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Triboluminescent composite microspheres consisting of alginate and EuD_4TEA crystals

Anıl İncel[1], Mustafa M. Demir*

Department of Materials Science and Engineering, Izmir Institute of Technology, Urla 35430, İzmir, Turkey

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ABSTRACT

Alginate is utilized to obtain luminescent composite microspheres containing europium tetrakis (dibenzoylmethide) triethylammonium (EuD_4TEA) triboluminescent (TL) crystals. Na alginate is initially treated with Ca(II) and then Eu (III) so that physically-crosslinked alginate microspheres were obtained. EuD_4TEA crystals are precipitated in situ on the surface of the spheres upon treatment with dibenzoylmethane (DBM) and triethylamine (TEA). The EuD_4TEA/alginate composite spheres are swollen in aqueous system, the diameter of the microspheres increases from 180 up to 405 μm in 48 h. TL intensity of the spheres swollen in 1 h decreases 4 folds compared to dry spheres; however, it systematically increases as the swelling time is extended step-wise to 48 h. Swelling may develop structural homogenity in the microsphere that supresses the optical scattering and may lead to better transmittance of the TL signal.
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1. Introduction

Damage sensing in situ attracts increasing attention in various fields such as material fracture [1,2,3], earthquake prediction and monitoring [4], and mechanobiology [5,6,7]. The sensor elements usually are powdery piezo/tribo luminescent materials placed on a substrate [8].The key point is the development of a suitable substrate material that allows obtaining a homogeneous distribution of the luminescent materials and maintaining the maximum transmittance of the optical signal created upon mechanical action. Hydrogels represent an important class of material that can be used for the formation of such substrates. Recently, it was shown that acrylamide-based synthetic hydrogels lead to achieve both distribution of the particles and radically extends the emission time of triboluminescence (TL) materials [9]. Naturally occurring polymers, on the other hand, can be good candidate for being hydrogel matrix for powdery optical elements [10–12]. Alginate ($(C_6H_8O_6)_n$) is a well-known polysaccharide, which is in fact linear copolymer consisting of (1–4)-linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues [13–19]. The derivatives of alginate readily allows to obtain physically-crosslinked hydrogel via polymer droplet gelation (or mill gelation) when alkaline earth metals such as Ca^{2+} and Ba^{2+} are involved into the aqueous system [20–22].They are combined with electrostatic interaction between the carboxylic acid pendant groups and the metal cations. Most of the alginate polymers are found in sodium salt and the gel formation is well established upon treatment with Ca salts. This is the most common method to synthesize hydrogels based on the combination of alginate with ionic cross-linking agents such as $CaCl_2$ and $CaCO_3$ [23–29]. The exchange mechanism of the cations with lantanides (Ln) instead of alkaline metals utilizes the applicability of these materials. For instance, the usage of lantanide allows to extent the technological feasibility of microspheres due to higher binding capability of carboxylate groups, characteristic emittive band, and color purity in the emission [30,31]. The combination of alginate polymers with Ln-based materials can potentially increase the application of the resulting composites in mechano-optical system.

Triboluminescent materials are usually in the form of both organic and inorganic noncentrosymmetric crystals which emit light under mechanical action [32,33]. Y_2O_3:Eu [34], EuD_4TEA [35–37], MgD_4TEA [38], $Cu(NCS)(py)_2(PPh_3)$ [39], ZnO micro sized particles [40], $CaAl_2O_4$ and $MgAl_2O_4$ [41], $SrAl_2O_4$ [42], Ln:$SrAl_2O_4$ [43] are TL materials used in mechnaosensor applications. They are in fact pigments and they are usually in powder form. The association of these crystals with polymers maintaining the TL character remains a challenge. The hindrance in preparation of TL composites is that TL feature is attenuated when they are associated with polymers. Attempts have been made to obtain polymer

* Corresponding author.
E-mail address: mdemir@iyte.edu.tr (M.M. Demir).
[1] Present address: Department of Biomedical Sciences, Biofilms Research Center for Biointerfaces, Faculty of Health and Society, Malmö University, SE 21432 Malmö, Sweden.

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consisting TL crystals such as ZnS:Mn encapsulated PDMS [44]; doped vinyl ester resin [45]; integration of EuD_4TEA into commodity transparent polymers [8]; entrapment of EuD_4TEA and $Cu(NCS)(py)_2(PPh_3)$ crystals into polyacrylamide-based hydrogels [9]; and the impregnation of the TL crystals on various polymer of electrospun mats [46]. Our recent findings showed that the way of preparation of composite materials is a critical factor to maintain triboluminescence for the resulting polymer composite [8,9,46]. For instance, when TL crystals are dissolved in a polymeric system in solution, TL signal disappears because the crystal structure is destroyed. Since the intensity of TL emission is associated with the bonds broken over a plane of crystal during the mechanical impact, TL behavior only show up for crystal materials. TL can be obtained if the crystals are impregnated onto the surface of polymeric substrate, i.e. maintaining the crystal structure. However, the distribution of the crystals does not occur evenly over the polymeric surface. A bottom-up approach is needed to achieve homogeneous distribution of the crystals on the polymeric system. In this study, novel luminescent composite micropsheres are synthesized using TL, EuD_4TEA crystals on alginate beads of aqueous solution. EuD_4TEA is known as one of the bright TL materials. Its molecular structure consists of one four-coordinated electrondonating group, 1,3-diphenyl-1,3-propanedione, as the lightharvesting and energy-transferring component, and one electron-withdrawing group, triethylamine, as an ancillary ligand to stabilize the crystal complex. On the other hand, alginate as natural polymer offers easily prepared and low cost hydrogel matrix. It has –COOH group attached to each repeating unit. This group brings several functionalities, for instance it shows high capacity to absorb water. The carboxylic acid group may also trigger H-bonding between TEA of EuD_4TEA crystals. The interaction may extend the emission time in hydrogels as alginate. The development of alginate-based mechano-sensing materials containing TL particles can receive considerable interest [47–56].

In this study, it is hypothesized that the TL crystals can be developed in situ over the surface of alginate beads homogeneously such that an intense TL signal is maintained and can be controlled by swelling ratio. Alginate beads were prepared by polymer gelation method. Na^+ of Na^+-alginate complex is replaced by firstly Ca^{2+} and then Eu^{3+}, the resulting Eu^{3+}-alginate complex is treated with DBM and TEA. EuD_4TEA crystals were precipitated in situ on the surface of the alginate beads. TL behaviour of the luminescent microspheres at different levels of swelling is examined with respect to TL emission upon mechanical impact at 0.05 N·s.

2. Experimental part

2.1. Materials and methods

Europium(III) nitrate pentahydrate (99.9% trace metal basis), 1,3,-diphenyl-1,3-propanedione (99.8%), triethylamine (≥99%), Sodium alginate (MW∼ kDa), were purchased from SigmaAldrich (St. Louis, MO, USA). The M:G of alginate is estimated 3:2 by ^1H Nuclear Magnetic Spectroscopy. Its weight average molecular weight is measured by Dynamic Light Scattering as 20.2 kDa. All other reagents and solvents are available at analytical grade and were used as they were. Scanning electron microscopy (SEM, FEI Quanta 250 Feg, Oregon, USA) was used to determine the morphology of the spheres. Fluorescence images were recorded via fluorescence microscopy (FM, Olympus IX2-ILL100, New Jersey, USA). The hydrated particles were characterized by optical microscope (OP, Olympus BX53F, Tokyo, Japan) to measure the diameter of the spheres. A lab-made drop-tower system was designed and prepared involving USB2000+ Preconfigured 200 – 850 nm UV–vis spectrophotometer and fiber optic cable (Ocean Optics, Florida, USA). Photoluminescence emission was registered by using a FS5 Spectrofluorometer (Edinburgh, UK).

2.2. Synthesis of triboluminescent microspheres

The schematic representation of the synthesis of TL microspheres is given in Scheme 1. Sodium alginate was dissolved in water at 3.0% (w/v). The hydrogel was prepared by slowly dropping of the dissolved sodium alginate solution into 0.1 M of aqueous $CaCl_2 \cdot 2H_2O$ solution. The precipitation of spherical beads has been performed by using a plastic syringe equipped with a neddle. Separately, 0.1 M of aqueous $Eu(NO_3)_3 \cdot 5H_2O$ solution was prepared. Alginate beads associated with Ca^{2+} were treated with Eu^{3+} salt in solution, Ca^{2+} ions are considered to be partially replaced by Eu^{3+}.

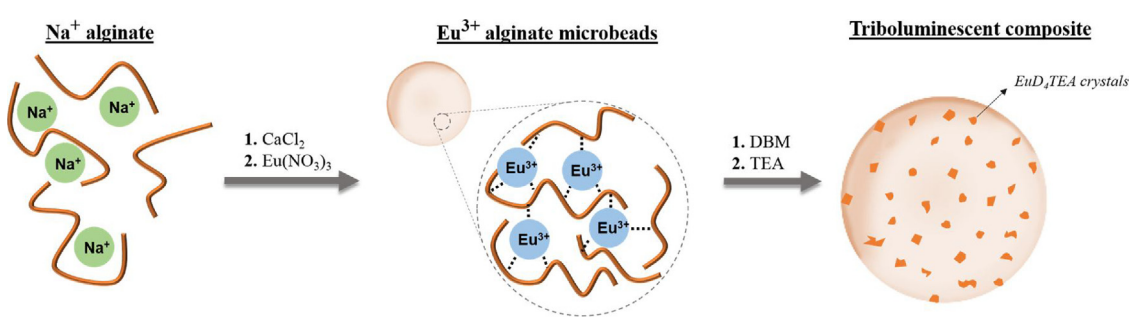
Ethanol solution of dibenzoylmethane (DBM, 14 mmol) and triethylamine (TEA, 13 mmol) were prepared in 50 mL. When both chemicals were completely dissolved in ethanol, and then Eu^{3+}-alginate microspheres were added into this solution and the solution was mixed for 6 h to form crystal particles. The obtained alginate-associated EuD_4TEA crystalline particles were dried in air. The diameter of the spheres from captured image was measured by ImageJ [57].

2.3. Swelling process

The synthesized TL microspheres were treated with deonized water at different time intervals from 1 h to 48 h. The mass of the hydrated bead was recorded to determine the swelling capacity at 25 °C. The swelling ratio of the spheres was estimated with the following formula:

$$\text{Swellingratio} = W_s/W_i$$

where W_i is the mass of the spheres before swelling and W_s is the mass of particle after swelling. Volumetric change was also registered based on optical microscopic images of a representative bead.



Scheme 1. The schematic representation of the entire process.

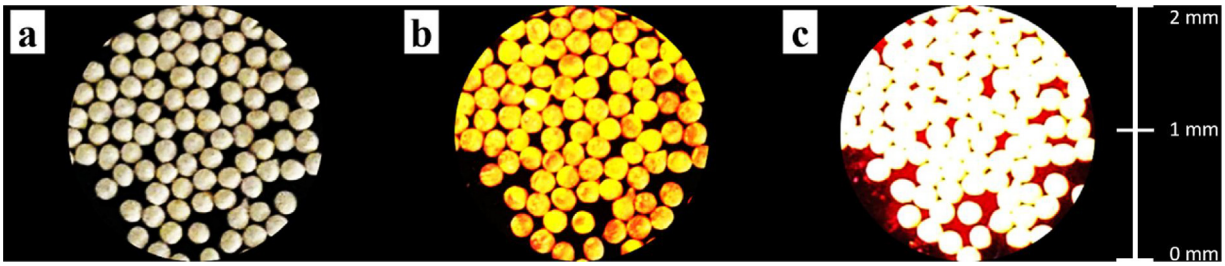


Fig. 1. The photographic images of synthesized microsphere under; (a) daylight, UV-light (b) λ = 254 nm, (c) λ = 365 nm.

2.4. Triboluminescence measurement

TL emission of the system was measured by a home-made drop tower system, which was detailly explained in our previous studies [8,9,46]. The compression force on particles was applied from 50 cm height by using 50 g mass metal ball. The produced TL signal was registered via fiber optic spectrometer. The spectra were processed by LabView program.

3. Result and discussion

3.1. Characterization of TL microsphere

A two step process was applied to obtain TL microsphere of alginate. The details of the process is shown in Scheme 1. *First*, Na^+ in Na^+-alginate complex is replaced by Ca^{2+}. Ca(II) are used to physically bind alginate molecules in situ in aqueous system. Divalent Ca cations are able to interact with negatively charged carboxylic acid groups of alginate chains. The chains surround the cations and form a physically cross-linked structure. The segregation of the interacted chains forms a physical network (gel) structure. Then, the gels are treated with Eu(III) for the exchanging of the ionic cross-linker, Ca(II). In contrast to Ca(II), Eu(III) is a trivalent cation that is able to interact with higher number of chains. So that the size of spheres is getting smaller when treated with Eu^{3+} because trivalent cations associate with higher number of chains. The denser the chains per unit volume of alginate solution, the smaller the resulting beads are. *Second*, Eu^{3+}-alginate complex is treated with TEA and DBM in pure ethanol. These reactants interact with Eu^{3+}-based beads and EuD_4TEA crystals are precipitated in situ. Since the diffusion of both molecules through alginate chains is limited, the crystals may develop on the surface or close to the surface of the microspheres. EuD_4TEA crystallizes in monoclinic crystal system with $P2_1$ space group [8]. The digital camera images of the microspheres under daylight (Fig. 1a) and UV-light (Fig. 1b and c) are illustrated. The beads seem spherical and uniform in size and shape.

A higher magnification microscopy images of a representative alginate/EuD_4TEA composite microsphere are shown in Fig. 2. The

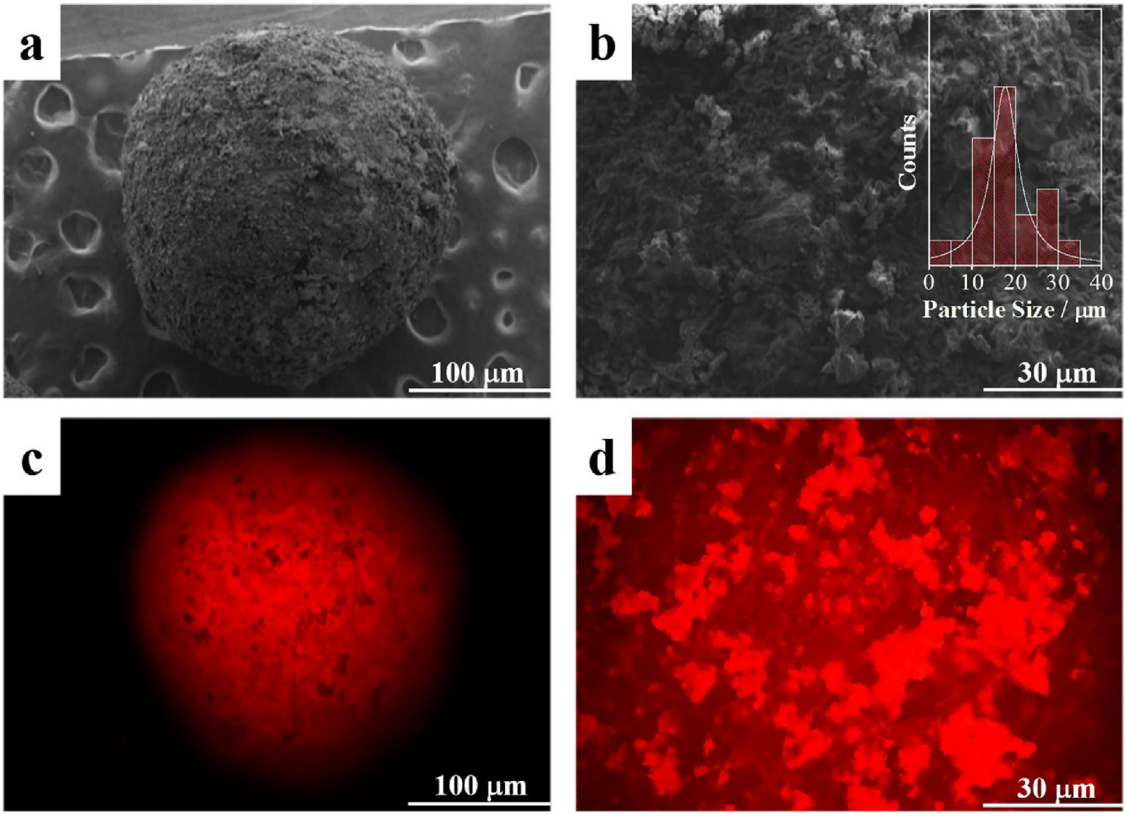


Fig. 2. (a) SEM images of a representative composite microsphere, (b) higher magnification image captured from the surface of the microsphere (inset: the particle size distribution of EuD_4TEA crystals), (c) FM image of the same microsphere, (d) higher magnification image captured from the surface. Thermogravimetric analysis of the composite spheres provides nearly 20% remaining by mass after thermal treatment above 700 °C.

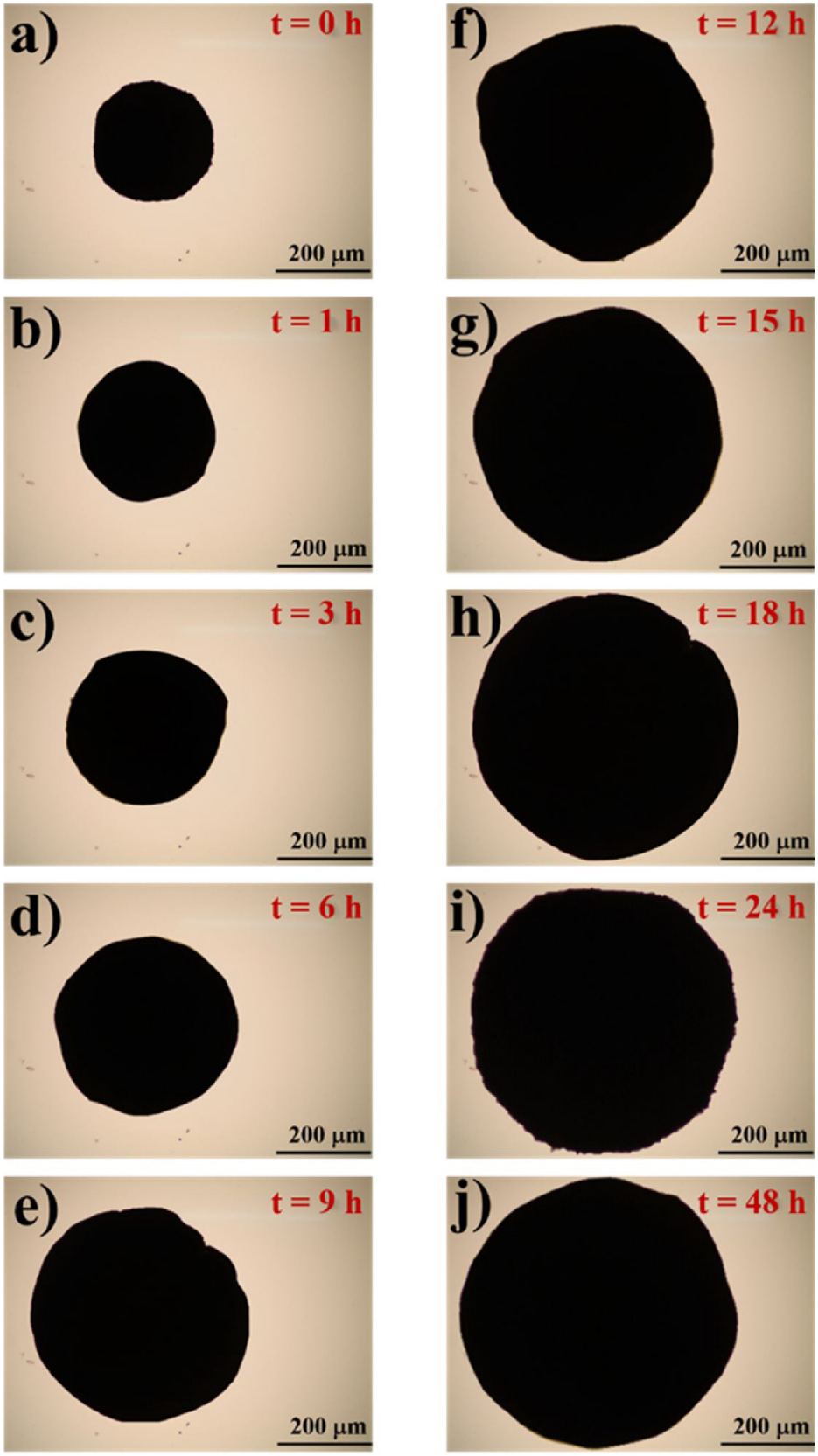


Fig. 3. The optical microscopy images of a representative microsphere (a) before and (b–j) after water treatment at various swelling time.

diameter of microsphere is nearly 180 µm (Fig. 2a). The surface of the spheres was found to be rough (Fig. 2b). The particle size distribution of EuD_4TEA crystals shows a classic Gaussian behaviour and the mean diameter appears to be 20 µm. The surface of obtained composite film has pores with submicron size (Fig. 2c). Photoluminescence (PL) and triboluminescence spectra of the microspheres

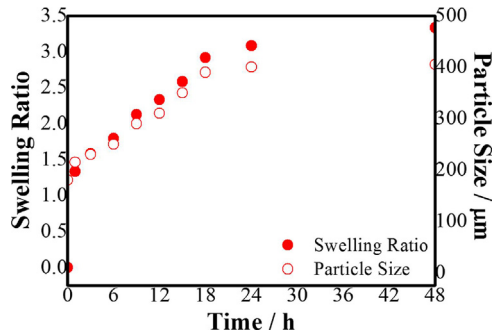


Fig. 4. The change in swelling ratio (left axis) and particle size of composite microsphere (right axis) with respect to the hydration time from $t = 0$ to $t = 48$.

depict similar spectral signal appearing at 614 nm (not shown). FM image shows a classical transition color (reddish-orange) of Eu(III)-based compounds (Fig. 2d). The presence of alginate does not remarkably change the characteristic of the composite system in terms of spectral colour. The interaction of EuD_4TEA and alginate is investigated by vibrational spectroscopy. The signals of Na^+-alginate are shifted when the cation is replaced with Ca^{2+} and then Eu^{3+}(not shown). This shift is also seen for the spectrum of the composite microsphere after precipitation of the TL crystals. This shift may hint about the interaction of alginate and TL crystals.

One can consider the direct replacement of Na^+ with Eu^{3+} (skipping the step of Ca^{2+}) to obtain EuD_4TEA crystal. This experiment has been performed in this study; however, TL emission appears very weak and hard to detect the resulting TL signal at least in this configuration of the experimental set-up. The reason behind this weak or no signal could be the small size of the EuD_4TEA crystals with submicrometer size. Meaningful TL signal could not be achieved from small crystals formed in situ because the TL performance is proportional with the crystal size.

3.2. TL and PL of the composite microsphere after water treatment

Alginates have carboxylic acid groups of each monomeric unit so that they have high capacity to absorb large volume of water. A representative particle is followed by optical microscopy through the swelling process from 1 h to 48 h. Fig. 3a-j exhibits the optical microscopy images of single microsphere with respect to swelling time (from $t = 0$ to $t = 48$).

The particle size is getting larger in swelling, the diameter shows a linear increase from 180 to 395 μm in 24 h. The size is not significantly changed after 24 h even the swelling time is extended to 48 h (the size of single particle is 405 μm) meaning that the system may reach equiblirium in nearly 24 h period (Fig. 4).

TL response of the microsphere is shown in Fig. 5a. The emission for the composite microspheres upon mechanical impact was registered for both dry and swollen hydrogel microspheres at 1–48 h. The wavelength and shape of the spectra is almost unchanged after the application of mechanical impact (0.05 N·s). The signal with a shoulder appears at 612 nm. TL intensity of pristine composite ($t = 0$) is around 3.2×10^4 count/second. The intensity of the sphere swollen in 1 h is decreased by 62% (1.2×10^4 count/second). The decrease of TL emission might be originated from the structural heterogenity of the medium upon swelling. Such that some regions of the microspheres structure are partially hydrated in 1 h; on the other hand, some other regions are less hydrated. This heterogeneity may arise optical scattering and a reduction of TL signal takes place.

As the time of swelling is extended under a fixed mechanical impact, a systematic increase of TL intensity is observed from the hydrogel beads. The enhancement of the TL signal can be

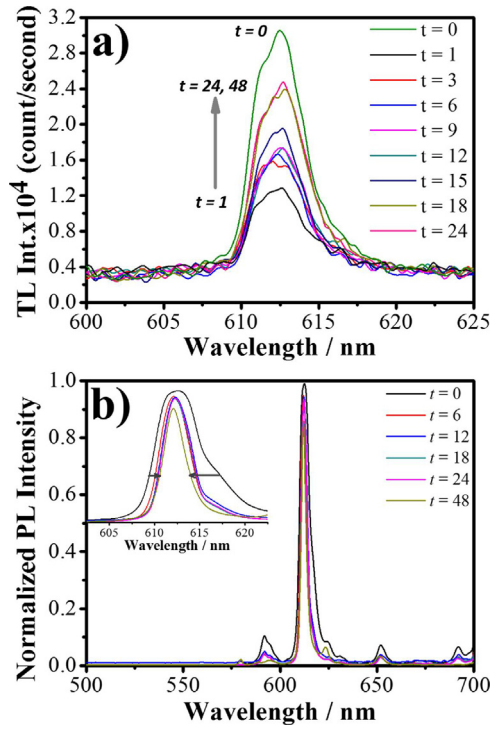


Fig. 5. (a) TL emission of the composite microsphere before and after swelling from $t = 0$ to $t = 48$ (the applied force for each time: 0.05 N·s) (b) PL spectrum of the composite microsphere before and after swelling in 6 h period.

originated by the simultaneous occurence of two reasons: One of them could be the development of a homogeneous medium for the transmittance of TL signal upon swelling. The development of the homogenity can be validated by the shape of the PL spectra of the swollen hydrogels [52]. Fig. 5b exhibits the PL emission of the composite before and after different level of swelling (measurement was done in 6 h period). The PL spectrum of the pristine complex displayed a broad distribution with a signal centered at 614 nm. The full width at half maximum (FWHM) is initially 12 nm. While the system approaches to 24 h in equilibrium, it is reduced to 4 nm. When the swelling time is extended to 48 h, the value of FWHM is further decreased to 2 nm. The systematic reduction of FWHM may prove the development of homogeneity of the microsphere and better dispersed particles in the alginate spheres as the system approaches to equilibrium of swelling. Another reason of the intensity increase upon swelling could be the improvement of the dispersion of crystalline particles in the microsphere volume. The EuD_4TEA crystals are stated on the surface of the alginate beads. Swelling enlarges the volume of the composite microspheres such that loosely-associated crystals and crystal aggregates are separated, i.e. interparticle distance between EuD_4TEA crystals increase. Each crystal domain may act as emitting center. The better distributed particles in composite sphere, the higher collective emission from the composite microspheres.

TL intensity is finally reached up to around 2.47×10^4 count/second at $t = 24$ h swelling and the maximum TL intensity remains unchanged for the microsphere swollen up to 48 h hydration under identical mechanical action. Although a clear systematic increase of the TL intensity is observed as the swelling time is extended, it never reaches to the initial TL value at dry state even the microspheres come into equilibrium of swelling. Since the polymeric system has viscoelastic feature, it absorbs certain amount of energy during the mechanical impact. The rest of the energy is transffered to the EuD_4TEA crystals; as a result, less mechanical force remains to be applied to the microspheres. Thus, weaker sig-

nal is registered for swollen gels compared to TL intensity at dry state.

4. Conclusion

A bottom up approach is presented to produce alginate microspheres covered by homongeneously-distributed TL EuD_4TEA crystals obtained in situ. The procedure is based on two consequtive steps: i) the formation of alginate/Eu^{3+} gels ii) in situ precipitation of EuD_4TEA by the treatment of the complex with the solution of TEA and DBM. The pristine TL microsphere has 180 μm-diameter which is more than doubled in 48 h hydration. The TL and PL performance of the alignate-EuD_4TEA are monitored throughout the sweeling process. As the swelling of the beads is getting equilibirium, the intensity of TL emission shows a systematic increase. There may be two origins of this enhancement. First could be the development of homongeneous medium in the course of the swellling process. The reduction of FWHM of the PL signal can be attributed to the validation of homogenous medium during swelling. Second could be the separation of the TL crystals in the bead structure. The volumetric increase of the alginate-EuD_4TEA bead inevitably increases the distance between the loosely associated individual crystals and aggregates developed over the surface of the microspheres in situ. Thus, the domains are separated and better dispersion of the particles is achieved. A collective response of the domains increases the TL emission upon the mechanical impact. Consequently, we confirm that TL crystals can be generated over the surface of alginate beads in situ and the resulting composite microspheres show intense triboluminescence. The composite spheres undergo remarkable swelling in 48 h. The spectral feature of TL signal (intensity and shape) can be controlled by the swelling ratio. The alginate/EuD_4TEA composite microspheres are promising candidates for mechanosensing platform and can be applied both in dry and aqueous systems.

Author Contributions

The manuscript was written through contributions of all coauthors. They have given approval to the final version of the manuscript.

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Biographies

Anil İncel has received his master degree from İzmir Institute of Technology in 2016 and he started his PhD study at Biofilms Research Center for Biointerfaces, Department of Biomedical Sciences, Faculty of Health and Society, Malmö University.

Mustafa M. Demir is full professor and chairman of Material Science and Engineering of İzmir Institute of Technology. His scientific activity includes material synthesis, electrospinning, polymer and inorganic composites, polymer processing. He is co/author of over sixty journal articles.