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Flexible and transparent nanocrystal floating gate memory devices using silk protein

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ABSTRACT

The charge storage behavior of a floating gate memory device using carbon nanotube-CdS nanostructures embedded in *Bombyx mori* silk protein matrix has been demonstrated. The capacitance – voltage characteristics in ITO/CNT–CdS-silk composite/Al device exhibits a clockwise hysteresis behavior due to the injection and storage of holes in the quantized valence band energy levels of CdS nanocrystals. The enhanced charge injection resulting in increase in memory window is observed at higher sweeping voltages. Nearly frequency independent hysteresis width over a wide range of 100 kHz–2.0 MHz, indicates its origin due to the charge storage in nanocrystals. The memory behavior of carbon nanotube–CdS nanostructures/silk nanocomposite devices has also been demonstrated on polyethylene terephthalate substrates, which may provide the way for flexible, transparent and printable electronic devices.

1. Introduction

Silk, a natural protein, fibre has been used widely in textiles due to their exceptional mechanical properties and shimmering appearance. Among various silkworms, the fibers extracted from *Bombyx mori* attractive for its wide availability, biocompatibility, robustness and implant ability [1–3]. Silk fibers contain two hydrophobic core protein fibroin fibers, which are covered with hydrophilic glycoprotein sericin [4]. Recently, silk fibroin has been reported as an attractive material for the application in several devices, optical fibers, photonic crystals and microfluidic devices [5–7]. However, only a few attempts have been made for the fabrication of silk-based sensors, electronic and optoelectronic devices [8–10]. Capelli et al. [8] reported the characteristics of organic thin film field-effect transistor and light emitting devices by using silk fibroin as a dielectric layer. Recently, metal and semiconductor quantum dots embedded in organic matrix have been demonstrated as charge storage nodes in floating gate nonvolatile memory devices [11–13]. These organic–inorganic hybrid devices are cheaper compared to their inorganic counterpart, easier to fabricate over a large area and flexible for applications in printable electronics. The use of silk protein for bioelectronic resistive switching has been reported for integration on clothes and flexible substrates [14,15]. The insulating characteristics and high dielectric permittivity ($\epsilon_s \sim 6$) [8] of silk protein, may be useful as a dielectric medium for nanocrystal based floating gate memory devices. Here we report the realization of a novel flexible and transparent floating gate memory devices using CdS–carbon nanotube composite embedded in a silk protein matrix. The proposed devices may be attractive due to the aqueous processing capability of the silk protein, optical transparency, biodegradability and higher

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dielectric constant of silk matrix comparable to conducting/insulating polymers.

2. Experimental details

Silk protein solution was prepared by following the established protocol [16,17]. In brief, the live fresh and white bivoltine cocoons of mulberry silkworm, *Bombyx mori* (BM) were cut into pieces, degumented (removal of glue protein sericin) by boiling for an hour in 0.02 M sodium bicarbonate (Na_2CO_3) solution and dissolved in the 9.3 M solution of lithium bromide (LiBr). The concentration of the obtained silk solution was quantified using Bradford method [18]. The solution was adjusted to 2.0 wt% with distilled water and finally stored in 4 °C for the experimentation. The detailed protocol followed is depicted in Fig. 1. The silk protein based memory device was prepared by using CdS decorated multi-walled carbon nanotubes (MWCNTs) dissolved in silk solution. CdS nanostructures were grown on MWCNT surfaces by a simple chemical reduction method at room temperature, the details of which were reported elsewhere [19]. In brief, 15 mg of purified MWCNTs were ultrasonically dispersed in 10 ml dry tetrahydrofuran (THF), which contained S powder and $CdCl_2$. Excess potassium borohydride (KBH_4) was slowly added to the flux under vigorous stirring and a dark green precipitate of CdS decorated MWCNT nanostructures was formed. In order to fabricate the floating gate memory device, transparent conducting ITO coated glass and flexible PET substrates were patterned by chemical etching. The patterned ITO glass and PET substrate were cleaned thoroughly by using acetone and de-ionized water. The active solution was prepared by dissolving 0.2 gm of CdS decorated MWCNT nanostructures powder in 5 ml of silk solution. MWCNT–CdS/silk protein active layer was deposited by spin coating (1000 rpm) followed by annealing at 60 °C for 30 min. Thermal evaporation at a base pressure of 10^{-6} torr was used to deposit aluminum top electrode with an active area of 0.04 cm^2. On the other hand ITO was used as the bottom electrode for electrical contacts.

Microstructural studies of embedded nanostructures in silk matrix were performed using a transmission electron microscope (JEOL JEM-2100F) with an accelerating voltage 200 kV. Room temperature photoluminescence (PL) measurements were carried out using a He–Cd laser of wavelength 325 nm, Triax310 monochromator and a multi-channel photomultiplier detector. The charge transfer dynamics in CdS–CNT nanocomposites was studied by photoluminescence decay measurements using time correlated single photon counting (TCSPC) technique with picosecond pulsed laser diode of wavelength ~404.2 nm (Edinburgh Instruments, spectra II). The electrical characteristics of the fabricated floating gate memory devices were measured using a KEITHLEY semiconductor parameter analyzer (model no. 4200-SCS).

3. Results and discussion

Fig. 2(a) represents the plane-view bright field TEM micrograph of CdS decorated MWCNT nanostructures. The attachment of CdS nanoparticles with the MWCNT is clearly evident from the micrograph. The high-resolution TEM micrograph (HRTEM) of CdS, decorated on the nanotube surface shown in Fig. 2(b) indicates the lattice fringes in crystalline hexagonal CdS. The selected area electron diffraction pattern (SAED) presented in Fig. 2(c) indicates the formation of CdS nanostructures with dominant diffraction from (100), (002), (102), (110) and (103) oriented hexagonal crystallites. Fig. 3(a) shows the photoluminescence spectra of control BM silk protein and after the attachment of silk with CdS and MWCNT–CdS nanostructures. Upon the laser excitation of 325 nm, the BM silk shows a strong emission at 403 nm, which may be attributed to trapped charges in silk protein. The intensity of this peak is significantly reduced when CdS nanocrystals are incorporated into the silk matrix. Inset of Fig. 3(a) shows the room temperature PL spectra of CdS–MWCNT nanostructures after attachment of silk protein. The PL spectrum has been deconvoluted into 3 peaks at 402 nm, 448 nm and 510 nm. The emission peak at 402 nm is attributed to the emission from trapped charges in the *Bombyx mori* silk protein, whereas the strong emission at 448 nm is due to the band edge emission from CdS nanocrystals attached with CNT surfaces. Band-edge emission is ascribed to the

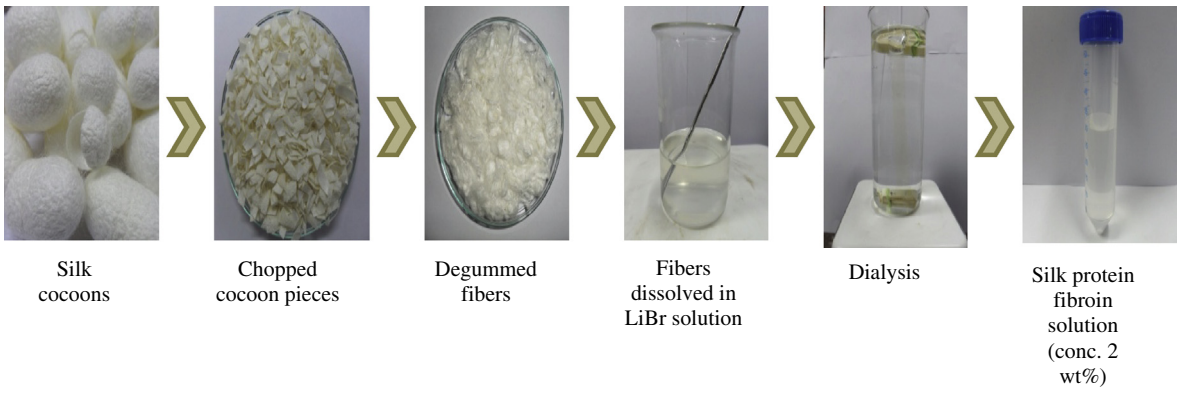

Fig. 1. Pictorial representation of silk protein fibroin solution preparation from cocoons of mulberry silkworm, *Bombyx mori*.