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A Comparative Study on Morphological and Optical Properties of Pure and Oleic Acid Added Organic Nanocrystal of DAST Embedded in PVA Matrix for NLO Applications

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Abstract

Organic nanocrystals exhibit enhanced nonlinear optical (NLO) properties over the bulk crystals of those organic molecules. In this article, an attempt has been made to prepare organic nanocrystal of DAST via two different approaches. In the first case, the synthesis of nanocrystal was explored via a cost effective and low temperature solvothermal method. In the second case, the DAST nanocrystal/PVA and oleic acid assisted DAST nanocrystal/PVA composite films were prepared in order to combine the enhanced nonlinear optical properties of the organic nanocrystalline material with flexible polymers. The structure and morphology of as-prepared DAST nanocrystal embedded in PVA matrixwere analyzed using powder XRD and scanning electron microscope (SEM). Fourier transform infrared (FT-IR) analysis confirms the presence of various functional groups. The optical property of the DAST/PVA composites was characterized by UV-Vis absorption spectrum. The addition of oleic acid significantly alters the crystal growth process of DAST nanocrystal, resulting in the generation and stabilization of regular nanosized DAST nanorods.

Keywords: Organic nanocrystals, functional groups, optical absorption, morphology, composite

1. Introduction

Terahertz (THz) technology has attracted much attention in the recent years due to its potential applications such as nonlinear optics, topographic imaging, label-free genetic analysis, cellular level imaging and chemical and biological sensing [1]. The most pressing component technology to be developed remains in the area of THz sources and many applications yet to be realized lie in wait [2]. Among the various classes of materials investigated worldwide, ionic organic crystals like 4-N, N-dimethylamino-4-N-methyl-stilbazolium tosylate (DAST) have been a recent source of interest as THz emitters due to its high nonlinearities in combination with a low dielectric constant [3]. The growth of high quality bulk DAST crystal is still a limitation and this hinders to exploit its high figure of merit. The use of organic materials for optical applications is generally limited by their insufficient chemical stability and mechanical resistance. In order to avoid these basic drawbacks and to take advantages of the optical properties of organic materials at the nanometer scale, Sanz and co-workers have developed hybrid (organic-inorganic) material by preparing organic nanocrystals in sol-gel glasses [4]. It has been proposed that organic nanocrystals could exhibit enhanced nonlinear optical (NLO) properties over the bulk crystals of those organic nonlinear molecules [5]. In this connection, DAST nanocrystals, which combine the unusual properties of nanocrystals have been prepared by dispersing them in a non-polar liquid using reprecipitation method [6]. However, only submicrometre DAST microcrystals have been achieved. Zheng et al. [7] have prepared DAST nanocrystals with enhanced NLO properties at nanometre scale due to influence of carbosiloxane dendrimer, employing the re-precipitation method. Stable and size controlled DAST nanocrystals were prepared and the size is reduced significantly below

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100 nm. Macchi et al. [8] have prepared DAST nanocrystals in a poly methyl methacrylate (PMMA) film by electric poling. However, it was found that the nanocrystal is not of high quality because of the instability caused by the PMMA polymer under the electronic beam. Hence, significant challenges are involved in the preparation of DAST nanoparticle to incorporate them into a matrix while preserving the size distribution. Poly vinyl alcohol (PVA) is one of the most frequently used host molecules and it forms a cross-linked structure that could hold cavities within [9].In the present work, an attempt has been made to prepare organic nanoparticles of DAST by two different approaches. In the first case, the synthesis of DAST nanoparticles was explored via a cost effective and low temperature solvothermal method. In the second case, the DAST nanocrystal/PVA composite films were prepared in order to combine the enhanced nonlinear optical properties of the organic nanocrystalline material with flexible reprocessability of polymers. The morphologies of the nanocrystals embedded in PVA matrix were analyzed by scanning electron microscope (SEM) and the structural characterization was carried out using powder XRD and Fourier transform infrared (FT-IR) analyses. The optical properties were characterized by UV-Vis absorption spectroscopy.

2. Experimental

2.1. Synthesis of DAST nanorods

DAST (0.088 g) was dissolved in 10 ml of methanol. To this solution, 1 ml of oleic acid was added and stirred for 1 h. After stirring, 100 ml of decalin was added to the above solution.The mixture was transferred into an autoclave and kept inside a furnace at 100°C for 2 h. After 2 h, the autoclave was taken out and allowed to cool to room temperature. The resultant precipitate was filtered and dried at 100 °C for 1 h.

2.2. Preparation of DAST nanocrystals in PVA matrix

An aqueous PVA (10 wt%) solution was prepared and stirred for 24 h. Simultaneously, an equal volume of saturated DAST-methanol solution was prepared at room temperature. Later, the DAST-methanol solution was added to the PVA gel and stirred for 1 hand then casted into a Petri dish. After drying at room temperature for 2 days, the film was kept in a furnace at 100 °C for 2 h in order to remove the water molecules. Later, the film was peeled off from the dish. The colour of the film appeared red, which is the typical colour of DAST (Fig. 1).

2.3. Preparation of oleic acid assisted DAST nanorods in PVA matrix

In another synthesis procedure, oleic acid assisted DAST nanorods were prepared. The same procedure was followed as in case of DAST in PVA but in addition to that an equal mole percent of oleic acid with respect to DAST was also mixed in the DAST-methanol solution. This solution is stirred for 30 min and then added to the PVA hydro-gel.

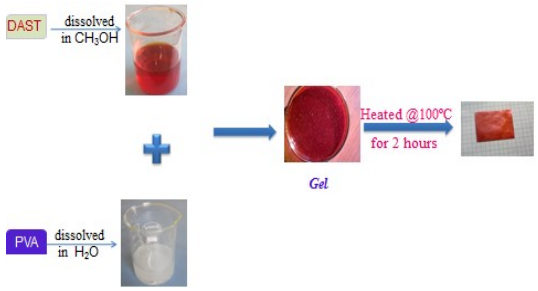

Figure 1. Synthesis scheme for preparation of DAST nanocrystals in PVA matrix

3. Result and discussions

3.1. Powder XRD analysis

Powder X-ray diffraction analysis was performed on the organic nanocrystals of DAST, at room temperature. The powder XRD pattern of DAST nanoparticles is shown in Figure 2. The (0 2 0) and (2 2 $\bar{2}$) planes are observed to be more intense than the (0 2 2) and (0 0 $\bar{4}$) which are the usually observed intense peaks for DAST crystals. At the same time, the peaks corresponding to the SHG inactive hydrated DAST crystal is not seen in the resulting pattern [5]. Further, the appearance of (0 2 0)

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and (2 2 $\bar{2}$) planes as dominant ones indicate the formation of good quality DAST nanorods. It is found that DAST crystallized into monoclinic system. The lattice parameters are; a = 10.219 Å, b = 11.328 Å, c = 17.859 Å, and β = 90.08° and V = 2067.45 Å^3. The XRD data for DAST nanocrystals obtained in this work is matching with those data for bulk crystals of DAST reported by Marder et al. [10].

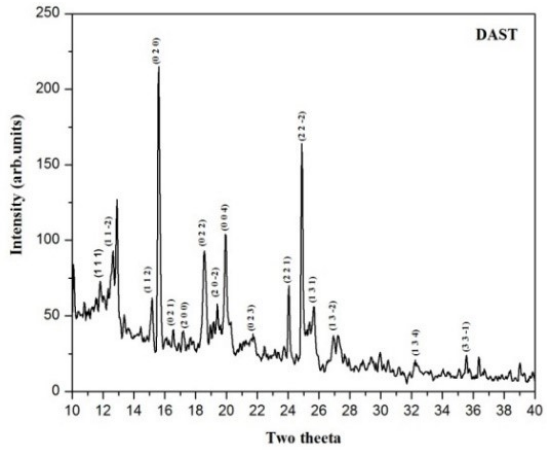

Figure 2. Powder XRD pattern of DAST nanorods

3.2. SEM analysis

SEM micrographs reveal different morphological behavior of DAST nanorods, nanocomposites of DAST/PVA and oleic acid assisted DAST/PVA (Fig. 3a-c). The size and shape of the nanocrystals embedded in PVA film was examined. The shape observed are rectangular plate-like crystals with size ranging from 200to 500nm. In an earlier report, the mean size distribution of DAST nanocrystals was found around 400 × 400 ×70 nm^3 and thus it is evident that the size of the DAST nanocrystals formed in the present work is better controlled than the previously repoterd work[6].It reveals the nanorod formation in the case of oleic acid assisted DAST/PVA matrix. In general, oleic acid assisted nanoparticles preparation helps to form onedimensional (1D) nanostructures. In the present case, the SEM picture reveals the domination of DAST nanorods along with few plate-like nano aggregates. The effect of oleic acid on the growth and morphology of the DAST nanorods is evident in the SEM micrograph (Figure 3c). It is clear that very distinct DAST nanorods with relatively high aspect ratio are obtained. The presence of DAST nanorods of diameter 300 nm – 1 μm and length 5-10 μm are evident. The images further reveal that the level of agglomeration is low for the DAST nanorods.

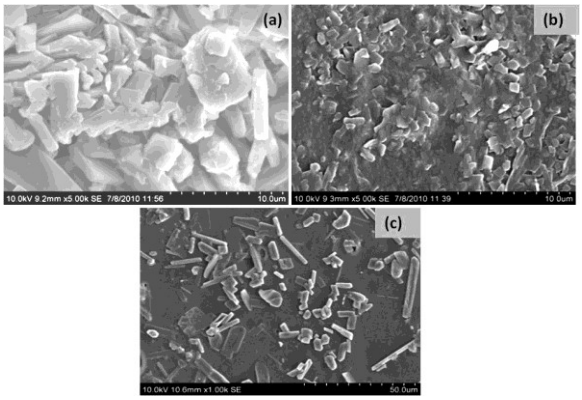

Figure 3. SEM micrograph of (a) DAST nanorods (b) DAST nanocrystals embedded in PVA matrix (c) oleic acid assisted DAST nanorods in PVA matrix

3.3. Optical absorption studies

UV-Vis absorption spectrum was recorded in the range 200 nm to 900 nm using SHIMADZU 2450 spectrophotometer. Figrue 4 shows the absorption spectra of DAST nanocrystal, DAST/PVA, oleic assistedDAST/PVA and DAST dissolved in methanol. The absorption for DAST in methanol is at 475 nm and for DAST nanorods, it is at 520 nm. When we compare the absorption spectrum of DAST nanocrystals with the DAST bulk crystal, the corresponding $\lambda_{(max)}$ is observed at 545 nm for bulk crystals. Thus there is a blue shift of 25 nm for the nanosample synthesized. The blue shift indicates the nanostructure nature of the developed sample. This result clearly indicates that the synthesized DAST nanorods are in between the molecular and bulk form. The absorption spectrum of the DAST nanocrystals embedded in PVA film is quite similar to that of bulk crystalline DAST. The narrow red shifted absorption band at 580 nm (475 nm is the cut off wavelength of DAST in molecular form) is the fingerprint of the J-type organization of the

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chromophore (4-N,N-dimethylamino-4-N-methylstilbazolium) within the crystalline structure of DAST [8]. The UV absorption spectrum of DAST nanorods prepared via oleic acid assisted synthesis reveals a strong absorption at 475 nm which is similar to that of DAST in molecular form. This result indicates that the addition of oleic acid significantly alters the crystal growth process of DAST nanocrystal, resulting in the generation and stabilization of regular nanosized DAST nanorods.

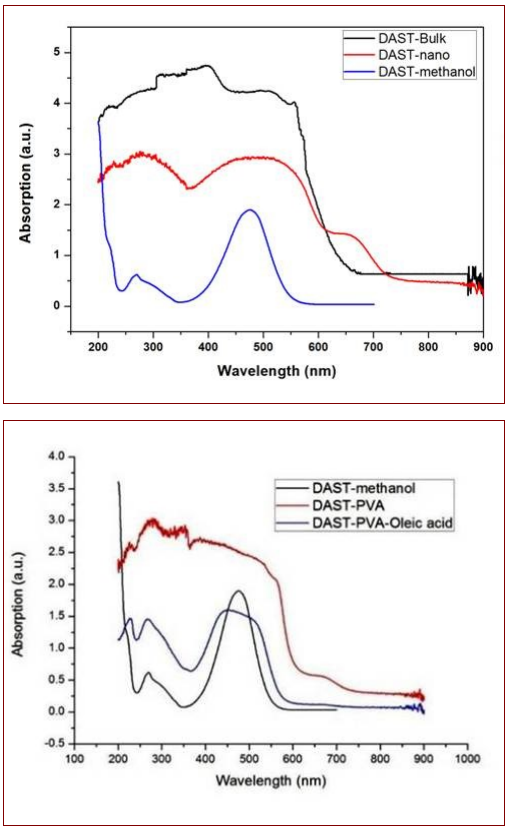

Figure 4. UV-Vis absorption spectra of DAST nanocrystal, DAST/PVA, oleic acid assisted DAST/PVA and DAST in methanol

3.5. FT-IR analysis

FT-IR spectrumof DAST/PVA and oleic acid assisted DAST/PVAwas recorded in the wavelength range 400 to 4000 cm^{-1}. For comparison, the spectrum of PVA is also provided in order to identify the functional groups and their corresponding vibrational characteristics (Fig. 5).The typical signatures in PVA which are due to O–H stretching (3435 cm^{-1}), C–H stretching (2912-2945 cm^{-1}), C–H bending (1638 cm^{-1}) and C–O (1050-1150 cm^{-1}) are observed in the FT-IR spectrum (Figure 5a). The presence of DAST nanocrystals/nanorods in PVA is confirmed by the identification of strong infrared active modes in DAST. The sharp peaks at 2924 cm^{-1} and 2919 cm^{-1} are due to the C–H stretching; the intensity of this peak is increased in DAST nanocrystals as well as in the sample with DAST nanorods. The peaks at 1585 cm^{-1} and 1581 cm^{-1} are typical C–C=C–C in-plane stretching frequency which are carbon backbone between the aromatic rings of the stilbazoliumchromophore, these peaks are also observed in both the cases. The peaks at 1179 cm^{-1}, 1163 cm^{-1} and 1179 cm^{-1}, 1165 cm^{-1} are assigned to the in-plane aromatic ring deformations, which are typical for para substituted benzenes [11]. The peaks at 564 cm^{-1} and 567 cm^{-1} are attributed to the vibrations of aromatic rings. In case of oleic acid assisted DAST nanorods in PVA, the peaks of DAST are more distinct and prominent when compared to DAST nanocrystals in PVA matrix.

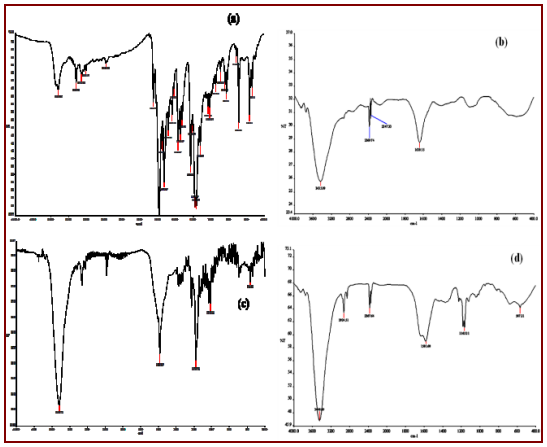

Figure 5. FT-IR spectra of (a) pure DAST (b) PVA (c) DAST nanocrystals embedded in PVA (d) oleic acid assisted DAST nanorods embedded in PVA

4. Conclusion

Organic nanocrystals of DAST, DAST nanocrystals embedded in PVA matrix and oleic acid assisted DAST/PVA matrix were successfully synthesized via cost effective and simple solvothermal method under

mild conditions. The structure of the nanoparticle was confirmed by powder XRD method. The surface features, morphology were investigated by SEM analysis. SEM analysis of nanocomposites of DAST/PVA, oleic acid assisted DSSS/PVA showed the formation of different morphologies.The UV-Vis absorption study on DAST nanoparticles confirms the blue shift of 25 nm when compared to the bulk DAST crystals.The stretching vibrations of the various functional groups were identified by FT-IR spectral studies. The flexible free-standing DAST/PVA film could be employed as potential material for THz applications.

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References

[1] Ferguson B, Zhang X.C, "Materials for terahertz science and technology", Nature Materials, 1 (2002) 26-33.

[2] Siegel P.H, "Terahertz technology", IEEE Transactions on Microwave Theory and Techniques, 3 (2002) 910-928.

[3] Jazbinsek M, Mutter L, Gunter P, "Photonic applications with the organic nonlinear optical crystal DAST", IEEE Journal on Selected Topics in Quantum Electronics, 5(2008)1298-1311.

[4] Sanz N, Baldeck P.L,Ibanez A, "Organic nanocrystals embedded in sol-gel glasses for optical applications", Synthetic Metals, 115(2000) 229-234.

[5] Oikawa H, Fujita S, Kasai H, Okada S, Tripathy S.K., Nakanishi H, "Electric field-induced orientation of organic microcrystals with large dipole moment in dispersion liquid", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 169 (2000) 251-258.

[6] Kaneko Y, Fukuda T, Onodera T, Kasai H, Okada S, Oikawa H, Nakanishi H, Matsuda H, "Anisotropic orientation control of nonpolar organic nanocrystal dispersion by external fields", Jpn. J. Appl. Phys., 42 (2003) L1343.

[7] Zheng M.L, Chen W.Q, Fujita K, Duan X.M, Kawata S, "Dendrimer adjusted nanocrystals of DAST: organic crystal with enhanced nonlinear optical properties", Nanoscale, 2(2010)913-916.

[8] Macchi R, Cariati E, Marinotto D, Roberto D, Tordin E, Ugo R, Bozio R, Cozzuol M, Pedron D, Mattei G, "Stable SHG from in situ grown oriented nanocrystals of [(E)-N,N-dimethylamino-N-methylstilbazolium] [p-toluenesulfonate] in a PMMA film", Journal of Materials Chemistry, 20 (2010) 1885-1890.

[9] Kim JM, Chae SK, Lee YB, Lee JS, Lee GS, Kim TY, Ahn DJ, "Ploydiacetylene supramolecules embedded in PVA film for strip-type chemosensors", Chemistry Letters, 35 (2006) 560-561.

[10] Marder SR, Perry JW, Schaefer WP, "Synthesis of organic salts with large second order optical nonlinearities", Science, 245(1989)626-628.

[11] Bosshard C, Spreiter R, Degiorgi l, Gunter P, "Infrared and Raman spectroscopy of the organic crystal DAST: polarization dependence and contribution of molecular vibrations to the linear electro-optic effect", Phys. Rev. B, 66 (2002) 205107-1-9.