



# One-step synthesis to photoelectric hybrid composite of N-vinylcarbazole–methyl acrylate copolymer and ZnO nanocrystals via nanocrystals-initiated polymerization

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## ABSTRACT

This study designs a polymerization, in which ZnO colloids are used to initiate a copolymerization of N-vinylcarbazole and methyl acrylate, to synthesize functional composites for fabricating photoelectric devices. It is proved that a block copolymer is synthesized and a nanocomposite consisting of the ZnO and copolymer is obtained simultaneously. As a result, the ZnO nanocrystals are finely dispersed in the polymer matrix. A film-device is prepared from the obtained nanocomposite which has good film-forming ability and measured about photocurrents under illumination.

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## 1. Introduction

Organic semiconductors are usually optically or electrically active materials. Hybrid composite materials of organic semiconductor polymers and inorganic nanocrystals, which exhibit different properties from those of individual components, have attracted much attention from the researchers in the field of photoelectric materials [1]. Poly(N-vinylcarbazole) (PVK), one of important semiconductor polymers, has good hole-transporting ability [2], which originates from  $\pi$ -stacking alignment of the pendent carbazole groups [3]. Composites of PVK and nanocrystals can find applications as functional layers in photoconductive devices and solar cells [4–8]. In these composite materials, PVK can transport holes while nanocrystals act as electron-trappers [5], and the interface between the two components plays an important role in charge transferring [6]. Organic functional layers in the photoelectric devices are prepared from solution, either by spin coating or via ink-jet printing. It should be pointed out that, being one of the rigid aromatic polymers, PVK has the glass-transition temperature ( $T_g$ ) as high as 208 °C [9]. As a result of the high  $T_g$  the coating prepared from PVK solution at room temperature is fragile. Moreover the presence of nanocrystals produces more fragile composites. It is urgent to improve the film-forming ability of PVK-contained composites because the lifetime of the devices largely depends on

the mechanical behaviors of functional layers, including strength, adhesion, and stability.

Photoexcitation of semiconductor nanocrystals yields electron and hole in pairs which generate surface-mediated reactions [10]. We have reported that photoexcited TiO<sub>2</sub> nanocrystals-initiated methyl methacrylate to polymerize [11], a new and promising polymerization technique. The nanocrystals-initiated polymerization offers a straightforward method to prepare polymer/nanocrystal composites because the composite was instantly formed once the polymerization was completed. A mechanism of surface polymerization was revealed for the nanocrystals-initiated polymerization [11–13]. Very recently, we have used ZnO nanocrystals to initiate a polymerization of N-vinylcarbazole (NVK) and obtained a novel ZnO–PVK composite [14]. We designed that composite based on the concept that the conduction band (CB) edge of ZnO [15] is 2.0 eV below the lowest unoccupied molecular orbital (LUMO) of PVK [7] and, thereby, the electron which was photoexcited to LUMO of PVK can easily be injected to CB of ZnO. The separation of electron and hole, as a result of the above charge-transfer, is important to photoconductive devices and solar cells [5,16]. Further, in this study we design a copolymerization, in which ZnO nanocrystals initiate a copolymerization of NVK and methyl acrylate (MA), to resolve the crucial issue of film-forming ability about PVK-contained nanocomposites. One reason for selecting MA is that its homopolymer (PMA) is a typical flexible polymer having  $T_g$  of 8 °C [17]. It should be mentioned that a copolymerization initiated by nanocrystals has not been reported as

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yet. This paper will report that we succeed in synthesizing the copolymer, and fabricate a film-device which exhibits photocurrents under illumination.

## 2. Materials and methods

### 2.1. Materials

N-vinylcarbazole (NVK, AR) was supplied by Aldrich Co. Lithium hydroxide monohydrate (AR) and methyl acrylate (MA, AR) were supplied by Sinopharm Chemicals Co. Zinc acetate dehydrate (AR) was supplied by Shanghai Meixing Chemicals CO.

### 2.2. Polymerization

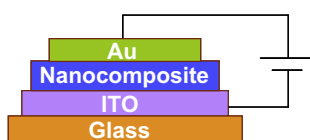
ZnO colloids were prepared through hydrolyzing zinc acetate [18], and zinc acetate dihydrate and lithium hydroxide monohydrate were used as starting reagents. In particular, the obtained ZnO colloids were further annealed by refluxing at 60 °C for 2 h in our experiments. A typical reaction procedure was as follows: 10 ml of ZnO colloids (0.1 M), 1.6 g NVK and desired amounts of MA were added to 90 ml of ethanol. The mixture was placed in a quartz-glass reactor which was equipped with a stirrer and a water jacket connected to a circulator of saturated CuSO<sub>4</sub> solution. After the mixture was degassed for 25 min, a mercury vapor lamp towards the reactor was switched on and the irradiation lasted for 3 h. The reaction mixture avoided being irradiated by the rays below 365 nm due to the cutoff of the CuSO<sub>4</sub> solution [12], and the light intensity was 13 mW/cm<sup>2</sup> at the wavelength of 365 nm and 0.085 mW/cm<sup>2</sup> at 254 nm at the reactor center. The light intensities were measured by inseting the cylindrical probe into the reactor.

### 2.3. Characterization

Transmission electron microscopy (TEM) was carried out with a Jeol JEM-2010 instrument which was equipped with a function of electron diffraction patterning. FTIR spectrum was recorded on a Nicolet Magna-IR™ 550 spectrometer. <sup>13</sup>C NMR spectrum was recorded on a Bruke DMX500 spectrometer with CDCl<sub>3</sub> as solvent. Differential scanning calorimetry (DSC) was carried out with Perkin Elmer Pyris 1 DSC instrument. Molecular weights were measured by gel permeation chromatography (GPC) Agilent 1100 Series calibrated with polystyrene standards. Scanning electron microscopy (SEM) was performed using a Hitachi S520 microscope. Devices with a sandwich-like structure which is shown in Scheme 1 were prepared as follows: a tetrahydrofuran solution of the composite was spin-coated on an ITO (Indium Tin Oxides) glass overlapped by 5-mm-wide Au bar-electrodes, and then the layer was covered with Au film through magnetron sputtering. A xenon lamp was used as the resource of white light with the intensity of 75 mW/cm<sup>2</sup> on the device. The effective area for photocurrent tests was 20 mm<sup>2</sup>.

## 3. Results and discussion

The size distribution of the prepared ZnO colloids is very narrow and the average size is around 5 nm. The ZnO nanocrystals are well

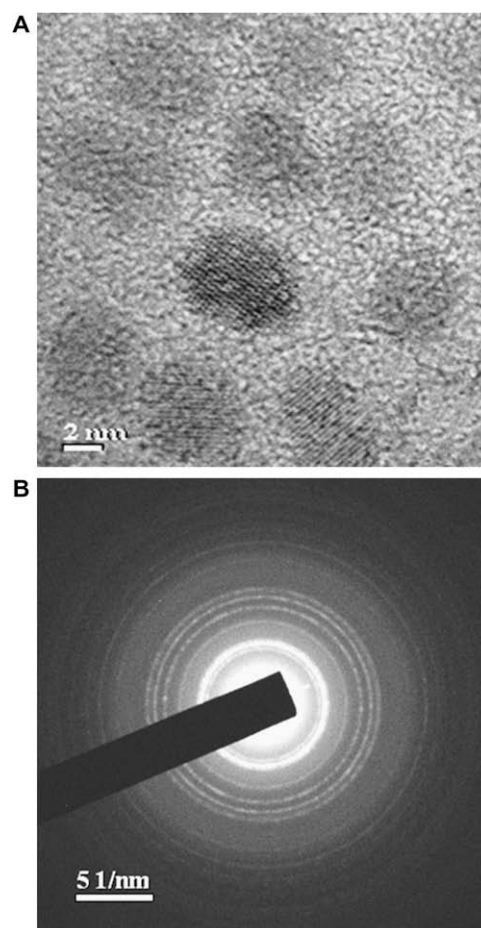


**Scheme 1.** Schematic configuration of the device fabricated for photocurrent tests.

crystallized with formation of highly regular crystal-lattices, as shown in Fig. 1. Crystalline stripes are clearly seen and have an interplanar spacing of about 0.26 nm (Fig. 1A), which indicates a hexagonal structure [19]. The ZnO nanocrystals are used to initiate the photochemical reaction as particularized in the Experimental section. Fig. 2, which shows the FTIR spectrum of the product, contains the characteristic bands of both PVK [20] and PMA [21]. The bands at 1478 and 1447 cm<sup>-1</sup> are assigned to the ring vibration of the carbazole groups, 1328 cm<sup>-1</sup> to C–H deformation of the vinylidene groups, and 1223 cm<sup>-1</sup> to C–H in-plane deformation of the aromatic rings. Moreover the strong absorption at 1730 cm<sup>-1</sup> is attributed to the C=O stretching of MA segments, and the peaks at 1268 and 1165 cm<sup>-1</sup> are attributed to the –C–O–C groups of MA. It is important to make clear whether the product is a copolymer or a mixture of PVK and PMA. Distinguished from a mixture of two polymers which exhibits two glass-transitions corresponding to the two components, the copolymer should have one *T<sub>g</sub>* which is approximately described by Fox rule [22]:

$$\frac{1}{T_g} \approx \frac{W_A}{T_g(A)} + \frac{W_B}{T_g(B)} \quad (1)$$

where *T<sub>g</sub>(A)*, and *T<sub>g</sub>(B)* are the glass-transition temperatures of homopolymers from A and B monomers, respectively. *W<sub>A</sub>*, and *W<sub>B</sub>* are mass fractions of A and B moieties, respectively. Fig. 3 shows the glass-transition behavior of the product measured by DSC. Only one *T<sub>g</sub>* is observed for each product. It is clear that the copolymer is obtained, called poly(VK-co-MA). Further, *T<sub>g</sub>* of the copolymer shifts to lower temperature when the feed ratio of NVK to MA is



**Fig. 1.** TEM image (A) and electron diffraction pattern (B) of the ZnO nanocrystals synthesized.

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