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Different approaches to PVP/graphene composite film fabrication using electrohydrodynamic atomization technique

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Abstract In this work a poly 4-vinlyphenol (PVP)/graphene composite film is fabricated by two different approaches i.e. blended and decorated (layer-by-layer i.e. LBL), using a reasonably inexpensive and less material consuming electrohydrodynamic atomization technique. Surface morphology of the fabricated composite film has been characterized by field emission scanning electron microscope and 3D Nano mapping. It has been observed that the film is uniform and has no voids and pores. Transmittance has been measured by UV–Visible spectroscopy, which showed nearly $\sim$88.5 % of transparency in the visible region. PVP/graphene film has sandwiched as dielectric layer between indium tin oxide and poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) as bottom and top electrodes, respectively, for capacitance measurement. PVP decorated graphene flakes (LBL) film showed better capacitance (1.22×10^{-2} F/cm^2) at 1 kHz in the voltage range of 0.1–0.2 V relative to a capacitance of 4.78×10^{-7} F/cm^2 at 1 kHz in the voltage range of −0.16 to 0.060 V fabricated by blended approach. It has been noticed that even at higher frequencies, a stable behavior as dielectric was observed. Besides this, a stable behavior was observed with the PVP/graphene (LBL) film even at higher frequencies.

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1 Introduction

Conventional (electrostatic) and electrochemical capacitors, batteries and fuel cells are systems which are widely used for energy storage [1, 2]. In fact, capacitors at nanoscale have been developed as one of the most promising energy storage mediums, whereby several orders of magnitude higher energy densities have been realized. They are able to store and release charge faster, can deliver higher amounts of charge at higher power rates as compared to conventional batteries and possess a longer life with short load cycles making them advantageous in various applications [3–7].

Recently, nanoscale dielectric capacitors (NDC) have rapidly developed and achieved properties, which are superior to other systems of energy storage. An ideal NDC should be composed of metallic layers that can store and release charge and a dielectric material in between these layers for increasing the capacitance value without increasing the dimensions of the structure.

From materials perspective, recent theoretical and experimental studies on graphene, carbon nanotubes and metallic nanowires have focused on understanding the dielectric properties of these structures and forming thin films that can serve as ideal charge holding metallic plates [7–10]. In polymers, poly 4-vinlyphenol (PVP) has been reported most frequently because of its better performance than other members of the family of gate dielectrics [11, 12]. Cross-linked PVP is investigated mostly for the fabrication of OTFTs due to the easy thin-film formation and to its excellent dielectric properties [13].

In fabrication techniques, EHDA technique is reasonably inexpensive and less material consuming, which involves the flow of a solution, containing nano particles or polymers of the material to be deposited (as a solute), under the influence of an electric field at ambient temperature [14, 15]. Due to the applied electric field, the liquid forms a cone at the exit of the capillary and a jet evolves from the cone apex. The stable jet further disintegrates into smaller droplets due to of coulombic forces; hence, a cloud of charged, mono-dispersed and extremely tiny droplets is achieved. The droplets generated from the spray are deposited on a substrate to form a uniform film of the solute present in the parent liquid. The stable cone-jet mode occurs when there is comparative impartiality in the electric field strength and the surface tension of the flowing medium. The applied voltage, flow rate and physical properties of the liquid (i.e. density, viscosity, surface tension, relative permittivity and electrical conductivity), control the droplet size generated from atomization under the cone-jet mode.

In this work, a composite film of PVP and graphene has been fabricated by two different approaches i.e. blended and layer-by-layer (LBL) approaches on ITO coated glass using electrohydrodynamic atomization (EHDA) technique [16]. The deposited PVP/graphene composite film is cured at 200 °C for 2 h. After curing, the PVP/graphene composite film was characterized using FE-SEM, UV–Vis–NIR spectroscopy and 3D-Nanomap. Electronic behavior is investigated by sandwiching PVP/graphene film in between ITO and PEDOT: PSS. Characterizations have shown that PVP/graphene composite film fabricated by using EHDA technique can be used in electronic devices for better charge storage.

2 Materials and experiments

Graphene platelets from cheap tubes (<4 layers and surface area >750 m^2/g), *N*-methyl-pyrrolidone (NMP) solvent and PVP from Sigma-Aldrich were purchased. The 0.84 mg graphene platelets and 0.40 g PVP were dispersed in NMP (4 ml) solvent by bath sonication for 30 min at room temperature followed by centrifugation at 3,000 rpm for 20 min. Supernatant containing PVP/graphene was collected and its viscosity was measured (22.3 mPa) via viscometer VM-10A system. The surface tension of the ink was found to be 20–24 mN/m. Surface-electro-optics (SEO)'s contact angle analyzer was used for the surface tension measurements. The electrical conductivity of the ink 19.4 μS/cm was measured using a conductivity meter (Cond6 + meter).

2.1 Taylor cone and spray formation

The EHDA experiments were initially performed with flow rates varying from 50 to 1,000 μl/h to determine the optimum spraying conditions with the stand-off distance fixed at 15 mm. At each flow rate, the strength of the electric field was increased by gradually increasing the potential difference between the anode nozzle and the grounded stage [17–19]. At each flow rate step, applying different magnitudes of voltage gave different modes of atomization and hence various modes were observed such as the dripping to the multi-jet [20–22]. Figure 1 represents higher solution and high-speed images of different atomization modes captured at a flow rate of 300 μl/h at different applied voltages. At a zero voltage, a stable meniscus was observed. When the voltage was gradually increased from zero up to 3.5 kV, only the dripping occurred. At 4.2 kV, the micro-dripping mode was observed. At 4.8 kV, the pulsating cone-jet mode was started. When the voltage was increased to 5.3 kV, stable cone-jet modes were observed while a further increase to 6.1 kV, the multi-jetting was observed.

Figure 2 provides the observed operating envelope of PVP/graphene dispersion representing different atomization modes with varying flow rates and corresponding applied voltages. It is evident from the envelope that as the flow rate increased the required applied voltage was increased from one mode to another. The reason behind this increase in applied voltage for obtaining a stable cone-jet is to overcome the surface tension i.e. 20–24 mN/m. A stable cone-jet region is shaded in operating envelope given in Fig. 2 to emphasize the possible flow rate and voltage combinations for optimized atomization. A flow rate of 300 μl/h was used throughout the experiments for the deposition of PVP/graphene films. A complete account of the deposition and characterizations of PVP and graphene flakes thin film fabrication by EHDA technique is given and explained in our previously published work [23, 24], respectively.

2.2 Film fabrication

The deposition of PVP/graphene was carried out using an electrospray deposition system [23, 24]. Before the PVP/graphene deposition, the silicone substrate was rinsed with deionized water and then dried. The flow rate with a combination of varying potentials was used in order to observe different modes of electrostatic atomization. The ink was then subjected to electrostatic atomization at an applied flow rate of 300 μl/h and a potential of 5.6 kV in the stable cone jet mode. The stand-off was changed from 5 to 20 mm to check for deposition area. The speed of the moving substrate was changed from 1 to 3 mm/s to find the

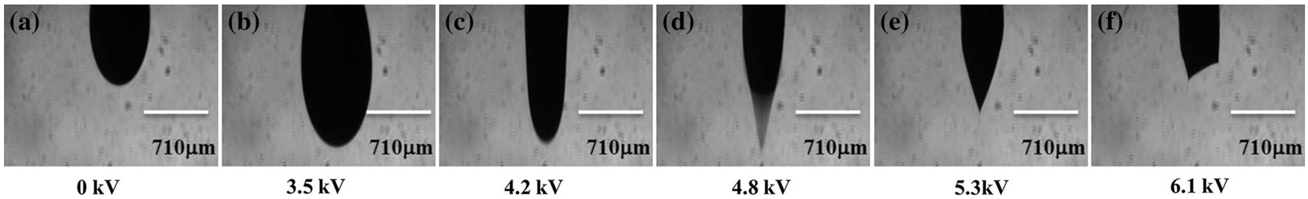


Fig. 1 Electrohydrodynamic modes of graphene dispersion observed during the deposition process. **a** Meniscus, **b** dripping mode, **c** microdripping, **d** unstable cone-jet mode, **e** stable cone-jet mode and **f** multi-jet mode

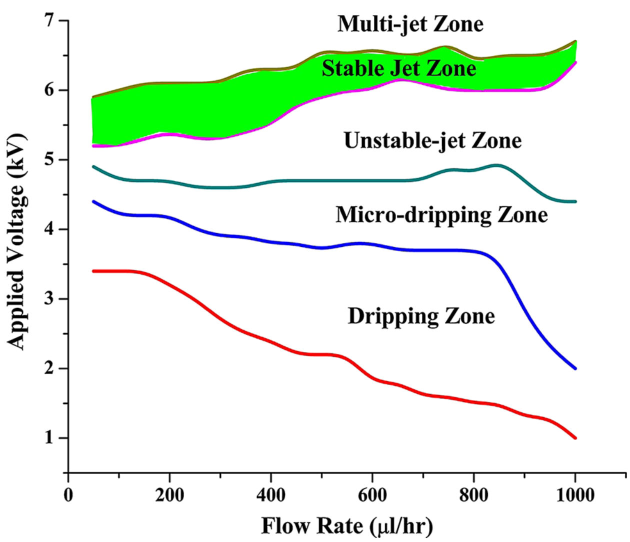


Fig. 2 PVP/graphene ink operating envelope

optimum value. It was noticed that the optimum parameter of stand-off and velocity required for covering the (2 × 2) cm^2 area on the ITO coated glass substrate were 15 mm and 3 mm/s, respectively. The deposited PVP/graphene film was cured at 200 °C for 2 h.

3 Results, characterizations and discussion

3.1 Morphological analysis

Figure 3a–c describes low to high resolution images of PVP/graphene (LBL) composite film. It is clear from the SEM images that the composite film is uniform throughout. The film did not show any unevenness, bumps, flaws or voids. This uniformity of the film, even at a nano-scale, enhances the stable dielectric behavior and eliminates the chances of short circuiting during voltage application. The capacitance behavior of the composite film as a dielectric film clearly showed a stable performance, both at low and high frequencies, while sweeping from low to high applied potentials. This performance may be attributed to interaction at interface due to high surface area per unit of uniform PVP/graphene film.

3.2 D-Nano mapping for surface roughness

NV-2000(Universal) non-contact surface profiler with nano-level accuracy was used for surface roughness measurement in phase shifting interferometry mode. In Fig. 4a, b the surface profile (2D and x-direction) of PVP/graphene is shown, respectively. It can be seen that the roughness of the film is 7.43 nm, while variations in film profile in the x-direction are mostly around 10.68 nm. In Fig. 4c, a 3D profile of PVP/graphene film is shown. It can be elucidated that PVP and graphene flakes deposited through EHDA technique are non-uniformly distributed and oriented in the film.

3.3 Optical properties

Figure 5a shows the transmittance spectrum of the PVP/graphene (LBL) composite film in the ultraviolet (UV), visible, and near-infrared spectral ranges. The maximum transmittance of the film has been observed at ~550 nm in the range of 85–88 % in the visible range. Absorption appears below 298 nm in the UV range. The transmittance spectrum reveals that the dielectric PVP/graphene composite film is more suitable for optoelectronic device applications due to its good transmittance. Based on the obtained data, the energy bandgap (Eg ~ 3.35 eV) was calculated, given in Fig. 5b.

3.4 Electrical behavior

The capacitance–voltage (C–V) curve was obtained for the device with different AC frequency, in order to investigate the charge storage mechanism. Figure 6a, b shows the C–V analysis of the composite films of PVP/graphene (LBL and blended approaches) as dielectric with an input frequency of about 1 kHz, respectively. It has been observed that the PVP/graphene (LBL) composite film shows a better dielectric nature with a maximum capacitance of 1.22×10^{-2} F/cm^2 within the voltage range 0.1–1.80 V. This behavior of the capacitor can be ascribed to the influence of capacitance dispersion, series resistance and bulk resistance [24]. In Fig. 6c, d capacitor performance at higher frequencies have been shown. The capacitance of

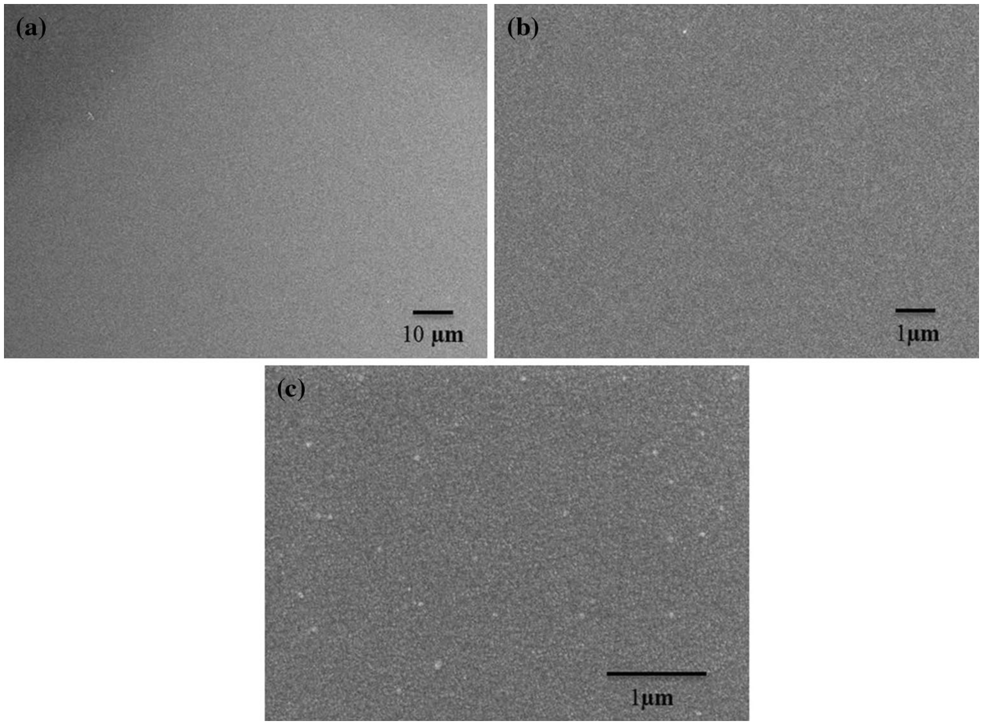


Fig. 3 (**a–c** Low to high magnification) shows the FE-SEM images of PVP/graphene composite thin film

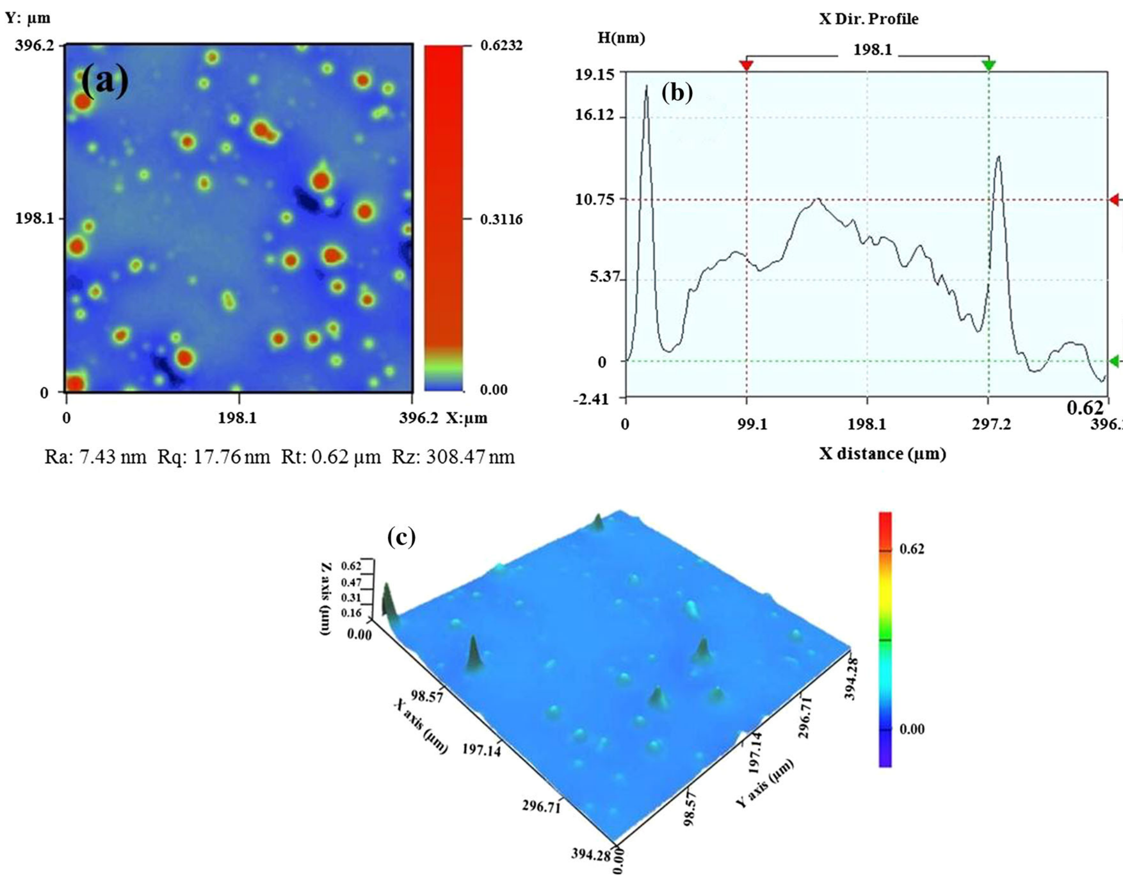
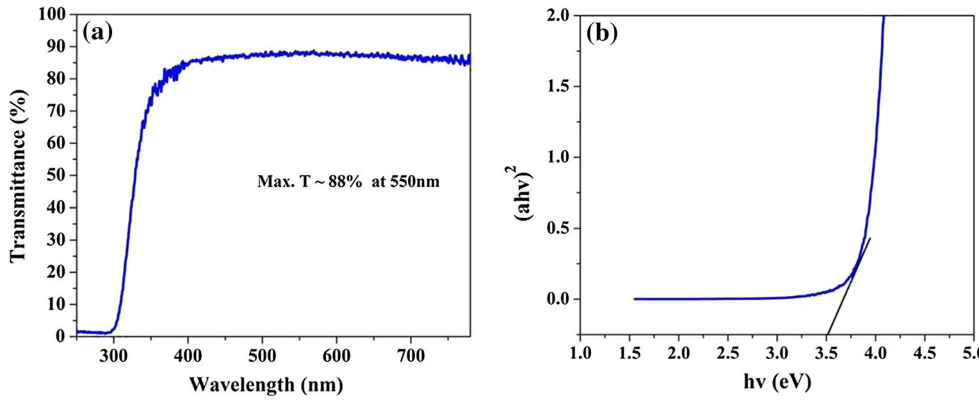


Fig. 4 3D-Nano mapping of PVP/graphene composite film

Fig. 5 **a** Transmittance spectra of PVP/graphene film **b** $(\alpha h\nu)^2$ versus $h\nu$ plot for bandgap estimation of PVP/graphene film



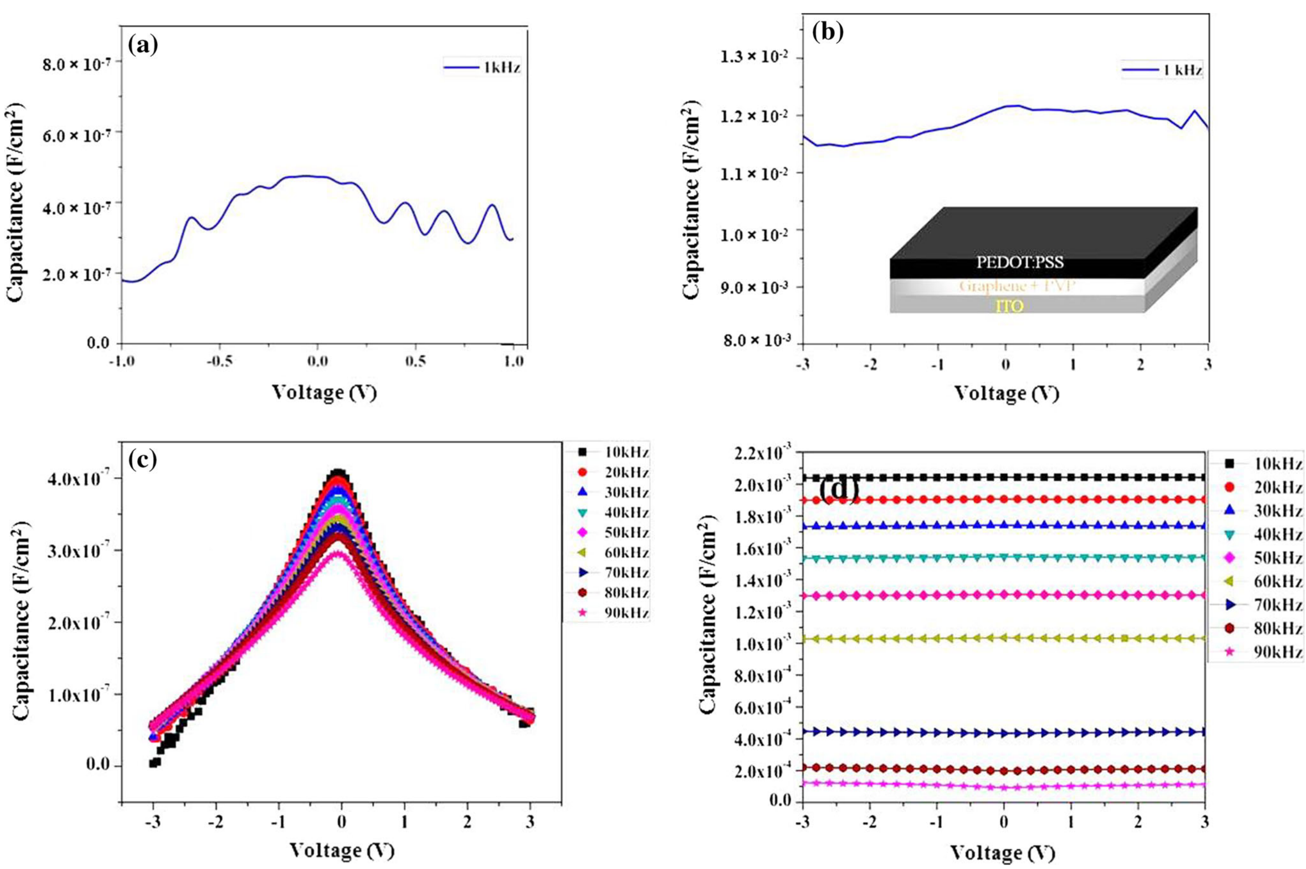


Fig. 6 Capacitance–voltage analysis of capacitor at 1 kHz when dielectric film is **a** PVP/graphene (Blended Approach) and **b** PVP/graphene (LBL approach) and Capacitance–voltage analysis of capacitor at higher frequencies when dielectric film is **c** PVP/graphene (Blended Approach) and **d** PVP/graphene (LBL approach), respectively

the capacitor has been decreased with an increase in AC frequency. Figure 6c, d also shows that the performance of the PVP/graphene (LBL) as dielectric film is $\sim 10^4$ orders better than the composite film fabricated through blended approach, at higher frequencies up to 90 kHz and a high voltage. This behavior is relatively better than using PVP or other PVP based composites films as dielectric layer. The characteristics confirm that the fabricated multi-layer printed device revealed a good charge storage mechanism for the PVP/graphene composite film through the LBL approach. Even at higher frequencies, a very minute change in capacitance has been observed using the PVP/graphene (LBL approach). The characteristics confirm that the fabricated multi-layer printed device shows a good charge storage mechanism for the PVP/graphene composite thin film fabricated through the LBL approach.

4 Conclusion

A PVP/graphene composite thin film is fabricated by two different approaches i.e. blended and decorated approaches with graphene flakes, using the EHDA technique. The PVP film decorated with graphene flakes showed better performance relative to the film PVP/graphene flakes obtained by blended approach as dielectric layer in capacitor having ITO and PEDOT: PSS as bottom and top electrode, respectively. It has been observed that the PVP film decorated with graphene flakes showed stable behavior at low as well as at high frequencies. Beside this, it portrayed a transmittance of $\sim$88.5 % in the visible region making it a strong candidate for optoelectronic devices.

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