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Near-infrared photopolymerization assisted by upconversion nanophosphors for biomedical applications

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Abstract. We present the concept and the experimental demonstration of near-infrared photopolymerization assisted by specially designed upconversion nanophosphors. The principle of this technique is based on conversion of 980 nm laser irradiation to ultraviolet photons subsequently absorbed by photoinitiator. The nonlinearity of upconversion allows for activation of the process locally in the laser beam waist. This approach enables precise fabrication of 3D constructs directly in the volume of photocurable composition. Furthermore, the presented technique is suitable for polymerization of a wide range of photocurable resins as well as gelation of hydrogels for biomedical applications.

A broad range of techniques based on photo-induced polymerization have been developed. The overwhelming majority of those employs the single-photon absorption. In this case, the polymerization of the exposed photocurable compositions (PCCs) is a linear process getting launched in every point within the irradiation penetration depth and depending only on exposure dose. This approach is widely used in laser stereolithography [1] and direct light processing [2] when the photocurable resin is patterned and recoated layer by layer. However, this technique is not always suitable for *in situ* formation of structures. In this case the two-photon photopolymerization can be implemented. The method is based on two-photon absorption of light by photoinitiator [3]. The nonlinearity of absorption process allows activation of polymerization locally in the laser beam waist. Furthermore, implementation of near-infrared light instead of UV exposure makes possible to increase the irradiation penetration depth. Two-photon polymerization represents a high resolution method for drawing structures directly in the volume of PCC. Nevertheless, the need to use complicated femtosecond laser systems in order to achieve the required high intensity in the beam waist limits the wide implementation of this technique.

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In this paper, we report on formation of structures in the volume of PCC using near-infrared photopolymerization. We propose to impregnate the photosensitive resin with upconversion core/shell $NaYF_4$:Yb^{3+},Tm^{3+}/$NaYF_4$ nanophosphors capable to absorb light at 980 nm and effectively convert it to ultraviolet lines (Fig 1 (left)) within the absorption band of photoinitiator launching the polymerization. The conversion coefficient was measured as $\eta_{UC}^{(UV)}$=2%. In comparison to two-photon polymerization the excitation action is performed via real energy states. Therefore, formation of 3D structures in the depth of PCC volume can be carried out at moderate intensities using simple semiconductor lasers instead of expensive femtosecond systems.

Figure 1 (right) illustrates the scaffolds produced by near-infrared photopolymerization in the depth of PCC on the base of oligocarbonate methacrylate (OCM-2) containing 1 % of TPO photoinitiator and upconversion nanoparticles. The standard Irgacure or chlorine P6 can be also used as photoinitiators.

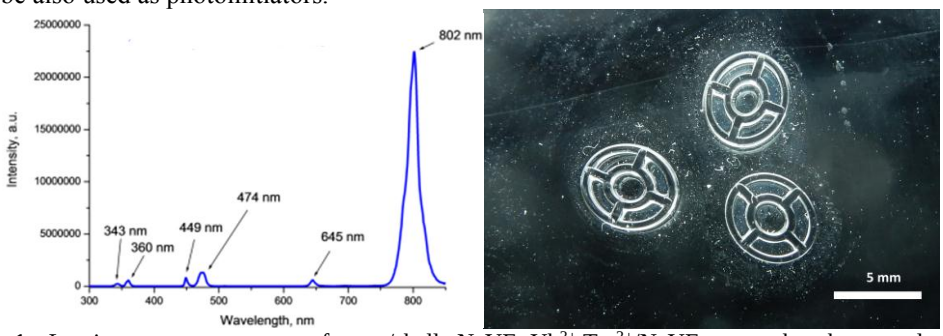

Fig. 1. Luminescence spectrum of core/shell $NaYF_4$:Yb^{3+},Tm^{3+}/$NaYF_4$ nanophosphors under excitation at 980 nm (left). Scaffolds on the base of oligocarbonate methacrylate produced by near-infrared photopolymerization (right).

Implementation of near-infrared photopolymerization assisted with upconversion nanophosphors has a great potential for gelation of biocompatible hydrogels, e.g. on the base of polyethylene glycol diacrylate. For this aim $NaYF_4$:Yb^{3+},Tm^{3+}/$NaYF_4$ nanophosphors can be modified with amphiphilic polymer in order to provide the hydrophilic properties. In this case the photoinitiator also should be water soluble. Therefore, the endogenous flavin mononucleotide [4] or chlorine P6 conjugated with polyethylene glycol can be the grate candidates. The ability to form the structures in the depth of biocompatible water-based PCCs makes the near-infrared photopolymerization assisted with upconversion nanophosphors extremely interesting for biomedical applications, when the polymerization process can be performed *in situ*.

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