and UC (up-conversion) acronyms (upper photographs in Fig 4). It should be emphasized that the particular election of the 0.2 % Tm^{3+}-doped K_2YbF_5 for our printable composition has been made in basis of the optimum overlap between their high intense UV-blue UC emissions of the fluoride microcrystals and the activation range of the photo-initiator (290-360 nm), presented in Fig. 1. Thus, the concurrence of this perfect spectral match accounts for a quasi-instantaneous “laser-writing” of 3D-printed structures by NIR laser diode. This implies a substantial improvement for photo-polymerization processes under NIR radiation with using UC phosphors in comparison to longer exposure times (in the order of tens of minutes[12] or even hours[11]) and higher nominal continuous laser powers needed around 1 W, as reported recently in the literature.[10] Moreover, due to the incorporation of UC emitting Tm^{3+}:K_2YbF_5 microparticles into the liquid resins, final polymerized objects exhibit visible luminescence under infrared light (lower photographs in Fig. 4). Therefore different objects of such a type can be directly used as novel 3D security-ink stamps[33-35] or as fluorescent labels for visual identification of dental adhesives for their safe removal after orthodontic treatments, as recently reported by Yamagata et al.[27] It should be also pointed out that resultant 3D-printed objects showing infrared-to-visible UC emissions, see authors´ previous results,[36] can be also used in the design and fabrication of up-converting-coated vessels, photoreactors or light-guiding structures to collect and, at the same time, to convert the incoming sunlight. They will have a direct implementation in up-conversion powered photocatalysis,[17-19] aimed at sustainable production of hydrogen to feed fuel cells[37] for artificial photosynthesis and solar-to-fuel applications.[38-39]

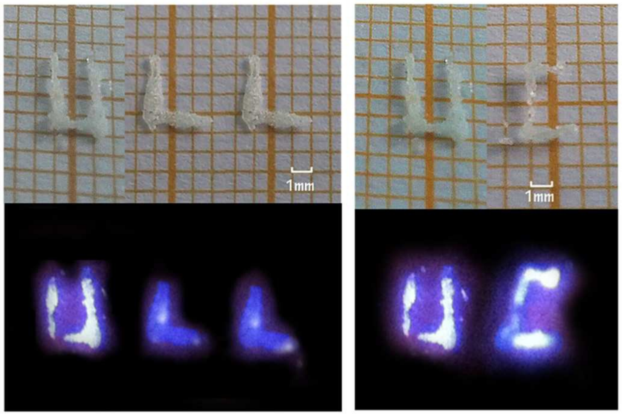

Fig. 4. 3D-printed structures obtained with low-power infrared laser-driven resin curing process as a quasi-instantaneous “laser-writing” procedure. Printed capital letters (upper photographs) correspond to the acronyms ULL, (University of La Laguna) and UC (Up-conversion), which show visible luminescence under infrared light radiation (lower photographs).

It should be reminded that we are a providing here a qualitative demonstration of our 3D system, in other words, our main goal has been to demonstrate the concept of infrared-light induced photo-polymerization of a commercial PEGDA-based organic resin by up-conversion processes. So 3D-printed structures presented in Fig. 4 are not intended to reflect the final printing resolution. The idea is to use this proved technique with any Desktop Stereolithography (SLA) 3D Printing, i.e. Form1+ from FORMLABS® or Pegasus from FSL3D®, or even more sophisticated ones, replacing the original UV laser for an IR laser. Then, in our proposed approach, a single particle or crystal will be attached to the optical fiber, producing UV-blue light by up-conversion processes to perform quasi-instantaneous "laser-writing".

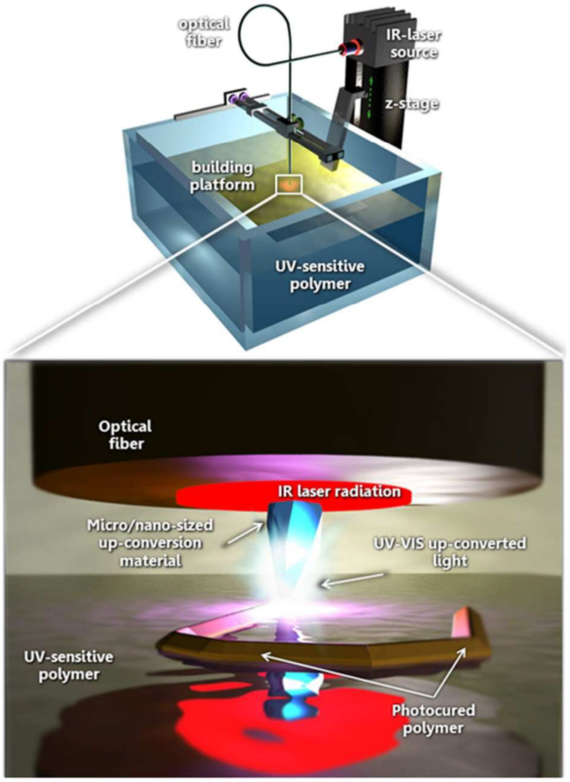

Fig. 5. Proposed approach of up-conversion nanoparticle driven 3D printing technique with enhanced spatial resolution through infrared-laser-induced curing of an UV-sensitive polymer resin. A flexible optical fibre is used to deliver radiation from a cost-effective low-power NIR laser diode to the building platform, while a high-efficient nano-sized up-conversion nano-sized particle is attached to the focal point. Intense UV radiation emitted just around the particle originates quasi-instantaneous curing of the photosensitive resin with that level of resolution, opening the door to photolithography at the nanometre scale.

Finally, based on above considerations, we pose an envisioned approach to control the spatial resolution of 3D-printed structures using of up-conversion nanoparticles (UCNP), see infographic scheme depicted in Fig. 5. In this advance step, the projected spatial resolution could be enhanced even further, within this cost-effective infrared-induced and significant less time-consuming approach, leading to a new way of additive fabrication technique that would help to open the door to photolithography on the nanometer scale, now barely explored.[11,12] As depicted in Fig. 5, a flexible optical fibre can be used to deliver the NIR laser radiation to the building platform, instead of the typical and expensive UV laser used in contemporary VµSL and PµSL devices.[6-9] While, the UCNPs are attached to the optical fiber, converting NIR photons into the UV photo-polymerization activity range just through the UC particles. Hence the resolution of the cured polymer structure depends just on the size of the UC particle/crystal, not on the NIR laser beam diameter, and therefore this technique should be able to produce 3D-structures at the nanoscale.

Conclusions

In summary, high-intense near-infrared to ultraviolet-blue up-conversion emissions from Tm^{3+}-doped K_2YbF_5 crystals allow the activation of light-sensitive resins with potential uses in cost-effective and low-power microstereolithography 3D-printing technology, as well as in dental implants. This infrared-light driven resin curing process has been ascribed to the very suitable overlap between high intense up-conversion emissions and the absorption of widely used UV-sensible photo-initiator added to the resin, such as Irgacure-819®. The reduced light-exposure requirements, along with lower nominal radiation needs, expand previous works reporting the use of analogous up-conversion processes for the photo-polymerization of organic resins. Moreover the present approach enables quasi-instantaneous "laser-writing"-like printing of luminescent 3D-structures and also the local polymerization of the resin, depending on the size of the up-converting particle/crystal, for promising applications in nano-photolithography.

Acknowledgements

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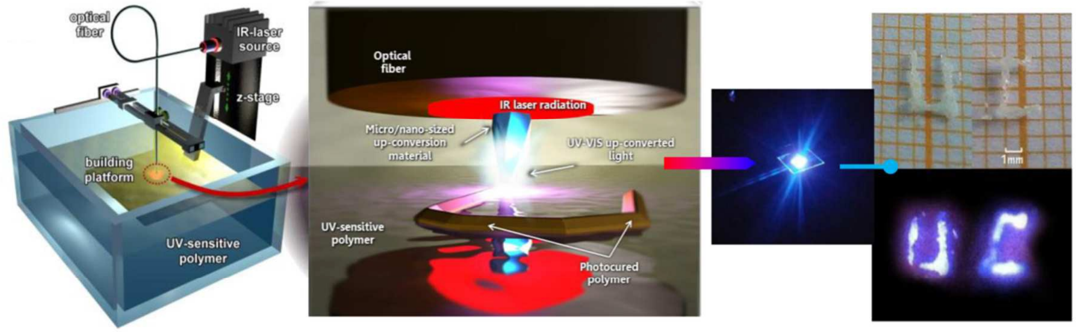

Cost-effective luminescent 3D-printing technology approach with enhanced resolution (left) through infrared-laser-induced photon up-conversion in rare-earth-doped luminescent materials, Tm^{3+}-doped K_2YbF_5 crystals (middle) for promising applications in nano-photolithography. Resultant quasi-instantaneous “laser-writing” of luminescent 3D printed structures by means of low-power infrared laser-driven resin curing process (right).