The photoresponse and photoconductivity of micron-sized C_{60} whiskers and sub-millimeter-sized C_{60} clusters*

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The photoresponse and photoconductivity properties of micron-sized C_{60} whiskers and sub-millimeter-sized C_{60} clusters are successfully studied by the microfabrication technologies. According to the ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopic study, a highly intense absorption is observed in the UV and visible light regions, which indicates probable applications in photoelectric devices. Furthermore, a large photocurrent is measured under the illumination of white light in nitrogen (N_2) atmosphere. The micron-sized C_{60} whiskers and the sub-millimeter-sized C_{60} clusters have different photoresponse curves under the same condition of measurement. A quick transformation of photoelectric response is detected in parallel multi-arranged micron-sized C_{60} whiskers, but the recovery of the photocurrent of self-assembly sub-millimeter-sized C_{60} clusters is much slower.

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Since the discovery of C_{60} by Kroto et al in 1985[1], fullerene C_{60} has attracted much interest due to its highly symmetrical structure and its novel conjugated π-π system[2-5]. After that, the discovery of carbon nanotubes in 1991[6] created a new era in nanoscience and nanotechnology, and led to many international researches on the synthesis of similar fullerene derivatives and the investigation of their properties and possible applications[7,8]. Recently, a study of electrical conductivity of a single C_{60} tube with diameter of 300 nm by Xing et al in 2005[9] indicated that the fullerene tubes may have a noticeable photoconductivity under the light illumination, which is promised to be applied in optical switching devices. Moreover, a significantly high photoresponse of C_{60} nanorod bundles in macroscopic scale was detected under illumination of white light by Zhang et al in 2010[10].

In this paper, we analyze the photoresponse and photoconductivity properties of micron-sized C_{60} whiskers and sub-millimeter-sized C_{60} clusters. The synthesis mechanism of C_{60} clusters from C_{60} whiskers is realized, and the photoconductivity properties of C_{60} materials with different diameters are explored. It is demonstrated that the photoresponse and photoconductivity properties of hundreds of micron-sized C_{60} whiskers in parallel are better than those of the self-assembly C_{60} clusters.

The micron-sized C_{60} whiskers and sub-millimeter-sized C_{60} clusters were successfully prepared by a process of liquid-liquid interfacial precipitation (LLIP) method through a mixture of C_{60}-saturated toluene and isopropyl alcohol[11]. The scanning electron microscope (SEM) of Raith E-Line is used to characterize the morphologies of C_{60} whiskers and C_{60} clusters as shown in Fig.1. The C_{60} nanorods shown in Fig.1(a) obviously exhibit a hexagon cross section, which reveals the hexahedral crystal structure of as-grown solvated C_{60} nanorods[12]. Fig.1(b) shows the morphology of well-synthesized micron-sized C_{60} whiskers with hexagon cross section. It is apparent that the sub-millimeter-sized C_{60} clusters shown in Fig.1(c) consist of amounts of micron-sized C_{60} whiskers. The expected mechanism fulfilling the growth of the C_{60} whiskers and clusters is assumed to be through Van der Waals interactions in the radial direction and via covalent cross-linking bonds in the longitudinal direction[13]. For that reason, the electron transmission would fade in the radial direction.

The electronic absorption properties of C_{60} whiskers and clusters are studied via ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy as shown in Fig.2. Both of the spectra have been normalized in intensity to the peak at ~328 nm which corresponds to the first allowed electronic transition in C_{60}. Significantly, the absorption spectrum of the sub-millimeter-sized C_{60} clusters reveals much broader and stronger absorption in Vis and NIR regions than that of the micron-sized C_{60} whiskers. A

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broad absorption band with peaks of ~620 nm and ~734 nm is identified clearly. These results suggest that the electronic structure of C_{60} clusters is violently perturbed in the course of formation of sub-millimeter-sized crystalline clusters from whiskers by means of the strong intermolecular π-π interactions[14]. Both of the C_{60} materials described above display a strong photoresponse to the white light.

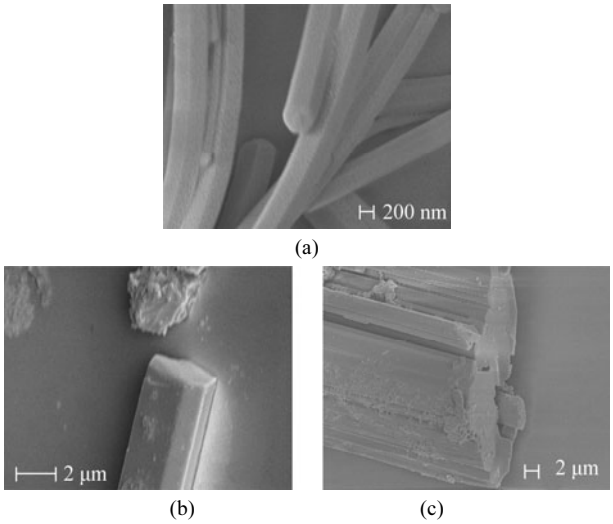


Fig.1 SEM images of (a) one-dimensional C_{60} nanorods, (b) micron-sized C_{60} whiskers and (c) sub-millimeter-sized C_{60} clusters obtained by LLIP method

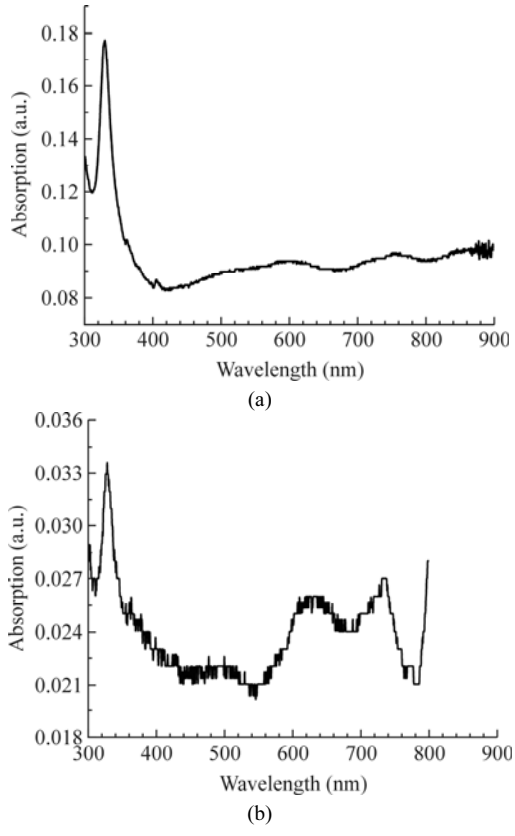


Fig.2 UV-Vis-NIR absorption spectra of (a) C_{60} whiskers and (b) C_{60} clusters dispersed in isopropyl alcohol

To determine the photoelectric properties of the micron-sized C_{60} whiskers and sub-millimeter-sized C_{60} clusters, a series of experiments were designed and conducted by Keithley instruments model 6485 picoammeter. The measurement was carried out on the micro-fabricated electrodes. The schematic diagram of the gold/titanium (Au/Ti) electrodes fabrication procedures is illustrated in Fig.3. In detail, the glass substrate sliced into square (50 mm×50 mm) was washed with detergent, rinsed in acetone and deionized (DI) water step by step, and dried on the heated platen at 120 °C for 30 min immediately. The 1 μm-thick positive photoresist (Suzhou Ruihong Co., China) was then spin-coated on the glass substrate as shown in Fig.3(a). After photolithography and development processes shown in Fig.3(b) and (c), a thin layer of Ti (20 nm) and a thick layer of Au (100 nm) were attached to the glass substrate by the ion beam sputtering deposition as shown in Fig.3(d). Subsequently, the remaining positive photoresist was removed by drenching in acetone for several hours as shown in Fig.3(e). After the microfabrication procedures, the totally integrated source and drain electrodes of Ti (20 nm) and Au (100 nm) were adhered to the glass substrate. A straightforward method for the placement of C_{60} whiskers and clusters was via drop-casting a single drop of the whiskers and clusters dispersed in isopropyl alcohol solution onto the pre-patterned substrate[15]. By annealing the whiskers and clusters on the substrates at ~150 °C in vacuum chamber for 24 h, the absorbed oxygen and residual solvents were removed. Moreover, the contact resistance between C_{60} whiskers/clusters and two electrodes is decreased due to manufacturing the heterostructures by means of solid-solid reaction[16,17].

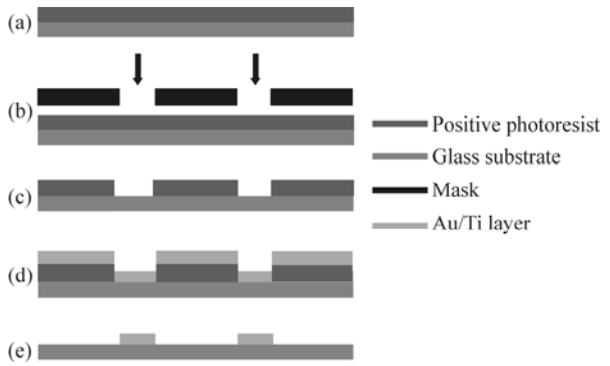


Fig.3 Microfabrication procedures of the Au/Ti source and drain electrodes, where (a) Spin-coating process of 1 μm positive photoresist; (b) Photolithography process; (c) Development process; (d) Sputtering deposition of Au/Ti; (e) Lift-off process

The photoresponse properties of micron-sized C_{60} whiskers in nitrogen (N_2) atmosphere are presented in Fig.4. The representative current-voltage (*I-V*) characteristics of hundreds of micron-sized C_{60} whiskers in parallel in the dark and under illumination shown in Fig.4(a) reveal that the photocurrent of device increases with the

illumination of white light. When C_{60} whiskers in parallel are irradiated by white light (1.35 mW/cm^2), the photocurrent is increased by more than 40 times at a constant bias voltage of 20 V. It is indicated that the periodic photoresponse of C_{60} whiskers shown in Fig.4(b) can be switched between high and low electrical conductivity states by turning the optical source on and off gradually. In this case, we conclude that the micron-sized C_{60} whiskers own strong and stable photoresponse, which indicates a new strategy for effectively fabricating amplifying optoelectronics devices.

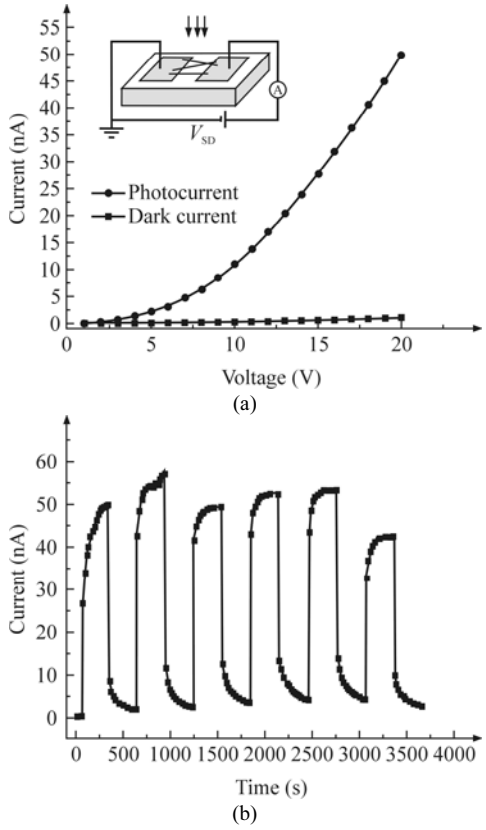
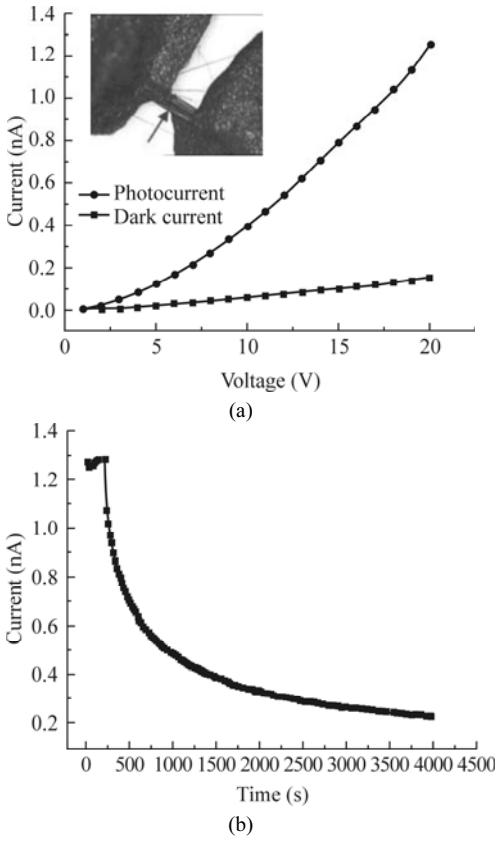
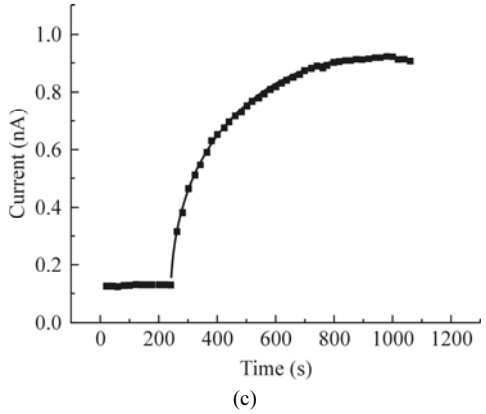


Fig.4 (a) Current-voltage characteristics in the dark and under illumination; (b) Periodic photoresponse under illumination (white light of 1.35 mW/ cm^2 at bias voltage of 20 V) for multi-arranged micron-sized C_{60} whiskers in N_2 atmosphere (The inset of (a) is the schematic diagram of the photoresponse measurement device containing hundreds of C_{60} whiskers in parallel.)

For comparing, we perform a two-end device fabricated by depositing silver conductive adhesive (SPI Supplies Inc., USA) on sub-millimeter-sized C_{60} clusters as shown in the inset of Fig.5(a), which consist of amounts of micron-sized C_{60} whiskers. Fig.5(a) shows a similar *I-V* characteristic of a single sub-millimeter-sized C_{60} cluster in the dark and under illumination in N_2 atmosphere. The photocurrent increases by more than 10 times at a constant bias voltage of 20 V when the C_{60} cluster is irradiated, which is a little less than that of the multi-arranged micron-sized C_{60} whiskers in parallel described above. The photoresponse recovery characteristics of C_{60} clusters are also studied at a bias of 20 V at room temperature. As shown in Fig.5(b) and (c), the recovery time of the photoresponse current is fairly long. It takes almost 2600 s to regress the current to 10% of its D-value between the maximum and minimum values as shown in Fig.5(b). In the same way, it takes almost 400 s to recover the current to 90% of its D-value as shown in Fig.5(c). Notably, the photoresponse current exhibits a slow recovery compared with the periodic photoresponse described in Fig.4(b). In this case, we arrive at a conclusion that the recovery of photocurrent by turning the optical source on and off becomes slower with the diameter of C_{60} fullerene materials increasing from whisker to cluster. Compared with the previous, the multi-arranged whiskers and the self-assembled clusters have different combinations, which contribute to the various photoresponses as well as the recovery properties. The specific surface area decreased with the increase of diameter is thought to be a possible reason influencing the photocurrent transmission and recovery characteristics. The multiple channels for shuttling the photogenerated electrons are considered to be divided into two states. One is thought to be through the single nanorods in the longitudinal direction, which represents a large conductance under the influence of covalent cross-linking bonds. The other is penetrating blocks between the nanorods in the radial direction, which performs a small conductance of Van der Waals interactions[18]. This gives us a good explanation of that the transformation of photoelectric response of the sub-millimeter-sized C_{60} clusters is restricted and delayed.





(c)

Fig.5 (a) Current-voltage characteristics in the dark and under illumination; (b) Light-off and (c) light-on photocurrent recovery characteristics under illumination (white light of 1.35 mW/cm^2 at bias voltage of 20 V) for a single sub-millimeter-sized C_{60} cluster in N_2 atmosphere (The inset of (a) is the optical microscope image of a device fabricated by a sub-millimeter-sized C_{60} cluster with diameter of about 100 μm.)

In conclusion, we successfully study the photoresponse and photoconductivity properties of micron-sized C_{60} whiskers and sub-millimeter-sized C_{60} clusters. Both of C_{60} whiskers and C_{60} clusters have an intense absorption and display a strong photoresponse under illumination of white light. But the transmission of photocurrent and transformation of photoelectric response of the sub-millimeter-sized C_{60} clusters are restricted and delayed due to the imperfect synthesis mechanism of Van der Waals interactions between C_{60} nanorods in the radial direction.

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