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Carbon Dot-Lanthanide Composite Based Smart Luminescent Anticounterfeiting Material

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ABSTRACT

In this emerging technology world, the counterfeit of products are increasing due to raising the economy of industry. Counterfeiting is as old as the human desire to create objects of value. There are number of products, which can be easily duplicated by simple processes and the product is accurate and precise. Counterfeit is a problem of product security, the rise and affects every product category from consumer goods to medicines and spare parts. Products can furthermore contain non-active or even toxic-ingredients. So, luminescent materials are useful to detect different counterfeit products at different wavelength. The carbon dots-lanthanide composite based gel formulation is used to coat on different subtract and according to the process their different characterization part for the prevention of counterfeit problems. Carbon dots-lanthanide composites are basically easy to synthesis and they have fluorescent property, which can help to make product unique and diverse. With help of UV chamber, the carbon dots-lanthanide composites are easily detected at some particular wavelength. So by using this property, the gel formulation can be fabricated to coat on different subtract and characterize different surface morphology for the future precepts. UV-Vis- spectrophotometer was utilized to differentiate optical properties and fluorospectrometer was exploited to differentiate fluorescent properties of carbon dots, carbon dots-lanthanide composite and CDs-lanthanide based fluorescent ink. FT-IR and viscometer were used characterized other properties of carbon dots-lanthanide based fluorescent ink. This research article is the revised article of one step synthesis of carbon dots based smart fluorescent security ink.

1. Introduction

Luminescent materials have drawn great attention because of their unique optical behaviour and diverse fluorescence properties in different sectors including bio-imaging, optoelectronic devices, security purpose, sensing applications etc. Carbon dots and lanthanide materials both have photoluminescence properties, which can be useful in many different ways [1]. Carbon dots (CDs) have emerged as most precious gifts in nanotechnology because of their magical properties and applications. CDs are typically carbon nanoparticles, most of them with average diameter less than 10 nm [2]. Lanthanides are becoming vital to many kinds of advanced optical materials and technologies based on a wide range of emission spectra covering the ultraviolet (UV)-visible-near-infrared (NIR) region, and those involving NIR luminescence have received growing interest in view of exciting applications in telecommunications and associated lasers and LED/OLED devices, as well as in bio-sciences, etc., [3,4]. Among the trivalent lanthanide ions, Nd³⁺, Yb³⁺, Er³⁺ and Ho³⁺ show UV emissions, while Eu³⁺ ions (red light) and Tb³⁺ ions (green light) can provide visible emission, which can be seen by naked eyes. However, lanthanide ions suffer from low luminescence quantum efficiency due to their low molar absorptive and narrow absorption band [5,6]. Considering their relatively low chemical, optical, and thermal stabilities, lanthanide complexes have been excluded so far from practical applications. In addition, the water soluble CDs can supplement the limitation of the hydrophobicity of lanthanide complexes, which is advantageous for optical bioimaging. However, there are rare reports on constructing a system based on CDs and lanthanide complexes, which offers and regulates different emission covering from visible to NIR spectral region [7-9]. In this paper, a new kind of carbon dots-lanthanide composite was synthesised and based on that smart fluorescent ink was fabricated for the prevention of the counterfeit of the products.

2. Experimental Methods

2.1 Materials

All the materials and solvents were purchased from commercial sources (Sisco research laboratories Pvt. Ltd., India) and used as received unless stated otherwise. Citric acid (anhydrous, extrapure AR, 99.5%) and ethanolamine (extrapure AR, 99%) were obtained from SRL company and used without further purification process. Terbium nitrate (extrapure AR, 95%) was purchased from Sigma Aldrich Company. Milli-Q water and spectroscopic grade solvents were used for all measurements. Fourier-transform infrared (FT-IR) spectra were measured on a JASCO FT-4600 spectrophotometer by putting directly the sample solution into it. Solution phase optical absorption spectra were recorded on a JASCO V-670 spectrophotometer by using a quartz cell with optical path length of 1 cm after diluting the sample in Milli-Q water. Steady state photoluminescence (PL) spectra were recorded using a JASCO FP-6500 fluorophotometer by using a quartz cell with optical path length of 1 cm. All solution phase PL measurements were carried out at room temperature (RT) and without removing dissolved O₂. Atomic force microscopy (Nanosurf C300) was used to find the particle size after diluting the sample into Milli-Q water and dried it on MICA sheet at room temperature. The gel was characterised by Brookfield viscometer after diluting the sample in 4:6 ratio with Milli-Q water.

2.2 Synthesis of Carbon Dots

The synthesis was followed by procedure reported by Gregory Ethan LeCroy et al. [10]. In brief, the one step hydrothermal process was used to synthesis crystalline carbon dots. 500 mg of citric acid (CA) was dissolved in 45 mL of Milli-Q water along with 1 mL of ethanolamine. The solution was mixed for few minutes on the stirrer and then it was transferred into the teflon coated 90 mL of white chamber, which was a part of small autoclave system. After that the autoclave was heated along with the solution in it in muffle furnace at 175 °C for 4-5 hours. The solution was cooled and characterised by FT-IR and AFM for structural property. The fluorescence property was characterised by UV-Vis-spectrometer and fluorospectrometer.

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2.3 Synthesis of Carbon Dots-Lanthanide Composite

For the synthesis of carbon dot-lanthanide composite, 10 mL of carbon dot solution was mixed with 5 mL of terbium nitrate aqueous solution; and stirred the solution for 3 hours. The solution's colour was changed. Centrifuged the solution with membrane filter and lyophilise the solution for overnight to get powder form [11].

2.4 Synthesis of Carbon Dot-Lanthanide Composite Based Gel Formulation

The gel formulation was synthesised by literature reported by Apostolos Koutsoukis et al. [12]. Previously, the crystalline carbon dots-lanthanide composite was synthesised, which was mixed with commercially available water base varnish NAB polyurethane in ratio of 1:9. The process went overnight for better mixing of the sample and solvent. The commercial varnish contains a mixture of styrene-acrylic-emulsion, acrylic resins, and emulsion of polyethylene wax.

3. Results and Discussion

3.1 Characterization of CDs

For analysing the structural property of carbon dots, the XRD instrument was not useful because of the hydrophilic property of carbon dots. So the structural property was analysed by the FT-IR instrument. FT-IR instrument can detect the functional group of the material, so different materials can be detectable by the FT-IR graph. Fig. 1 shows the FT-IR graph, which concluded the different carbon, oxygen and hydrogen bonds.

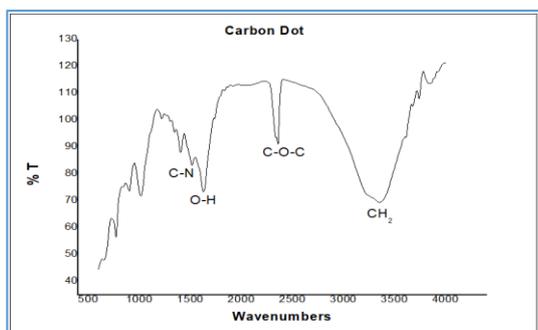


Fig. 1 FT-IR spectra of carbon dots

Here the absorption band 3450 cm^{-1} shows the presence of methylene group, which correspond to the saturated hydrocarbon from amorphous carbonic framework in the CDs. And $3500\text{--}3100\text{ cm}^{-1}$ concludes the O-H and N-H stretching vibrational peaks. Due to little bit vibration of the O-H group, small peak can be detected on 3441 cm^{-1} [2]. The peaks at around bands 1600 cm^{-1} and 2400 cm^{-1} conclude the carboxylic group. Here another stretching vibration peaks found nearest to the 1500 cm^{-1} with O-H and C-N group. A strong absorption peak nearest to 2450 cm^{-1} is assigned to C-O stretching vibration peak, revealing the existence of abundant C-O or C-OH groups. Further, the fluorescence property of CDs was analysed by the UV-Vis-spectrometer and fluorospectrometer. Fig. 2 shows the UV-Vis spectrometer spectra of CDs. The graph shows some oscillator peaks between 300 nm to 500 nm wavelength.

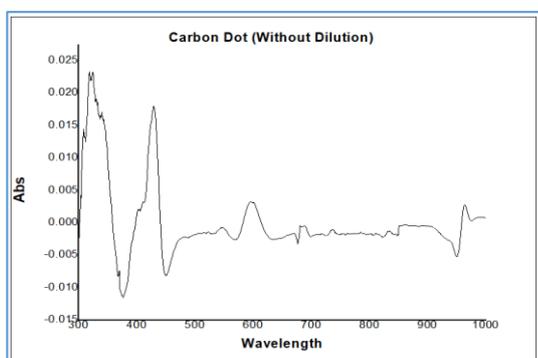


Fig. 2 UV-Vis spectra of carbon dots

The graph also indicates little bit dissociation energy after 650 nm wavelength. It has maximum intensity around 350 nm to 400 nm wavelength. The blue fluorescence absorbs at its highest intensity at 380 nm wavelength. But it is also depend on the parameters of the spectroscopy. Similarly, Fig. 3 shows the fluorescence spectra of the CDs.

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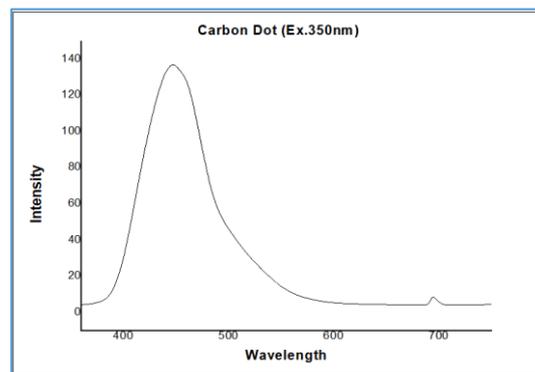


Fig. 3 Fluorescence spectra of carbon dots

Carbon dots have their own excitation peak at 459 nm wavelength. After putting the excitation wavelength 350 nm in spectroscopy parameter, the typical and diverse fluorescence absorption shows at the 459 nm wavelength. In contrast, the absorption peak of CDs in water is at 350 nm and the luminescence spectra between 400 nm to 500 nm show a maximum at 459 nm with strongest intense peak [2]. The absolute QY of CDs in water is between 10-17% higher than of the pure CDs. When further increasing the absorption wavelength of CDs in water, the luminescence peak will become broader and shift to its original position.

The CDs particle size were analysed by the AFM instrument. Fig. 4 shows the AFM image of CDs. Fig. 4 shows the particle size of CDs, which is in between 30 nm to 40 nm. The particle size was calculated by the Nanosurf C3000 model software. The software can be easily detected the height of the particle, which was placed and dried at the top of the MICA plate. CDs have hydrophilic property, so some particles become clusters to joint with each other in atmosphere. The size can also be calculated from the 3D image of CDs, which shows the surface of the MICA plate and some CDs particles are placed on it.

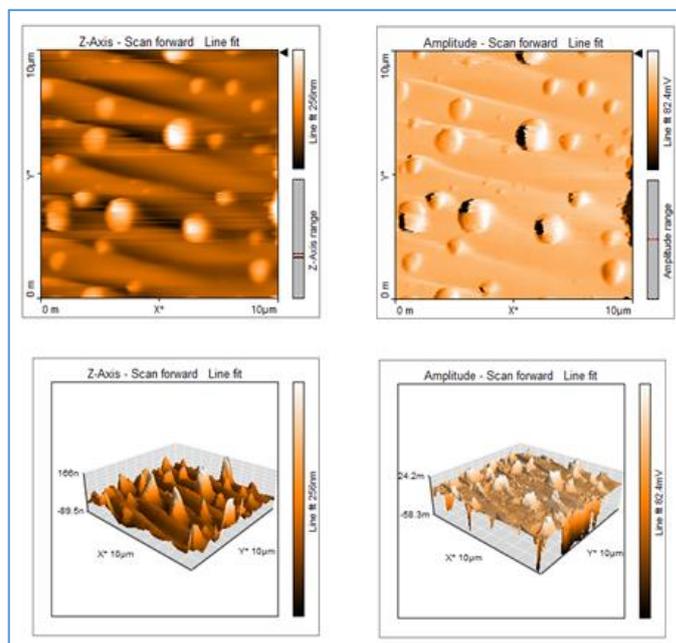


Fig. 4 AFM images of CDs (2D & 3D image)

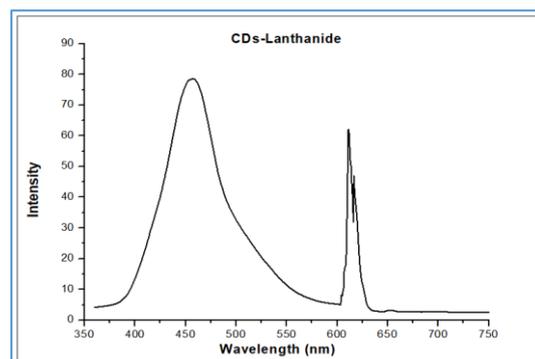


Fig. 5 PL spectra of carbon-dot-lanthanide composite

3.2 Characterization of CDs-Lanthanide Composite

Fig. 5 shows PL spectrum of the composite. The PL spectrum shows the presence of carbon dot and lanthanide. Carbon dots and terbium have their own excitation peak nearest to 450 nm and 613 nm respectively. For the low quantity of terbium in the solution, the peak is not that type intense, but it is clearly showed the fluorescence of the terbium nearest to 613 nm. The UV spectrum shows some oscillator peaks between 200 nm to 400 nm wavelength. Because of terbium, the peak is shifted from the 300-500 nm to 200-400 nm (Fig. 6).

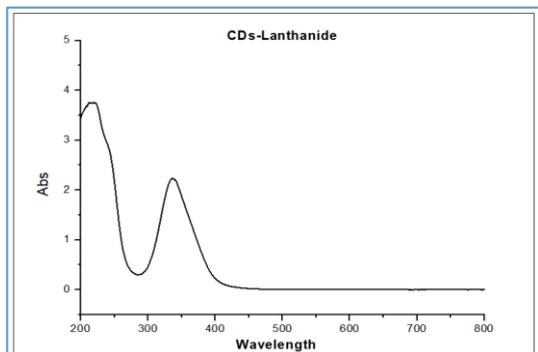


Fig. 6 UV-Vis spectra of carbon dot-lanthanide composite

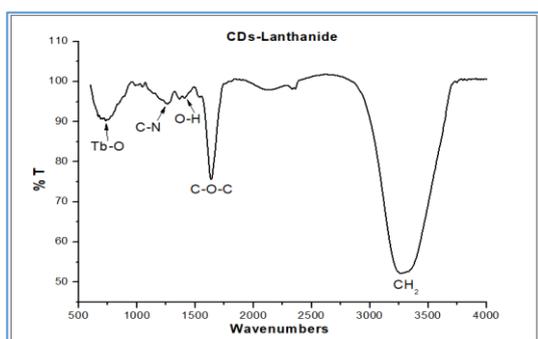


Fig. 7 FTIR graph of carbon dot-lanthanide composite

In FT-IR graph (Fig. 7), the absorption band 3450 cm^{-1} shows the presence of methylene group, which correspond to the saturated hydrocarbon from amorphous carbonic framework. Here another stretching vibration peaks found nearest to the 1500 cm^{-1} with O-H and C-N group. A strong absorption peak nearest to 750 cm^{-1} is assigned to Tb-O stretching vibration peak, revealing the existence of terbium means lanthanide group.

3.3 Characterization of CDs-Lanthanide Composite Based Gel Formulation

As discussed previously, the characterisation study of CDs-lanthanide composite based gel formulation has been done and Fig. 8 shows the UV-Vis spectra of the gel/ink. The graph shows the presence of the polymer, which was mixed with the carbon dots to form gel formulation. The graph shows some oscillator peaks between 650 nm to 750 nm wavelength.

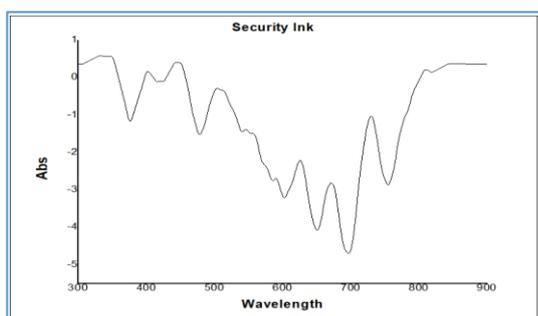


Fig. 8 UV-Vis spectra of gel/ink

The graph also indicates little bit dissociation energy before 650 nm wavelength. It has maximum intensity at 700 nm wavelength. The peak is shift after mixing the carbon dot into polyurethane solution. The absorption peak shows between 350 nm to 450 nm, which is shifted between 650 nm to 750 nm. But still it has blue fluorescence absorbs at its highest intensity. But it is also depend on the parameters of the spectroscopy.

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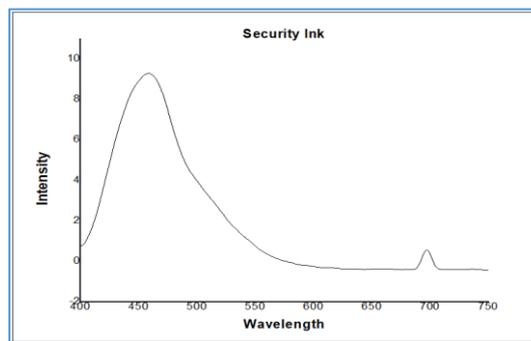


Fig. 9 Fluorescence spectra of gel/ink

Fig. 9 shows the fluorescence spectra of the gel, which concluded that after mixing the polymer with the carbon dots; it gives blue fluorescence colour at the highest and intense absorption peak at 400 nm. The fluorescence absorption peak is shifted from 380 nm to 400 nm because of the presence of the polymer in the solution. The blue fluorescence colour is easily visible in the UV-Vis chamber. Fig. 10 shows the comparison of fluorescence property of carbon dot and carbon dot based gel formulation.



Fig. 10 Fluorescence comparison of carbon dots and carbon dot based gel formulation

In the image Fig. 10, the first beaker on the left hand side shows the blue fluorescence of carbon dot-lanthanide composite based gel formulation and on the right hand side beaker shows the fluorescence of carbon dots-lanthanide composite. The right hand side beaker clearly shows the intense blue colour fluorescence of CDs and the left hand side beaker has blue colour fluorescence, but the intensity is bit low because of the presence of the polymer in it. With changing the quantity of the carbon dot in polyurethane solution, the fluorescence spectra and intensity are also changed.

The fluorescence spectra of the gel concluded that after mixing the polymer with the carbon dots-lanthanide, it gives blue-green fluorescence colour at the highest and intense absorption peak at 400nm. The blue fluorescence colour is easily visible in the UV-Vis chamber. The quantity of the terbium is less so the green emission spectra are not intense as compare to the carbon dot blue emission spectra. Thus the image shows the comparison of the carbon dot-lanthanide solution and carbon dot-lanthanide based ink.

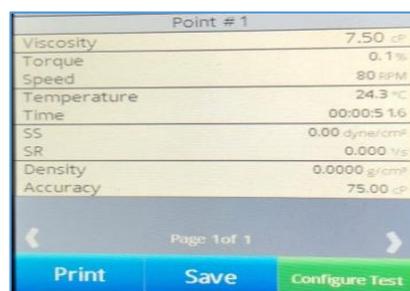


Fig. 11 Viscosity property of the synthesised ink

By Brookfield viscometer instrument (Fig. 11), the viscosity is accurately measured in centipoises (cp) unit. The gel/ink formulation has to be viscous in between 8-20 cp and it is also depending on the application part of the gel/ink. Here, the gel/ink solution has the viscosity around 7-8 cp, to be precise 7.50 cp, which is good for the security ink application purpose. Also the results got 75-80% accuracy by this instrument.

4. Conclusion

For one step synthesising carbon dots and carbon dot-lanthanide composite, the hydrothermal method is very accurate and precise. It gives the crystalline and much fined nanoparticles and nanocomposite of carbon and carbon dot-lanthanide respectively. By one day process of synthesising, having blue fluorescence carbon dots-lanthanide composites are ready for further characterisation. It has 30 nm to 40 nm particle size with high intense luminescence peak at 380 nm. With the help of the ethanolamine as a precursor, the carbon dot solution made as transparent. Synthesis process of carbon dot-lanthanide based ink is very easy and less time consuming. By mixing 3 solutions together, the ink will be ready. The lanthanide-carbon dots based security ink is very easy to synthesis and has wide broad application area. Since the solution is transparent, so it can be coated on different substrate for different applications. The gel formulation is very unique with dual fluorescence. So it is very tough to counterfeit it and counterfeit products can be easily detectable in less time. The transparent ink has fluorescence solution, which has many applications in bio-imaging, energy sector, security purpose (anti-counterfeiting), drug delivery utility, etc.

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