

Supporting Information

A Positive Synergetic Effect Observed in SnO₂-P3HT Composite

Semiconductor: The Striking Increase of Carrier Mobility

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S1. Specific surface area and pore-size distribution of SnO₂ PNS

Specific surface area (SSA) and pore-size distribution are two important parameters to characterize SnO₂ PNS. These parameters were determined by nitrogen adsorption/desorption isotherms obtained at -196 °C on an Accelerated Surface Area and Porosimetry 2000 Analyzer. The SSA value of the typical sample was calculated to be 7.9 m²/g using Brunauer-Emmett-Teller (BET) model. Fig. S1 shows the nitrogen absorption/desorption isotherm and pore-size distribution of this SnO₂ PNS sample. It can be seen that the slopes of both absorption and desorption curves are very steep, and the hysteresis loop is rather narrow, indicating that the pressures of condensation and evaporation are quite close to the saturation vapor pressure. The inset of Figure S1 demonstrates that the size of the pores mainly distributed within the range of 40~140

nm.

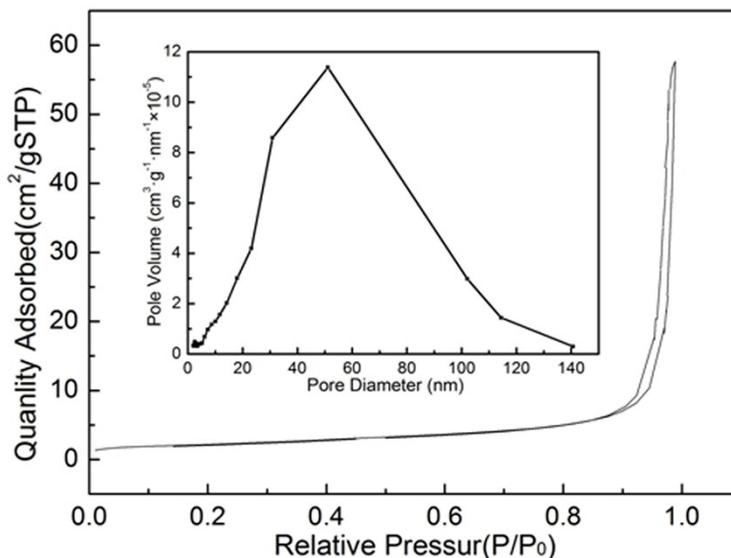


Figure S1. Nitrogen adsorption/desorption isotherms and pore-size distribution (inset) of a typical SnO₂ PNS sample.

S2. Correlation between the mobilities of SnO₂ PNS and P3HT-SnO₂ composite semiconductor

According to the model proposed in Fig. 3, SnO₂ PNS should serve as the major transportation path for the electrons, thus the mobility of P3HT-SnO₂ composite semiconductors would positively correlate with that of SnO₂ PNS. In other words, the higher the SnO₂ PNS mobility is, the higher the P3HT-SnO₂ composite semiconductor mobility is. On the other hand, it is also well known that oxygen vacancy is the major defect in SnO₂, and a semiconductor possessing perfect crystalline structure would exhibit much higher mobility. So, the mobility of SnO₂ PNS can be improved by reducing the oxygen vacancies. Here the SnO₂ PNS samples were annealed at 350°C in

high-pressure oxygen, and the resultant “pre-treated” SnO₂ PNSs were used in preparing P3HT-SnO₂ composite semiconductors. The results presented in Fig. S2 clearly indicate that, the SnO₂ PNS annealed at 350 °C in 4.0 MPa oxygen exhibits the highest electron concentration and mobility, and the corresponding composite semiconductors also exhibit the highest electron concentration and mobility values. It should also be noted that both the electron concentration and mobility of the annealed SnO₂ PNS increased initially with the increase of oxygen pressure, reaching their maximum values at 4.0 MPa. Accompanying the further increase of oxygen pressure, the electron concentration and mobility decreased instead. This phenomenon may be resulted from the interstitial oxygen (also serves as crystal defect) in SnO₂ formed in higher pressure oxygen.

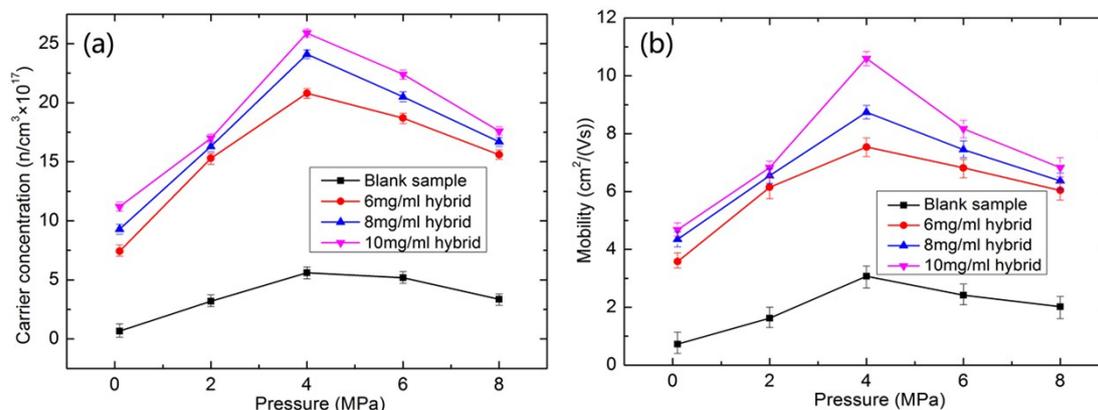


Figure S2. Electron concentration (a) and mobility (b) of SnO₂ PNSs annealed in high-pressure oxygen and the corresponding P3HT-SnO₂ composite semiconductors.

S3. Verifying the repeatability of above experimental results

Furthermore, we carried out several series of experiments to verify the repeatability

of the above results. Among the samples presented in Table S1, SnO₂ PNS (1) was prepared by hot-pressing the mixture of SnO₂ nanocrystals and dioxane at 60 MPa, 200 °C for 3 h, while SnO₂ PNS (2) and SnO₂ PNS (3) were prepared under similar conditions except the ratio of SnO₂:dioxane. Besides, the preparation processes of these composite semiconductors were all the same. It is clear that all the composite semiconductors possess much higher carrier concentration and mobility than the corresponding pristine SnO₂ PNSs.

Table S1 Carrier concentration and mobility of some SnO₂ PNS and their corresponding composite semiconductors.

Samples	SnO ₂ PNS (1)		SnO ₂ PNS (2)		SnO ₂ PNS (3)	
SnO ₂ nanoparticles / dioxane	3g/4ml		3g/5ml		3g/6ml	
Hybridization States	Before	After	Before	After	Before	After
$n / \times 10^{17} \text{cm}^{-3}$	1.21	5.17	1.65	10.3	1.14	4.26
$\mu / \text{cm}^2/\text{Vs}$	0.4	1.1	0.7	3.3	0.3	0.9

Note: “before” and “after” hybridization refer to SnO₂ PNSs and P3HT-SnO₂ PNS composite semiconductor, respectively.

S4. Distinguish the effects of pre-treatment in chloroform and forming composite semiconductor with P3HT.

In fact, the potential reasons for the increase of both carrier concentration and mobility of P3HT-SnO₂ PNS composite semiconductors might include two aspects: the pre-treatment of SnO₂ PNS in chloroform and the formation of composite semiconductor with P3HT. In order to clearly distinguish these two aspects, we

conducted control experiments in which the SnO₂ PNSs were treated under the same conditions with that of preparing P3HT-SnO₂ PNS composite semiconductors, except that no P3HT was used. In a typical experiment, a SnO₂ PNS was heated at 150 °C in a three-necked bottle for 3 h, under a vacuum of 2.3×10^{-3} Pa. Then the SnO₂ PNS was cooled naturally to room temperature, and 20 ml chloroform was injected into the bottle. After being immersed for 24 h, the SnO₂ PNS was recovered and annealed at 140 °C in argon for 20 minutes. By comparing the results of SnO₂ PNSs with and without the pre-treatment in chloroform, it was found that the carrier concentration of SnO₂ PNSs remained almost unchanged while the mobility decreased after such a treatment process. Namely, the carrier concentration of SnO₂ PNS remains at 1.65×10^{17} cm⁻³, but the mobility decreased from 0.7 cm²/Vs to 0.5 cm²/Vs.

Therefore, it is reasonable to believe that the increase of carrier concentration and mobility of P3HT-SnO₂ PNS composite semiconductor should arise from the synergetic effect of P3HT and SnO₂, rather than from the treatment in pure chloroform.