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Functionalized surfaces created by perturbation in luminescent polymer nanocomposites: Materials for forensic and security ink applications

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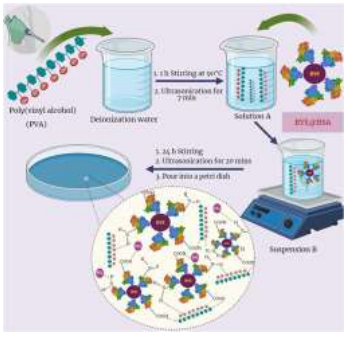
Abstract

Europium ions doped pearl white dispersed effectively in PVA binder using Bovine Serum Albumin (BSA) as a stabilizer. Nano-powders (NPs) were synthesized by using propellant chemistry approach. Further, these NPs were incorporated into the polymer binder matrix by solvent casting approach to obtain nanocomposites (NCs). BSA stabilizer made any avenue for the perturbation to the secondary protein chains leading to functionalized surfaces. This helped in obtaining the uniform dispersion of the filler added. Different proportions of (2–10wt%) functionalized BiOCl-Y_2O_3:Eu^{3+} NPs were loaded into PVA matrix. X-ray diffraction profile shows the effective incorporation of the NPs into the polymer. Upon exciting at 398nm near UV light, the NC shows strong red emission at 612nm along with other three peaks were due to the transition from $^5D_0$ to ^7F_j (j=1, 2, 3 and 4). The highest PL intensity was registered for 8wt% NPs in PVA matrix. The optimized NCPs were further utilized for various technological applications namely solid-state lighting, forensic and security ink preparation. The latent fingerprints developed on commonly encountered objects were investigated from the functionalized BiOCl-Y_2O_3:Eu^{3+} NCPs by powder dusting method. The results undoubtedly revealed all the Type – I – III ridge details irrespective of surfaces. Anti – counterfeiting ink has been developed and testified on various surfaces. The overall results clearly revealed that surface functionalized NCs were quite suitable for multifunctional applications.

Graphical Abstract



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Introduction

Forging is that the second biggest cause of transnational corruption, making up 39% of all global crime income. Not exclusively is forging a colossal financial weight, yet it's anything but a major danger to human wellbeing and security. The World Health Organization reported that about 10% of medicines sold in non-industrial nations was fake. Indeed, even fake electronics represent a huge danger to protection,

particularly for the military and space productions, as items around there commonly have an all-encompassing term of utilization between examinations [1], [2], [3], [4]. Because of these issues, the occasion of most recent enemy of forging marks is of foremost significance [5], [6]. Flow against duplicating techniques incorporates such methodologies as watermarks, visualizations, and electronic following recurrence recognizable proof. By and by, novel methodologies should be continually formed and fused into new items to stay at least one stage before the forgers [7].

As of late, practical gadgets with special optical or fluorescent properties have accumulated interest in making security marks with simple visual analysis. Methodologies for fostering this optics-based enemy of duplicating labels range from exploiting the photo bleaching impact of colorants to the difficult to mimic optical impacts of underlying shadings [8], [9].

Recently, the photoluminescence (PL) anti-counterfeiting technology supported many rare earths (RE) doped fluorescent phosphors, dyes, and quantum dots etc, have been established [10]. In any case, these advancements actually have faults in photograph fading, helpless deprived thermal and photo steadiness, and notable luminescence quenching by means of lattice changed, which seriously prevent their huge scope of industrial applications. Lanthanide ions caped nanocrystals, particularly europium and terbium particles, were utilized as, high fluorescence efficiency with prolonged fluorescence life time [11], [12], [13]. Consequently, the PL phosphors reinforced in lanthanide-based nanocrystals have probable applications to anti-counterfeiting; meanwhile their compensations in improved security, easy identification, and struggle of replication. Anti-counterfeiting resources comprising trivalent lanthanide RE element ions were broadly useful in anti-counterfeiting for its outstanding luminescence strength and free from harmful radiation [14].

Recently several studies indicated that pure and nanomaterials integrated polymer NCs were tremendously improved the material properties. Further, the NMs also showed superior properties to the polymers with the addition of appropriate quantities. The resultant NCs which were efficient for various applications consists of matrix and filled with more than two or more phases, in which the dimension of the filler is nano-range owing to its superior properties (mechanical, thermal, optical). They can be used for biomedical and optoelectronic applications etc. [15]. The NMs in general slow aggregation owing to their nano dimension with huge surface area. Hence it is obvious that aggregation can be minimized for technically polymeric NCs. Therefore, it is necessary for chemical and physical functionalization to enhance the interaction between nanofiller and polymer matrix [16]. Polyvinyl alcohol (PVA) is a semicrystalline, glassy, low cost, less toxic, and biodegradable with extraordinary water soluble [17]. Hence, it is quite useful in many applications such as sensors, drug delivery, degradation of heavy metal ion, PVA contains polar -OH groups in every alteration C-atoms, it is easily reacting with organic/inorganic phosphors via physico- chemical interactions.

The finger marks establish perhaps the main classes of actual proof in the field of forensic science, and valuable piece of proof on the grounds that every individual has an interesting unique finger impression [18], [19]. Periodically, these imprints were faintly noticeable dormant prints that should be created utilizing techniques like powders, synthetic vapor or elective light sources. The advancement of nanophosphor materials with novel and synergetic physicochemical properties has established substantial consideration because of their broad use in optoelectronic devices and biomedical applications [20], [21], [22], [23], [24].

Due to large surface to volume ratio of NPs, it is obviously expecting aggregation. Sonochemical irradiation along with natural protein (BSA) satisfies can lead to uniform distribution with the PVA matrix. Surface functionalization with numerous modifiers is an efficient route to enhance the preparation of NCs [25]. BSA was driven from serum cow having high stability with low cost, which is often more used for biological studies. This protein contains 583 amino acid units. This heart shaped protein has free sulfhydryl group that facilitates to trap active oxygen and nitrogen for instance biocompatibility, biodegradability, heat resistance up to 62°C for 10h and high solubility at pH of 7.4. These properties combined with non-toxicity and good ligand-connection trait which made it as an eligible bio-safe modifier for modification of the NPs. Recent published papers clearly showed that ultrasound irradiation is quick and efficient to produce homogeneous eco-friendly NCs films [26], [27]. During perturbation, the secondary structures of the protein occurs due to the disrupting the disulphide bonds and leads to partial loss of α-helix or change in the polarity of the environment. These changes results in differed molecular interactions viz., excited-state reactions, energy transfer collision quenching or molecular rearrangements which end up with structured metal oxide NPs.

Ultrasound route in fabrication of nanostructured materials were highly effective because it leads to heterogeneous crystallization and rates counting on the frequency were repeated when liquid is sonicated via high-intensity sound waves [28]. During these progressive cycles, when the bubble arrives at a specific size, it's strengthened by ultrasonic waves and expansions in size, then; at that point the bubble gets unsteady and firmly crumbles and makes a problem area inside the fluid. Since these progressive cycles happen so quickly, they were doing not permit the core to develop and in each falling bubble, a few cores were framed, whose development is confined by short deterioration. Further, ultrasound enables crystal nucleation and decreases the width of the stable region to supply uniform and lesser particles [29], [30], [31].

In this paper, Bismuth Oxychloride-Y_2O_3 doped Eu^{3+} (BYE)@BSA/PVA films were prepared by solution casting method and characterized by XRD, SEM, FTIR, DRS, TEM/ HRTEM PL spectroscopy etc. The results show that the use of optimized NCs in an orange–red emanating fluorescent security ink upon UV excitation shows an accomplished development in anti-counterfeiting technology. Table 1 shows the comparative analysis among the various host materials which were doped with Eu^{3+} ions and their luminescence/forensic importance was reported which includes the importance of our prepared samples also [32], [33], [34], [35], [36], [37], [38], [39], [40], [41], [42], [43], [44], [45], [46], [47], [48], [49], [50], [51].