

Preparation of Ligand Free Au NPs/PPV Composites with High Stability and Photo-electric Response^{*}

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Abstract A novel kind of ligand free aurum nanoparticles (Au NPs)/poly(*p*-phenylene-vinylene) (PPV) composites was prepared *via* a simple approach. Although there were no ligands coating on the surface of the Au NPs, the Au NPs/PPV precursor composite exhibited excellent stability that no obvious variance was found as long as 6 months at ~4 °C in aqueous and alcohol mixed solutions. This was attributed to the strong interaction between Au NPs and PPV precursor, which was further strengthened after heat transformation. Fourier transform infrared (FTIR) and Raman spectra showed the interaction between benzene ring in PPV and Au NPs led to the part transformation of the sp² hybrid orbital into the sp³ one during the composite formation. As a result, the photoluminescence (PL) life time of PPV in the composite was longer than that of pure PPV. The Au NPs/PPV composite exhibited good photo-electric response, indicating their potential application in the area of the photoelectric conversion devices.

Keywords: Au; Nanoparticle; PPV; Composite; Photo-electric.

INTRODUCTION

The composites of nanoparticles (NPs) and polymers have attracted much attention because they not only have luminescent, electrical or magnetic properties of inorganic NPs but also the convenience to tailor the structure, facility to process and low cost of polymers^[1–6]. Many methods of preparing composites have been developed including directly mixing^[7], layer-by-layer assembly^[8], electrochemistry^[9], sol-gel^[10] and ultrasonic irradiation^[11], *etc.* These composites can find applications in electroluminescent (EL) devices, photovoltaic (PV) cells as well as temperature sensor, *etc.*^[7–13]. However, the ligands which are essential to stabilize the NPs often hinder the transport of the charge carriers and hence limit the improvement of the device efficiency. Therefore, we try to get rid of these ligands by heat treatment after the formation of the composites, but it is difficult to remove all of the ligands^[14]. *In situ* approach can solve this problem in which the matrix material and metal ions are mixed in solution and then exposed to the counterion (such as S²⁻ or Se²⁻, *etc.*) in the form of gas or as ions dissolved in solution^[15]. The shortcoming of this method cannot really realize the function integration of NPs

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and polymers. On the contrary, it often sacrifices the properties of the components in the composites. For example, the photoluminescence (PL) of the resulting NPs/polymer composites is dramatically quenched as a result of the absence of efficient passivation^[16]. Therefore, it still remains challenge to prepare ligand free NPs/polymer composites with desired properties.

Noble metal NPs have been widely investigated in recent years because of their potential application in catalysis, sensor, electronics and nanobiomedicine, *etc*^[17–20]. Among these NPs, Au NPs are one of the most popular noble metal NPs for their unique optical, electrical and electrochemical properties^[17, 21]. In order to improve the properties of Au NPs and explore their application, people normally combine Au NPs with conducting polymers. For example, Carroll added small amount of Au NPs capped by dodecylamine into poly (3-octylthiophene)/C₆₀ blends and enhanced the photovoltaic device efficiency^[22]. Kim *et al.* reported that Au NPs/multi-walled carbon nano-tubes/polyvinylidene fluoride nanofibrous composites showed excellent electrocatalytic activity towards oxidation of ascorbic acid^[23]. Poly(*p*-phenylene-vinylene) (PPV) is one of the most famous conducting polymers due to its excellent PL, EL, PV, and non-linear optical properties^[24]. However, there are few reports about the Au NPs/PPV composites.

In this paper, we used a novel route to prepare Au NPs/PPV composites. HAuCl₄ was reduced in the presence of *p*-xylene-bis(tetrahydrothiophenium chloride) and almost simultaneously, the monomer was polymerized to get the Au NPs/PPV precursor composite, followed by heat transformation to obtain the Au NPs/PPV composite at last. The advantage in this system was that there were no ligands on the surface of the Au NPs, which ensured the closed contact between Au NPs and PPV. The direct interaction between them was confirmed by the results of FTIR, Raman spectra and PL life time, as well as the photo-electric response properties.

EXPERIMENTAL

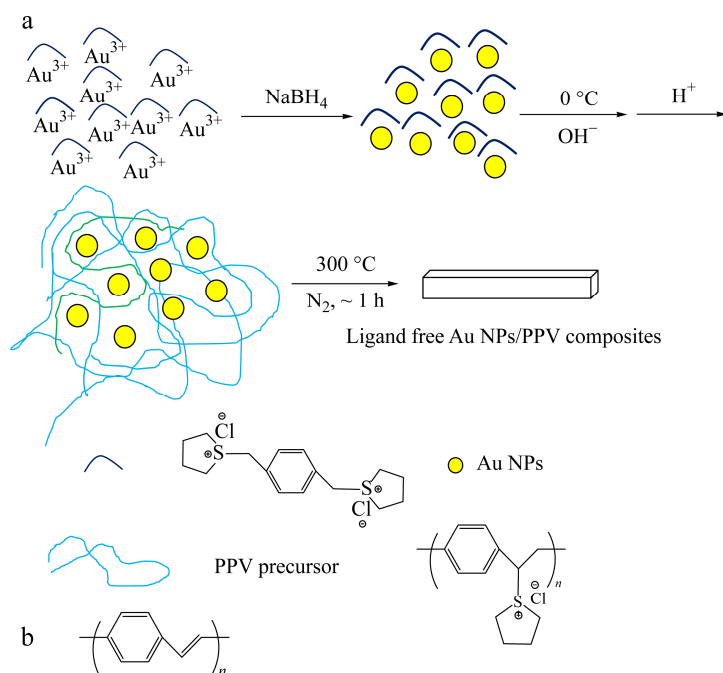
Materials

p-Xylylene dichloride (98%) was purchased from Alfa Corporation, tetra-hydro-thiophene (98%) was purchased from Aldrich Corporation, MoO₃ was purchased from Acros Corporation, chloroauric acid (HAuCl₄·4H₂O) was bought from Shanghai Chemicals Corporation, and sodium borohydride (NaBH₄) was bought from Tianjin Chemicals Corporation. All reagents were directly used without further purification.

Preparation of PPV Precursor and Au NPs/PPV Precursor Composites

The preparation of PPV precursor can be found elsewhere^[24]. Briefly, 10 mL 0.4 mol/L NaOH was added into 10 mL of 0.4 mol/L *p*-xylylenebis(tetrahydrothiophenium chloride) methanol solution. This solution was cooled to 0–5 °C in an ice bath under nitrogen atmosphere. The reaction proceeded for 1 h and then was terminated by the addition of 0.4 mol/L HCl aqueous solution to neutralize the reaction solution. The PPV precursor aqueous solution was dialyzed against deionized water for about one week and ethanol for three days.

A certain amount of 1 wt% HAuCl₄ was added into the methanol solution containing 0.5 g *p*-xylene-bis (tetrahydrothiophenium chloride) and then excessive 2 wt% NaBH₄ solution was rapidly added under vigorous stirring. The solution changed into black blue immediately. The polymerization was initiated by dropping 40 mL 0.4 mol/L NaOH solution to obtain Au NPs/PPV precursor composites. The reaction proceeded for 1 h and then was terminated by the addition of 0.4 mol/L HCl aqueous solution to neutralize the reaction solution. The whole reaction procedure was carried out in ice-water bath and under nitrogen atmosphere. The prepared Au NPs/PPV precursor composite aqueous solution was dialyzed against deionized water for one week and ethanol for three days (Scheme 1). Therefore, the Au NPs/PPV precursor composite was kept in aqueous and alcohol mixed solution.



Scheme 1 (a) The preparation process of ligand free Au NPs/PPV composite, (b) the structure of PPV

Fabrication of Photovoltaic Device

First, prepare the TiO_2 precursor. In a typical synthesis, 4 mL tetrabutyltitanate was dissolved in 2 mL isopropanol in a conical flask for 5 min. 210 μL water and 17 μL concentrated HCl were mixed with 4 mL isopropanol for 5 min. Then, this solution was dropped into the conical flask over about 10 min, and the mixture was stirred for 12 h at room temperature. Before use, the resultant TiO_2 precursor was diluted with isopropanol. Second, fabricate the device. ITO-coated glass substrates were first treated with chloroform, acetone and isopropanol consequently by ultrasonic. The substrates were rinsed with deionized water before drying in an N_2 flow, followed by oxygen plasma treatment for 5 min. Then, TiO_2 was spun-coating on the substrate and heated at $350\text{ }^\circ\text{C}$ for 15 min. The thickness of TiO_2 layer was about 30 nm. After spin-coating the Au NPs/PPV composite precursor at 1000 r/min, the blend film was annealed at $300\text{ }^\circ\text{C}$ for 60 min in the glove box under nitrogen atmosphere and the thickness of the blend film was about 80 nm, followed by evaporation of 5 nm MoO_3 and 60 nm Au electrode with a 5 mm^2 mask.

Characterization

UV-Vis spectra were acquired using a Shimadzu 3100 UV-Vis-near-IR spectrophotometer. TEM on the selected areas of the samples was performed on a Hitachi H-800 electron microscope operating at 175 kV and a JEOL-2010 electron microscope operating at 200 kV. FTIR spectra were recorded from a KBr window on a Nicolet AVATAR 360 FTIR spectrophotometer. Resonant Raman scattering spectra were recorded at room temperature with a JY HR-800 Lab Ram confocal Raman microscope in a backscattering configuration with an excitation wavelength of 633 nm. The fluorescence lifetimes of Au NPs/PPV and pure PPV films were measured with a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using a 325 nm laser (pulse width = 4 ns) from a Sunlite OPO (Continuum) pumped by a Nd: YAG PP-8000 as the excitation source. Atomic force microscopy (AFM) images were recorded in tapping mode with a Digital Instruments NanoScope IIIa under ambient conditions. The current density-voltage (J - V) characterization of photovoltaic devices under white-light illumination from an SCIENCETECH 500-W solar simulator (AM 1.5 G, $100\text{ mW}/\text{cm}^2$) was carried out on computer-controlled Keithley 2400 Source Meter measurement system in a glove box filled with nitrogen atmosphere ($\text{H}_2\text{O} < 0.08\text{ mg}/\text{m}^3$ and $\text{O}_2 < 0.14\text{ mg}/\text{m}^3$).

RESULTS AND DISCUSSION

UV-Vis Spectra of Au NPs/PPV Precursor Composites

Figure 1 shows the UV-Vis spectra of Au NPs/PPV precursor composites and PPV precursor (a). Spectrum (b) is the UV-Vis spectrum of Au NPs/PPV precursor composites just prepared and the spectrum (c) is for the composite placement over 6 months. There is an obvious new peak at about 546 nm in the composite spectra in comparison with that of pure PPV precursor, which results from the surface plasma resonance (SPR) absorption of Au NPs. This indicates that the Au NPs have been successfully formed in the PPV precursor matrix. Generally speaking, Au NPs with diameter in the range of 5–50 nm show a sharp absorption band in the region of 520–530 nm^[17]. It is red-shift in our system due to the affection of PPV precursor because SPR of metal NPs is sensitive to the surrounding environment, indicating the strong interaction between Au NPs and PPV precursor. Insets of Fig. 1 give the photos of Au NPs/PPV composite solutions with weight ratio of PPV to Au NPs equal to 75. It is observed that Au NPs homogeneously distribute in the solution although we didn't use any alkyl thiol or surfactant to protect Au NPs in this experiment process. Moreover, alcohol was introduced into the system during the dialysis process, which would have led to the precipitation at most cases. However, the Au NPs/PPV precursor composite solution can keep stable over 6 months. Inset of Fig. 1, the upper photo shows no obvious change for the solution after 6 months' placement at ~4 °C except for some solvent evaporation. The SPR peak in the UV-Vis spectrum becomes more obvious after 6 months (the line in Fig. 1) because the concentration increased due to the solvent evaporation. The formation of Au NPs and PPV precursor is almost at the same time, and this step is the key to control the size and homogeneous distribution of the Au NPs in the composites. Therefore, it is important to immediately initiate the polymerization of *p*-xylylenebis (tetrahydrothiophenium chloride) after the formation of Au NPs. This is because the molecular chains of PPV precursor stagger in solution and result in the improvement of the solution viscosity, which makes Au NPs limited in the PPV precursor chains and can't freely move. As a result, the Au NPs/PPV precursor composite solution possesses good stability.

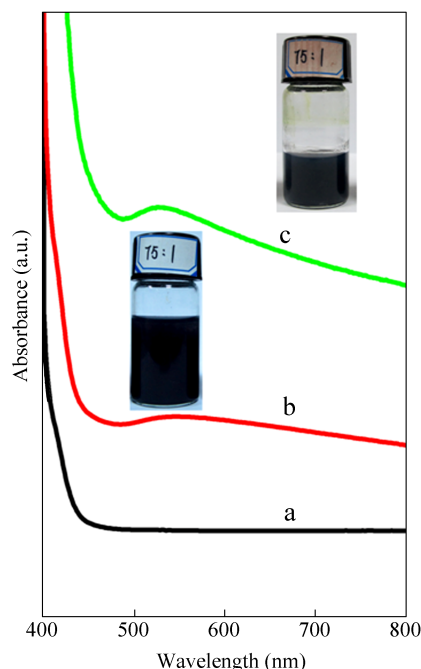


Fig. 1 UV-Vis spectra of pure PPV precursor (a), Au NPs/PPV precursor composite (b, just prepared) and Au NPs/PPV precursor composite (c, 6 months after preparation). Insets are the photos of Au NPs/PPV precursor composite solutions: the lower is the one just prepared and the upper is the one placement for 6 months.

Morphologies of Au NPs/PPV Composites

The composites with different weight ratios of PPV to Au NPs including 25, 75, 125 and 250, were prepared in order to investigate the morphology and properties. Figure 2 exhibits the TEM images of Au NPs/PPV precursor composites with different ratios. For the ratio of 25 (Fig. 2a), serious aggregation is observed during the evaporation of the solvent. It is impossible to distinguish the size of the composite. The Au/PPV precursor composite with diameter of ~ 20 nm is observed when the ratio increases to 75 in Fig. 2(b), although they aggregate to form branched chains. For the ratio of 125 and 250, the distribution of composite NPs becomes much better. These results suggest that the interaction between Au NPs and PPV precursor is not strong enough to stabilize Au NPs during the process of film formation. Fortunately, the situation is different after heat transformation of Au NPs/PPV precursor at 300 °C for 60 min. Figure 3 gives the TEM images of Au NPs/PPV composites. It is observed that Au NPs homogenously distribute in the PPV matrix for all of the ratios, although some aggregation (~ 50 nm) can still be seen. The diameter of the Au NPs/PPV composites ranges from 15 to 20 nm and the morphology is sphere-like. The large difference after heat transformation implies that the interaction between Au NPs and PPV has changed into much stronger one, which motivates us to further investigate their interaction.

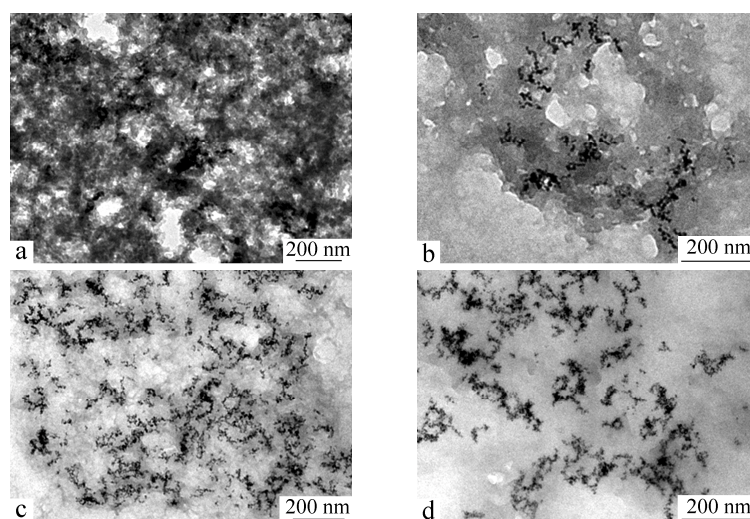


Fig. 2 TEM images of Au NPs/PPV precursor composites with weight ratios of PPV to Au: (a) 25, (b) 75, (c) 125 and (d) 250

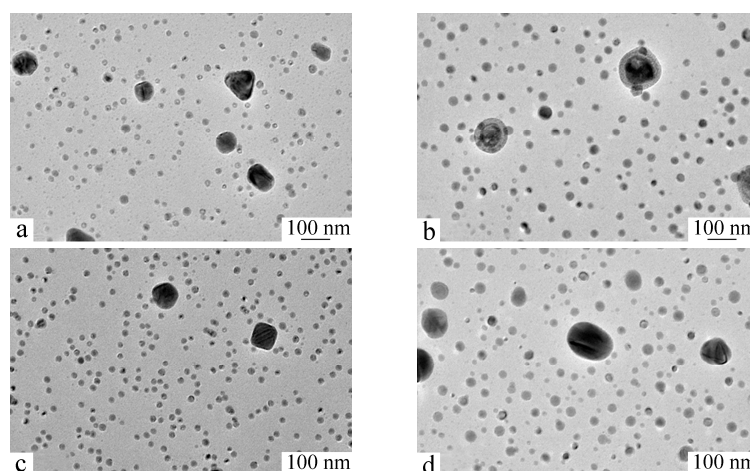


Fig. 3 TEM images of Au NPs/PPV composites with weight ratios of PPV to Au: (a) 25, (b) 75, (c) 125 and (d) 250

FTIR and Raman Spectra of the Au NPs/PPV Composites

Figure 4 shows the FTIR spectra of Au NPs/PPV composite and pure PPV, respectively. The two spectra are almost similar with each other. The bands at 3020 and 2950 cm^{-1} are assigned to the stretch vibration of trans-vinylene C—H. The bands at 836 and 1516 cm^{-1} are attributed to C—H out-of-plane bend vibration and C—C ring stretch vibration in *p*-phenylene, respectively. These results indicate that PPV has been successfully formed by this method. It is observed that there is a new peak emerged at 783 cm^{-1} in Au NPs/PPV composite, which results from the interaction of 6S orbital of Au atom with benzene ring in PPV chain. During the procedure of interaction, part of benzene ring in PPV is affected by Au NPs because this procedure leads to the introduction of sp^3 hybrid orbital into the sp^2 hybrid orbital of the benzene ring. The results of FTIR spectra indicate the direct interaction between Au NPs and PPV is realized by using our method, which is important for their photo-electric property.

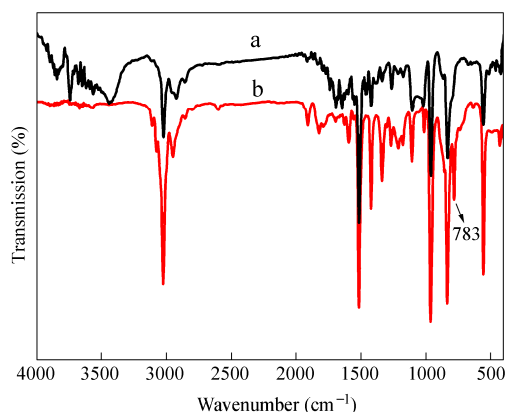


Fig. 4 FTIR spectra of pure PPV (a) and Au NPs/PPV composite (b)

Raman spectra can be used to prove the contribution of sp^2 hybrid orbital. According to Fig. 5(a), the peaks at 1328, 1546 and 1625 cm^{-1} mainly attributed to C=C stretching vibration^[25]. The peak at 1328 cm^{-1} generates from the defect of sp^2 hybrid orbital while the peaks at 1546 and 1625 cm^{-1} originate from sp^2 hybrid orbital. If the 6S orbital of Au atom has interaction with benzene ring in PPV chain, the relative intensity of peak at 1328 cm^{-1} will increase. Therefore, the contribution of peak at 1328 cm^{-1} (the ratio of peak intensity at 1328 cm^{-1} to peak intensity at 1546 and 1625 cm^{-1}) can directly prove the transformation of sp^2 to sp^3 hybrid orbital^[25–27]. In our system, the ratio in pure PPV is 0.46 (Fig. 5b). As expected, introducing Au NPs into PPV leads to a great enhancement in the intensity of the Raman spectrum. The ratio increases to 0.51 (Fig. 5a). Therefore, there might be the transformation of sp^2 to sp^3 hybrid orbital during the formation of Au NPs/PPV composites, which will bring important influence on its stability.

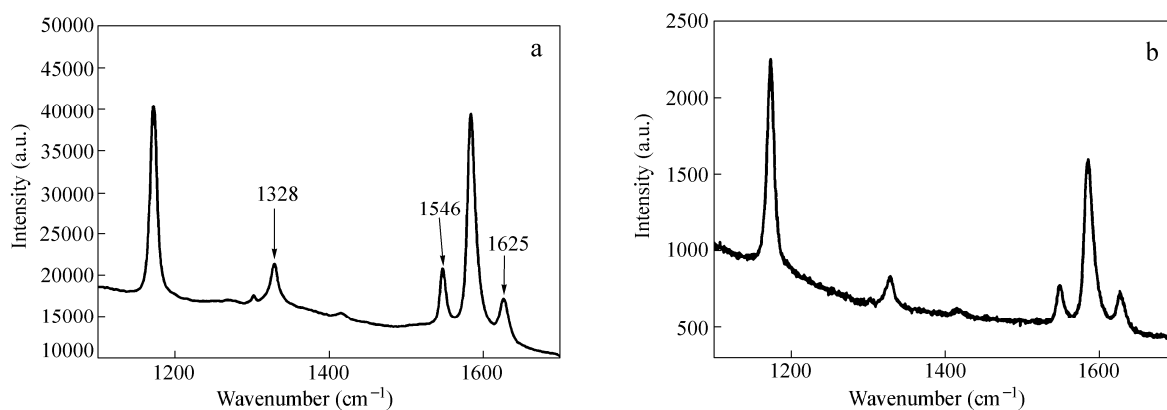


Fig. 5 Raman spectra of (a) Au NPs/PPV composite and (b) pure PPV

The Photo-electric Properties of Au NPs/PPV Composites

The fluorescence life times of Au NPs/PPV composites with 25, 75, 125, 250 ratios are 1955, 1974, 1957, and 1942 ps while that of pure PPV is 1805 ps at 516 nm (Fig. 6). The life time increased ~ 150 ps by doping Au NPs, which is in accordance with the results reported by Lim^[28]. This result indicates the photo stability is enhanced in the Au NPs/PPV composite. It is believed that the photo-oxidation of PPV begins with the formation of singlet oxygen *via* energy transfer from long-lived triplet excitons. Triplet exciton energetics and dynamics play a primary role in the photo-oxidation process. The oxygen is excited to a highly reactive singlet site, which reacts with the conducting polymer backbone, resulting in the formation of luminescence-quenching defects and decrease of fluorescence lifetime. In our system, however, the 6S orbital of Au NPs and benzene ring have interaction which results in the excitons restricted to move along the conjugated chain of PPV. The number of excitons trapped by defect in the chain decreases due to the formation of the Au NPs/PPV composite. Consequently, more excitons transit to ground state from excited single state and the fluorescence life time becomes longer.

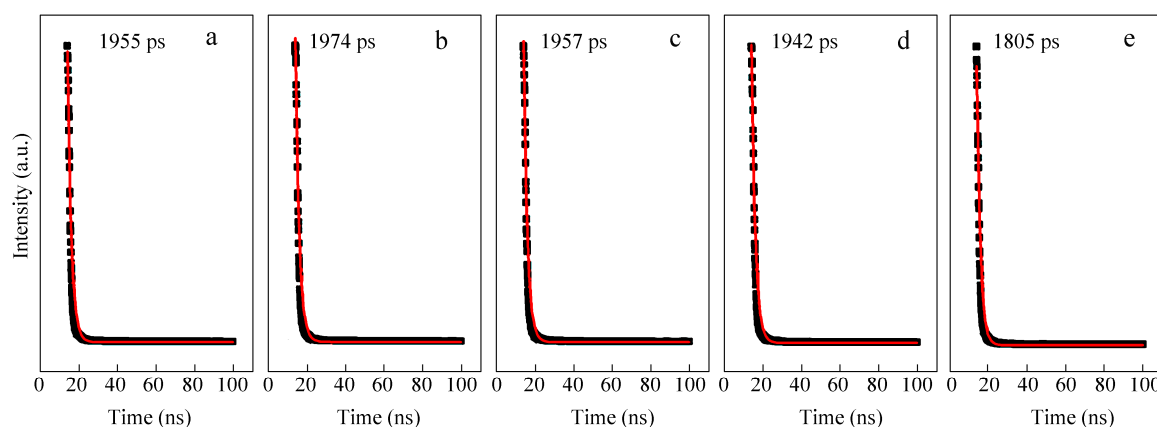
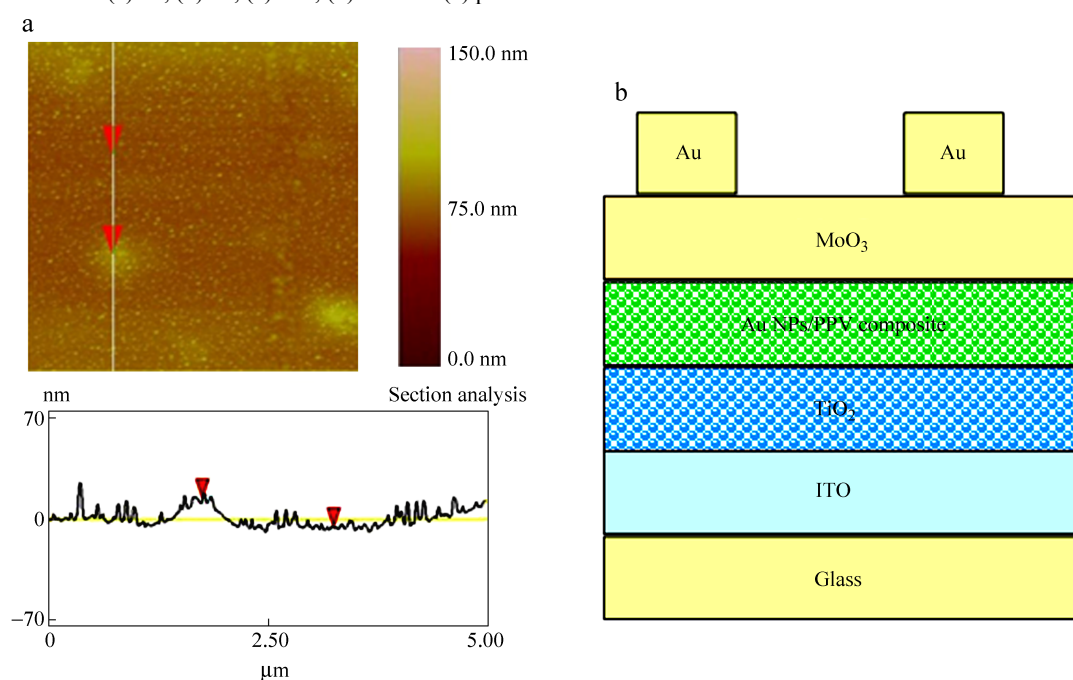


Fig. 6 Fluorescence lifetime decays of Au NPs/PPV composites with ratios of PPV/Au: (a) 25, (b) 75, (c) 125, (d) 250 and (e) pure PPV



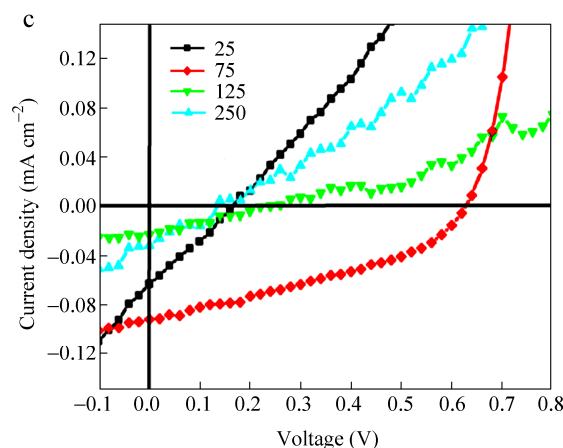


Fig. 7 (a) AFM image of Au NPs/PPV composite, (b) device structure, (c) current density-voltage curves of Au NPs/PPV composites with different ratios of PPV/Au NPs

From Fig. 7(a), the AFM image of the Au NPs/PPV composite exhibits that the height is lower than 100 nm, which satisfies the requirement of device fabrication. The devices with the structure of ITO/ TiO₂/Au NPs and PPV composites/MoO₃/Au (Fig. 7b) were fabricated. All of them show a clear photo-electric response under illumination at standard conditions, namely, illuminating with an SCIENCETECH 500-W solar simulator (AM 1.5 G, 100 mW/cm²) at the same distance. In comparison with other ratio composites, the Au NPs/PPV composite with 75 ratio shows good rectifying properties. The photo-current of Au NPs/PPV composite films are obviously enhanced and power conversion efficiencies increase by about 20 times at the ratio of 75 in comparison with that of pure PPV. The reason for the improvement of the photo-electronic response of the composite material might be attributed to the interaction between the Au atom and the π system of PPV. Photo-generated excitons dissociate to electrons and holes more easily in the composite than those in pure PPV. As a result, the density of photo-generated current is improved by doping appropriate dose of Au NPs.

CONCLUSIONS

In summary, a novel kind of ligand free Au NPs/PPV composites was prepared. Part of benzene ring in PPV was affected by Au NPs in which the sp³ hybrid orbital was introduced into the sp² hybrid orbital. Such structure of the composites led to the improvement of the stability, the increase of the PL life time and the enhancement of the photo-electric response of the Au NPs/PPV composite, which indicated their broadly potential application in organic photo-electronic area, such as LED, solar cells, and sensors, *etc.*

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