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Electrical bistability of copper (I) sulfide nanocrystals blending with a semiconducting polymer

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Electrically bistable devices were fabricated based on blends of *n*-dodecanethiol capped copper (I) sulfide (Cu_2S) nanocrystals and a semiconducting polymer using a simple spin-coating method. Reproducible electrical bistability and negative differential resistance effects were observed in current-voltage characteristics. A large ON/OFF current ratio of 10^4 at negative voltages could be obtained by applying different amplitude of sweeping voltages and varying the mass ratios of Cu_2S nanocrystals to polymer. The observed conductance switching was speculated to be resulted from electric-filed-induced charge transfer between the nanocrystals and polymer, and negative differential resistance behavior could be attributed to the charge trapping in the nanocrystals. © *2009 American Institute of Physics*. [doi:10.1063/1.3243981]

In the past few decades, electrically bistable devices based on organic materials have been extensively studied due to their potential applications in the next-generation of nonvolatile memory devices.[1,2] In these devices, two kinds of different stable conducting states are generally observed when different voltage-sweeping directions are applied.[3–6] With the progress of synthesis and properties of nanoparticles, nanoparticle-polymer composites have been widely used in organic bistable devices.[7–12] To date, a lot of studies were reported on the applications of nanoparticles in organic bistable devices with various device architectures, such as polymer-metal nanoparticle blends structures[7–9] and organic/metal nanocrystal/organic sandwich structures,[10–12] in which, the metal nanoparticles were mainly synthesized and stabilized by alkanethiol with different chain lengths.[9,10] In recent years, semiconductor nanocrystals including CdSe,[13,14] ZnO,[3,15] and CdSe/ZnS[16,17] were embedded into an organic matrix and were used to fabricate electrically bistable devices by a simple solution process, which have become particularly attractive. In these reports, however, the semiconductor nanocrystals were mainly distributed in an insulated polymer. It is rarely reported that the semiconductor nanocrystals capped by alkanethiol molecules embedded in a semiconducting polymer were used in the organic bistable devices. In this letter, we prepared copper (I) sulfide (Cu_2S) nanocrystals in *n*-dodecanethiol by one-pot approach, and fabricated bistable devices utilizing the blends of Cu_2S and poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (MEH-PPV). Current-voltage (*I-V*) characteristics were employed to study the electrical bistability properties of the devices with different Cu_2S concentrations in polymer, and two different conducting states were observed at the same sweeping voltage. Meanwhile, the negative differential resistance (NDR) effects were observed in the negative voltages region, which is attributed to the charge-trapping in the nanocrystals.

Cu_2S nanocrystals capped by *n*-dodecanethiol were synthesized from decomposition of copper(II) acetylacetonate ($Cu(acac)_2$) precursors in *n*-dodecanethiol at high temperature (200 °C). Figure 1(a) shows x-ray powder diffraction patterns (XRD) of the as-obtained Cu_2S nanocrystals, which indicate the resultant nanocrystals are orthorhombic chalcocite Cu_2S [Ref. 18, the lines at the bottom of Fig. 1(a)]. It is also confirmed by the corresponding selected-area electron diffraction pattern shown in the inset of Fig. 1(b). Transmission electron microscopy (TEM) studies [shown in Fig. 1(b)] show that the nanocrystals are spherical in shape with the mean size of 19.5 ± 1.2 nm. Figure 1(c) gives a UV-visible absorption spectrum of the resultant Cu_2S nanocrystals with a wide absorption up to about 800 nm. The inset of Fig. 1(c)

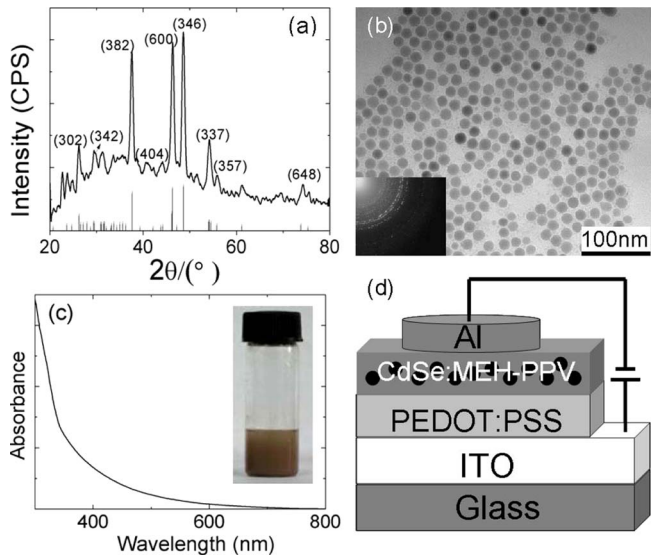

FIG. 1. (Color online) (a) XRD pattern of Cu_2S nanocrystals, which can be indexed to orthorhombic bulk Cu_2S (Ref. 18, bottom lines). (b) TEM image of Cu_2S nanocrystals with a mean diameter of 19.5 ± 1.2 nm, and the inset shows the selected-area electron diffraction pattern of Cu_2S nanocrystals. (c) Optical absorption spectrum of Cu_2S nanocrystals dispersed in chloroform, and the inset shows the image of as-prepared Cu_2S nanocrystals dispersed in chloroform. (d) Schematic diagram of the device structure studied in this work.

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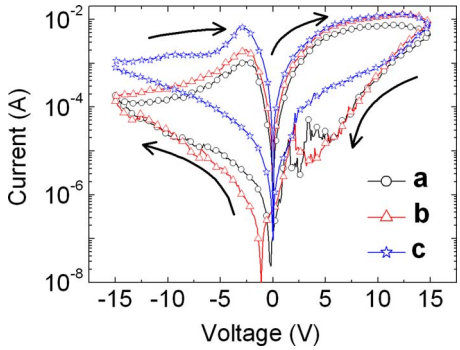

FIG. 2. (Color online) *I-V* characteristics of the bistable devices containing different mass ratios of Cu_2S to MEH-PPV: (a) 1:2, (b) 1:1, and (c) 3:1. Arrows represent the direction of the sweeping voltages.

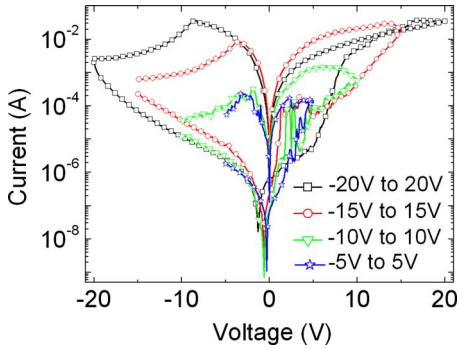

FIG. 3. (Color online) *I-V* characteristics of the device based on the blends of Cu_2S and MEH-PPV (1:1 in mass ratio) for different amplitude of sweeping voltages.

shows a photograph of Cu_2S nanocrystals dispersed in chloroform at room temperature, showing a brown color due to their strong absorbance for visible light.[19]

A schematic diagram of the bistable device in our work is shown in Fig. 1(d). The bistable devices were fabricated on glass substrates precoated with an indium tin oxide anode (sheet resistance 20 Ω/sq). The substrates were cleaned with deionized water, acetone, and isopropanol sequentially, and then treated in ultraviolet ozone before spin-coating a layer of poly(3,4-ethylenedioxythiophene):poly-(styrene-sulfonate) (PEDOT:PSS). After spin-coating and annealing PEDOT:PSS layer at 150 °C, the blends containing Cu_2S nanocrystals and MEH-PPV were spin-coated from chloroform solution onto the top of PEDOT:PSS layer, in which the mass ratios of Cu_2S to MEH-PPV are 1:2, 1:1, and 3:1, respectively. Finally, a top Al electrode layer with a thickness of 100 nm was deposited using high vacuum thermal evaporation.

To clearly understand the role of Cu_2S nanocrystals in the bistable devices studied in our work, we compared the *I-V* characteristics for the devices with different mass ratios of Cu_2S to MEH-PPV. Figure 2 gives the *I-V* curves of the devices with different Cu_2S concentrations measured from −15 to 0, 0 to 15, 15 to 0, and 0 to −15 V. It is clearly observed an electrical hysteresis with different currents of a high-conducting state (ON state) and a low-conducting state (OFF state) at the same sweeping voltages. Such an electrical hysteresis behavior is an essential feature for a bistable device.[2,20] For the bistable device with 50 wt % Cu_2S nanocrystals concentration, the amplitude of the hysteresis of the *I-V* curve is larger than that for the other two devices. The ratio between the ON state and OFF state at the same sweeping voltage (the ON/OFF ratio) is the highest at an optimum mass ratio of Cu_2S to MEH-PPV. It is noted that the ON/OFF ratio for the device with 50 wt % Cu_2S concentration can reach 10^4 at −1 V, which is equivalent to a reading process in a digital memory cell.[20] However, for the devices with 33.3 and 75 wt % Cu_2S concentrations, the ON/OFF ratios are about 10^2, which is two orders smaller than that for the device with 50 wt % Cu_2S concentration. On the other hand, the device without Cu_2S nanocrystals in the polymer did not exhibit the current hysteresis. This indicates that the *n*-dodecanethiol capped Cu_2S nanocrystals play an important role in the electrical bistability of the bistable device. In addition, the application of a negative sweeping voltage region leads to a significant NDR in the *I-V* characteristics of the devices with different mass ratios of Cu_2S to MEH-PPV. In the NDR region (from 0 to −5 V), the current increases rapidly to its peak value. The NDR behavior has been recently reported in organic bistable devices with metal nanoparticles capped by alkanethiol molecules, and the NDR behavior is associated with the trapped charges in the nanoparticles.[21] As to our work, we believe that the traps of the nanoparticles become filled with the injected electrons in the negative voltages region, which leads to the formation of the NDR region.[21,22]

Figure 3 gives the *I-V* curves of the bistable device containing 50 wt % Cu_2S concentrations in MEH-PPV by varying the amplitude of maximum sweeping voltages (−5 to 5 V, −10 to 10 V, −15 to 15 V, and −20 to 20 V). The results indicate that electrical hysteresis behavior is repeatable, and the magnitude of the *I-V* hysteresis increases with increasing amplitude of the maximum sweeping voltages. Furthermore, as shown in Fig. 3, in the different negative sweeping voltages region, the NDR characteristics are also observed. This suggests that the repeated observation of NDR behavior can be reliably regarded as an evidence of charge trapping and detrapping in charge-trap centers of Cu_2S nanocrystals. Because the application of different sweeping voltages lead to NDR effects in *I-V* characteristics and produce different conducting states, these electronic properties of the fabricated devices result in the multilevel memory capability.[22]

To further understand the current switching from the ON state to the OFF state, we have tried to fit the *I-V* characteristics in both states in terms of different theoretical models. Figure 4 show the *I-V* characteristics on a double logarithmic scale for both states. The *I-V* curve for the off state can fit to

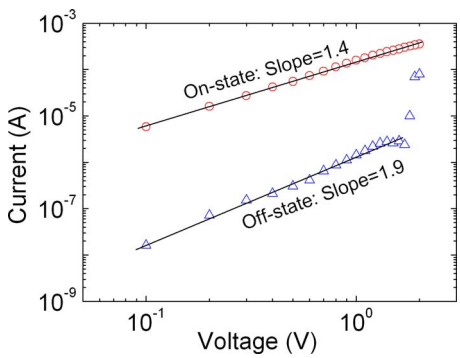

FIG. 4. (Color online) *I-V* curves of the Cu_2S:MEH-PPV (1:1 in mass ratio) bistable device on a double logarithmic scale. The scatters are experimental data, and the straight lines show linear fits to the OFF state and ON state with slopes of 1.9 and 1.4, respectively.

a straight line following the space-charge limited current (SCLC) model. According to this model, current density is expressed as follows:[4]

$$J = \frac{9\varepsilon\varepsilon_0\mu V^2}{8d^3},$$

where J is the current density, q is the electronic charge, ε is the dielectric constant of the material, ε_0 is the permittivity of free space, d is the thickness of the film, and μ is the carrier mobility. The fitting plot yields a slope of 1.9, which is very close to that expected from the above model. This indicates that the current injection of the off state is dominated by the SCLC model. On the other hand, the *I-V* curve for the ON state exhibits a straight line with a slope of 1.4. This suggests that the current injection for the ON state is no longer dominated by SCLC model as in the OFF state, but partially determined by the Ohmic conduction. Therefore, to some extent, the current switching from the ON state to the OFF state is a process of transition from Ohmic current to SCLC.[4]

Electrical bistability in the device using gold nanoparticles and a semiconducting polymer has been explained in terms of electric-field-induced charge transfer between nanoparticles and polymer.[8,23] Based on the aforementioned experimental results and discussions in our work, electrical bistability of our device is also due to the field-assisted charge transfer between Cu_2S nanocrystals and MEH-PPV. When the external electric field is high enough, the charge transfer will occur between Cu_2S and MEH-PPV. As a result, Cu_2S nanocrystals are negatively charged and MEH-PPV is positively charged, leading to the formation of an internal electric field. Therefore, the trapped charges in this process result in the transition of the device from OFF state to ON state. The negative charge on the nanoparticles may be stable due to the presence of insulating *n*-dodecanethiol capping layer on Cu_2S nanocrystals, which prevents the charge recombination after removal of external electric field. When a reverse electric field is applied to the device, the OFF state can be recovered because the trapped charges can be transported from nanoparticle to polymer.[8,12,23] It is noted that the current-injection mechanism of our device is very different to that of the device using gold nanoparticles and polymer. This maybe arising from the different electrodes used and different nanoparticles used in our work. The different electrodes with different work functions determine the barrier height for charge injection. Furthermore, the gold nanoparticle and Cu_2S nanocrystals are two different materials with different electrical conductivity and different dielectric constant, which determine the different capability of charge transport and injection.

In summary, a bistable device using blends of MEH-PPV and Cu_2S nanocrystals capped by *n*-dodecanethiol has been demonstrated. The devices exhibit repeated electrical bistability and NDR behavior in current-voltage characteristics at different nanocrystals concentrations and the different amplitude of sweeping voltages. The electric-field-induced charge transfer is responsible for the electrical bistability and the charge trapping effect in Cu_2S nanocrystals results in NDR effect. The maximum ON/OFF ratio of the device can reach 10^4 by suitable manipulation. These results indicate that the semiconductor nanocrystals capped by *n*-dodecanethiol hold promise for potential applications in next-generation nonvolatile memory devices.

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