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Facile Synthesis of Germanium Nanocrystals and Their Application in Organic–Inorganic Hybrid Photodetectors

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Group IV semiconductor nanocrystals (NCs) have attracted much attention in recent years for applications in different areas, including photodetectors,^[1–3] field-effect transistors,^[4,5] lithium-ion batteries,^[6,7] and solar cells.^[8,9] In particular, germanium NCs have drawn special attention because of its inherent properties: Firstly, Ge is a narrow bandgap semiconductor with a bulk bandgap of 0.67 eV at 300 K, which can be easily tuned by quantization to technologically important wavelengths. Secondly, it has a large exciton Bohr radius (≈ 24 nm), which provides a strong quantum confinement effect^[10,11] as well as a large absorption coefficient ($\approx 2 \times 10^5$ cm⁻¹ at 2 eV).^[12] Considerable efforts have been recently directed towards the preparation of Ge NCs. The available methods so far include etching, molecular beam epitaxy, plasma-enhanced chemical vapor deposition, and ion implantation, which are characteristically high cost processes and limit the wide applications of Ge NCs.^[13]

Solution-based routes hold great promise for the synthesis of NCs, considering their advantage in large scale production and flexibility in product quality control. Recent progress reveals the possibility to overcome the big hurdle in liquid phase synthesis, i.e., the high crystallization temperatures of Ge NCs that originate from their strong covalent bonding.^[14] However, the reported methods either need a specially designed organic Ge precursor for thermal decomposition, or use strong reducing agents such as hydrides and butyllithium, which are extremely dangerous and environmentally unfriendly. Until now, it remains a big challenge to develop a simple and safe approach to synthesize high quality Ge NCs in solution.

Organic–inorganic hybrid photoelectric devices have drawn considerable attention from the scientific community. Such devices show the capability to take advantage of both inorganic and organic devices, while overcoming their own shortcomings.^[15,16] Different prototypes of hybrid photodetectors have been constructed and tested for their photoelectric properties.

For example, polymers in conjunction with different inorganic components such as CuInSe₂ NCs,^[17] TiO₂ NCs,^[18] and ZnO quantum dots^[19] have been developed as promising photoelectric devices. To our surprise, few reports have utilized Ge NCs as the inorganic component, which should be favorable for photoelectric devices with respect to their low toxicity, high absorption coefficient, high carrier mobility, and large Bohr excitation radius. A possible reason may lie in the lack of simple and benign methods for Ge NC synthesis, and therefore their further characterization and application are delayed.

In this paper, we report the facile synthesis of high quality Ge NCs by using a solution method, as well as the successful construction of a hybrid photoelectric device based on the conjunction of the Ge NCs and a conjugated polymer such as poly(3-hexylthiophene) (P3HT). P3HT was selected because of its high electrical conductivity and strong absorption in the visible range.^[20] Ge NCs are prepared from a simple and environmentally benign process without using toxic and expensive metal-organic precursors or reducing agents. The device constructed using the hybrid P3HT-Ge NCs shows high performance and is promising for large-area photodetector applications.

In a typical synthesis, GeBr₄ and oleylamine were added to a three-neck flask in air, and degassed by bubbling with Ar gas while stirring. After heating to 260 °C and aging for 2 h, a black colloidal solution forms, indicating the formation of NCs. Oleylamine is the only solvent used in the synthesis, which plays an important role in the formation of uniform NCs. In addition to its well known role as a stabilizer, its lone electron pair in its amine group provides the necessary electron charge for the reduction process.^[21] A blank experiment in which oleylamine was substituted with 1-octadecene leads to no Ge NCs.

The as-synthesized powder was characterized by X-ray diffraction (XRD). **Figure 1a** shows its pattern and it can be identified as diamond cubic Ge (JCPDF No. 04-0545). The crystal domain size estimated from the full width at half maximum of the (111) peak by the Scherrer equation is 10 nm.

Figure 1b shows a typical transmission electron microscopy (TEM) image of the Ge NCs. The as-synthesized NCs are nearly monodispersed with an average diameter of ≈ 10 nm, which is in good agreement with the particle sizes from XRD analysis. The high-resolution TEM (HRTEM) image in **Figure 1c** reveals that the Ge particle is single-crystalline with (111) lattice fringes (d -spacing = 0.33 nm).

The selected-area electron diffraction (SAED) pattern (**Figure 1d**) also reveals the NCs have a diamond cubic structure. The observed and calculated d -spacings from the SAED pattern

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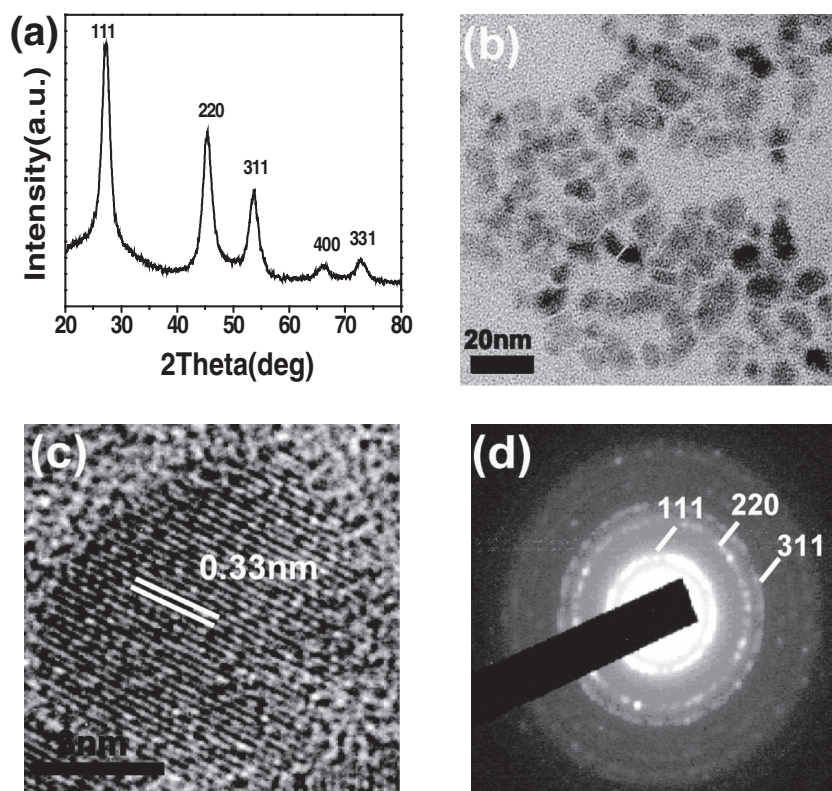


Figure 1. a) XRD pattern of Ge NCs. b) TEM image of Ge NCs. c) HRTEM image of a single Ge NC. d) SAED pattern of Ge NCs.

are 0.33, 0.2, and 0.17 nm, which match well with the *d*-spacing values for bulk Ge of (111), (220), and (311), respectively.

The Ge NCs are then mixed with P3HT to form a hybrid film. A prototype photoelectric device is constructed to investigate its photoresponse characteristics. A schematic illustration of the hybrid device is shown in Figure 2a. Current-voltage (*I*-*V*) characteristics of the devices were recorded with a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a clean and shielded box at room temperature. An iodine-tungsten lamp was used as a white light source. Figure 2b shows the photocurrents of the device during repetitive switching of light illumination, or on/off switching. The photocurrent increases and decreases as a response to the on/off operation, and shows very high photosensitivity. After a number of cycles, the photocurrent can still be changed as a result of the illumination switching. The response characteristic of the constructed device is proven to be fairly stable and reversible. In the dark, the current was only 0.05 pA. At an incident light density of 8.03 mW cm⁻² and a bias voltage of 10 V, the current jumps to 7.8 pA, giving an on/off switching ratio of >100. Further experiments show that the photocurrent is very sensitive

to the intensity of the incident light. A tiny change in light intensity can lead to a remarkable change in the photocurrent (Figure 2c), which may lie in different photon densities from the incident lights. As shown in Figure 2d, the device current is strongly related to the light intensity and demonstrated a power dependence of ≈ 1.15 (i.e., $I \approx P^{1.15}$), indicating superior photocurrent capability of the hybrid material. These results prove the promising potential of the hybrid device as a photoswitch and a highly photosensitive detector. It is worth noting that the applied bias voltage influenced the on/off ratio of the devices as well, considering that the exciton dissociation and the background current usually depend on the applied bias voltage. In addition, it was found that the average size of Ge NCs could be tuned by varying the concentration of GeBr₂ and reaction time. Experiments concerning the size effects of Ge NCs on the device performance are now in progress, which will be reported in future work.

To understand the photoresponse mechanism of the hybrid material, a blank test based on a pure Ge film is carried out and the constructed device showed no obvious photoresponse (Figure 3a). The photocurrent originating from pure P3HT was also very low as previously reported.^[17] However, the hybrid

material based on P3HT-Ge NCs shows a sharp increase in photocurrent under light illumination. It is clear that the single components of Ge NCs or P3HT can not contribute

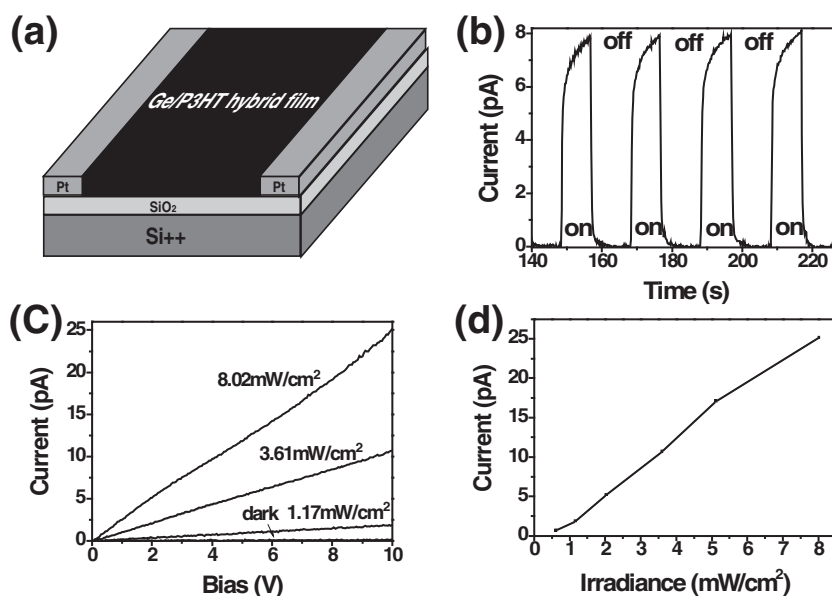


Figure 2. a) Schematic illustration of the hybrid device. b) On/off switching of the hybrid device (incident light density: 8.03 mW cm⁻², bias voltage: 10 V). c) Dark currents and photocurrents at different incident light densities. d) Photocurrent vs incident light density at a bias voltage of 20 V.

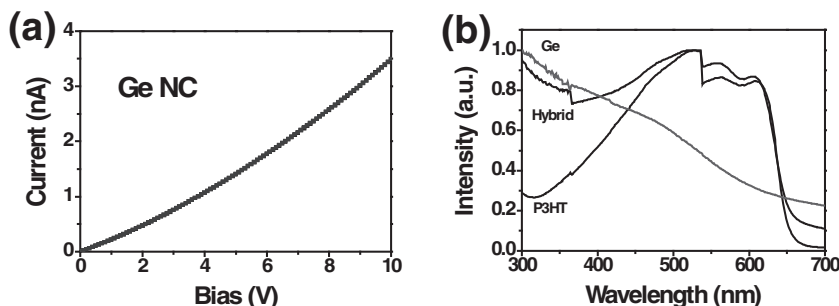


Figure 3. a) Typical I - V curves for an Ge NC film in the dark (incident light density: 8.03 mW cm^{-2}). b) UV-vis absorption spectra of P3HT film, Ge NC film, and P3HT-Ge hybrid film ($\approx 3:5$ weight ratio).

alone to the resultant high photocurrent, and therefore a logical explanation for the photoresponse is the existence of a synergistic effect between Ge and P3HT.

In order to explore the reason for this synergy effect, we measured the UV-vis absorption spectra of a pure Ge film, P3HT film, and P3HT:Ge hybrid film ($\approx 3:5$ weight ratio), respectively (Figure 3b). The result indicates that the inlay of Ge NCs into the P3HT film significantly broadens the absorption spectrum. While the spectrum of the pure P3HT film shows a characteristic wide peak in the range of 300–650 nm, the absorption spectrum of the P3HT-Ge hybrid film exhibits a stronger absorption in the range of 300–510 nm as well as a significant absorption at wavelengths longer than 650 nm. It is reported that exciton dissociation can occur efficiently at the interface of two semiconductors, such as in the system of an inorganic semiconductor of CdSe and an organic conjugated polymer of P3HT in a hybrid film because of their different natures.^[17–19,22,23] Similarly, in the present system, the Ge NC could act as the photoelectron acceptor because of its high electron affinity, while the P3HT serves as a hole acceptor as well as an electron donor upon photoexcitation. In addition, in the hybrid film, the Ge NCs are highly dispersed in the P3HT matrix, forming a three-dimensional interconnected network, which leads to a large interface area for charge separation. Therefore, long-lived charge separation and high transport might be achieved in the hybrid device. It should be noted that the hybrid photodetector also showed an outstanding stability. No obvious degradation was observed during scores of cycles. The high sensitivity and stability of the hybrid device is promising for large-area photodetector applications.

In conclusion, we have developed a new solution-based method for the synthesis of colloidal Ge NCs. By using a one-step synthetic route, high quality Ge NCs are prepared without using any extra reducing agents such as hydrides or butyllithium. Photodetectors based on P3HT and Ge NC hybrid films have been constructed. The hybrid device exhibits high performance such as a high photoresponse ratio ($I_{\text{light}}/I_{\text{dark}} > 100$), high sensitivity, and high stability, which is promising for large-area photodetector applications.

Experimental Section

Synthesis of Ge Nanocrystals: To synthesize Ge nanocrystals, GeBr_2 (0.1162 g, 0.5 mmol) and 10 mL of oleylamine were added to a 25 mL

three-necked flask in air, and degassed at $\approx 120^\circ\text{C}$ for 30 min by bubbling with Ar gas while stirring. The mixture was heated to 260°C and aged for 2 h. Finally, a black colloidal solution formed, indicating the formation of NCs. The flask was then cooled to room temperature and excess ethanol was added to precipitate the NCs, which were easily harvested through centrifugation at 9000 rpm for 5 min. The precipitates were washed three times with a mixture of ethanol and toluene. The final products were dispersed in toluene for further characterization.

Fabrication of Photodetector Devices: P3HT (45 mg) was dissolved in 3 mL of toluene. A Ge NC solution (100 μL , $\approx 50 \text{ mg mL}^{-1}$) and P3HT solution (200 μL) were mixed to form the final solution. Photodetector devices were fabricated by dropping

1 μL of the final solution onto pre-cleaned platinum electrodes and dried naturally.

Characterization of Materials: The size and morphology of the NCs were characterized by HRTEM using a Tecnai G2 20S-TWIN working at an accelerating voltage of 200 kV. The phase and the crystallographic structure of the NCs were characterized by powder XRD using a Regaku D/Max-2500 diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). UV-vis absorption spectra were recorded at room temperature with a Lambda 950 UV-vis spectrometer. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al $K\alpha$ radiation. Current-voltage (I - V) characteristics of the devices were recorded with a Keithley 4200 SCS and a Micromanipulator 6150 probe station in a shielded and clean box at room temperature. An iodine-tungsten lamp was selected as a white light source in view of the significant absorption of the hybrid film in the visible wavelength range.

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