

Synthesis of Poly(styrene)-TiO₂ Hybrid Submicrospheres and Their UV Photoconductivity Properties

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Abstract In this paper, poly(styrene)-TiO₂ hybrid submicrospheres were synthesized via a simple method. The photoconductivity of a double-layered photoreceptor (P/R) was also studied, in which the triphenylamine derivative (MTPD) was used as a carrier transportation layer and TiO₂ nanoparticles coated on polystyrene beads as a carrier generation layer. The P/R shows excellent photoelectronic properties under ultraviolet irradiation: charge potential reaches 660V, residual potential is about 100V and its photosensitivity is 0.106 (lx·s)⁻¹ with dark decay of 9V/s. This kind of UV-sensitive device shows great potential in many fields such as copying and printing.

1 Introduction

Inorganic/organic polymer nanocomposites have attracted the interest of a number of researchers, due to their properties of both the inorganic nanoparticles and the polymer by combining thermal stability, mechanical strength, or optical properties with flexibility and the ability to form films[1]. Nanocrystal TiO₂ is a typical n-type semiconductor potentially applicable to photochemical electrodes for energy conversion from solar into other forms such as H₂ gas and electricity[2]. However, it has the intrinsic trend to agglomerate and is hard to form dense and smooth film. Coating the colloidal particles on the polystyrene (PS) cores represents probably the simplest and most versatile strategy for increasing the diversity and complexity of a colloidal system[3] because formation of colloidal particles on the cores may dramatically alter the charge, functionality, and reactivity of their surfaces and thus enhance the stability and compatibility of the shell particles[4].

In this paper, hole-transport material triphenylamine derivatives were also used for photoconductivity measurements.

2 Experimental

The synthesis of titania-coated PS was similar to the literature[5]. Monodispersed positively charged PS spheres were synthesized by dispersion polymerization in an ethanol/water medium as follows: 5 g of water, 0.2 g of AIBN, 1.5 g of PVP, 5 g styrene (St), and 22.5 g of ethanol were charged into a 250-mL three-necked flask equipped with a mechanical stirrer, thermometer with a temperature controller, N₂ inlet, Graham condenser, and a heating mantle. The reaction solution was deoxygenated by bubbling N₂ at room temperature for about 30 min and then heated to 70 °C under a stirring rate of 100 rpm for 1.5 h, followed by the addition of the solution of 5 g St, 22.5 g EtOH, 0.22 g acrylic acid, and 1.14 g CTAB. The reaction was continued for another 12 h and then cooled to 50°C. 4 mL ammonia were then added and the mixture was stirred at 100 rpm

for 5 min. 19.6 g tetra-n-butyl titanate (TBT) was added quickly and the mixture was reacted at 50 °C for 2 h with constant stirring. The obtained spheres were separated from the reaction medium by centrifuging at 3000 rpm, washed three times with ammonium/ethanol, and then redispersed in deionized water for further examination.

The morphology of titania-coated PS was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Thermogravimetric Analysis (TGA) was performed using a TA Instruments SDT Q600 thermogravimetric analyzer under N₂ at a scan rate of 20°C/min heated from 30 to 650°C.

Photoconductivity was studied in function-separated dual-layer photoreceptors. Fig. 1 gives the structure of photoreceptors applied for measurement of photoconductivity. The photoreceptors were made by coating the charge generation layer (CGL) and the charge transportation layer (CTL) in turn on an aluminum substrate. The CGL was formed of titania-coated PS and the CTL consisted of 50 wt% triphenylamine derivatives (seen in Figure 2) in polycarbonate matrix. Photoconductive properties were evaluated by the standard xerographic photo-induced discharge method on the GDT- II model photoconductivity measuring device with a 500 W xenon lamp with a filter as a UV light source, and the photosensitivity was expressed as (E_{1/2})⁻¹ (E_{1/2}=I×t_{1/2}, I: light intensity, t_{1/2}: time from the initial potential to half under exposure). A good desired photoreceptor should have a large photosensitivity value first of all.

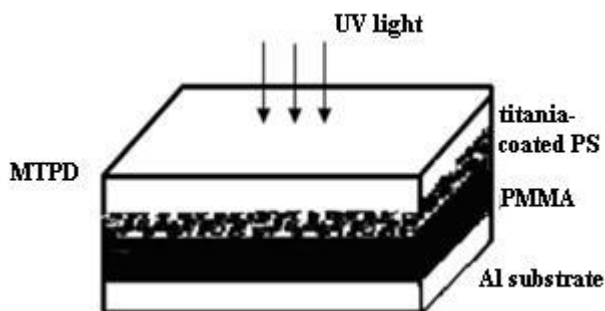


Fig. 1. Schematic diagram of the double layered photoreceptors

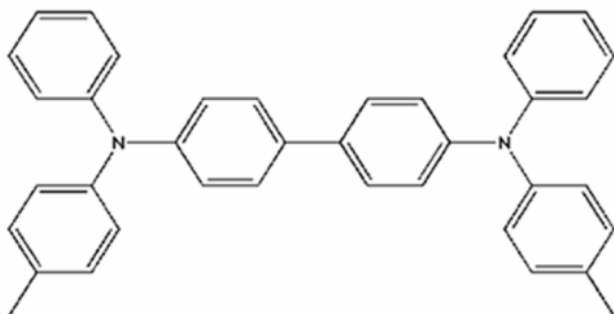


Figure 2. Molecular structure of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine.

3 Results and Discussion

3.1 Surface morphology of the PS and titania-coated PS

First, monodispersed positively charged PS particles were prepared by dispersion polymerization on the basis of the procedures described in the experiments. The TEM image, as demonstrated in Figure 3a, showed that uniform spherical PS particles with an average diameter of about 500 nm were obtained.

In the subsequent coating process, ammonia and TBT were added to the PS suspension for the sol-gel reaction. Under this condition, all titania formed as the shell on the core particle via the ammonia-catalyzed hydrolysis and condensation of TBT, which could be shown in Figure 3b.

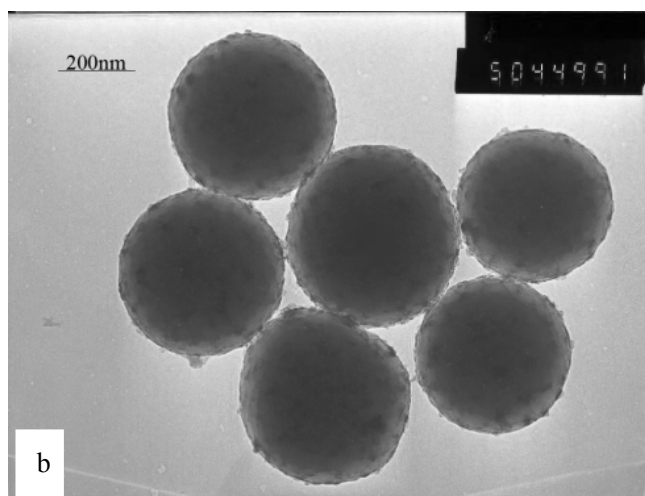
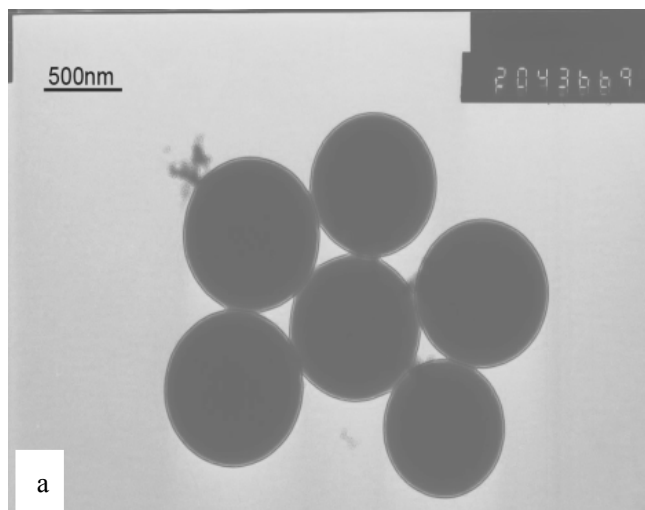


Figure 3. TEM images of the original PS particles (a) and all the coated spheres obtained(b)

Figure 4 further illustrated the SEM image of the titania-coated spheres prepared. It was found that all the spheres maintained the spherical morphology. However, some protuberances were clearly seen on the surfaces of the titania shells, probably because of the formation of the secondary particles as a result of faster hydrolysis and condensation of TBT. Also some titania aggregates can be found.

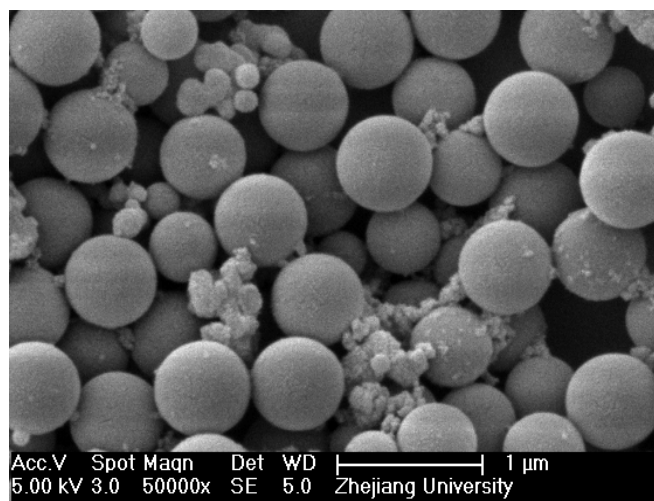


Figure 4. SEM image of the typical coated spheres obtained

3.2 TGA curve

The thermogravimetric curve of the titania-coated PS composite particles was shown in Figure 5. For the titania-coated PS composite particles, two weight loss stages (below 370, and 370-470°C), were observed, corresponding to the evaporation of physically absorbed water and residual solvent in the samples, and the decomposition of PS, respectively. There were almost no residuals at much higher temperatures for PS samples, so the content of TiO₂ was calculated to be 14.1%, which was similar to the theoretical result.

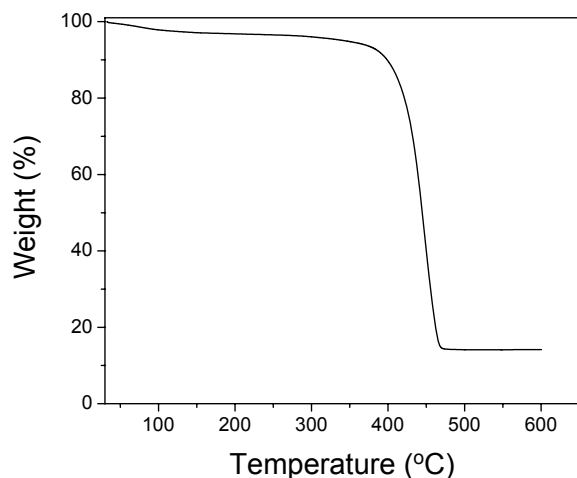


Figure 5. TGA curves for the selected titania-coated PS particles

3.3 Photoconductivity results

PS, as nonconducting polymer, has no photoconductivity. However, MTPD is a conventional hole-transporting material as well as carrier-generation material under UV irradiation. The results in Table 1 show the photoconductivity data of pristine PS

and titania-coated PS. From the results we can see there was a higher charge acceptance ($V_c=671$ V) and a lower residual potential ($V_r=105$ V) for modified PS than for pure PS. Furthermore, the time of half discharge of titania-coated PS is 0.47 s, which is a much lower value than that of PS (0.96 s) and indicates much better photoconductivity and photosensitivity than for corresponding PS. Chen et al. [6] investigated the photoconductivity of PS-co-CuPc(NO₂)₂. Zhang et al. [7] also investigated the photoconductivity of PS bonded with CuPc. They think that there is interaction between the PS main chain and CuPc(COOH)₄; this is beneficial for charge occurring by light transfer and hence is beneficial for promoting the photoconductivity property of this kind of polymer. In the titania-coated PS spheres there is also interaction between PS and TiO₂, so titania-coated PS showed better photoconductivity than PS.

Table 1 Photoconductivity of PS, titania-coated PS

CGL	V _c /V	V _r /V	t _{1/2} /s	E _{1/2} ⁻¹ /(lx•s) ⁻¹
PS	546	136	0.96	0.0519
titania-coated PS	671	105	0.47	0.106

Interface material: PMMA;

Charge transportation material (CTM) is N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (MTPD);

Exposure intensity is 20 lx.

From the above data, it can be concluded that photoconductivity is improved by the presence of TiO₂ in the polymers, and this type of polymer can be used as photoconductivity material directly.

4 Conclusion

Polymer submicrospheres coated with TiO₂ nanoparticles were synthesized by dispersion polymerization in an ethanol/water medium followed by hydrolysis and condensation of TBT. The photoconductivity results showed that modified PS submicrospheres have much better photoconductivity as well as photosensitivity compared to their counter parts. This kind of photoconductivity UV material may be used in many areas such as copying and printing.

5 Acknowledgements

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References

- [1] Ming Zhang, et al. Titania-Coated Polystyrene Hybrid Microballs Prepared with Miniemulsion Polymerization. *Langmuir*, 2004, 20(4):1420-1424.
- [2] B. O'Regan, M. Gratzel. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*, 1991, 353(6346):737-740.
- [3] F. Caruso. Nanoengineering of Particle Surfaces. *Advanced Materials*, 2001, 13(1):11-22.
- [4] M. Ohmori, E. Matijevic. Preparation and Properties of Uniform Coated

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- Inorganic Colloidal Particles: 8. Silica on Iron. Journal of Colloid and Interface Science, 1993, 160(2) :288-292.
- [5] Xinjian Chen, et al. Novel and Facile Method for the Preparation of Monodispersed Titania Hollow Spheres. Langmuir, 2006, 22(8) : 3858-3863.
- [6] Hongzheng Chen, et al. Synthesis and photoconductivity study of phthalocyanine polymers. II. PVK-co-CuPc (COOH)₃. Journal of Polymer Science Part A: Polymer Chemistry, 1993, 31(5) :1165-1170.
- [7] Junhua Zhang, et al. Synthesis and characterization of magnetic polymer microspheres with photoconductivity. Colloid and Polymer Science, 2002, 280 : 674-677.

Author Biography

Yan-gang Han received his BS in polymer science and engineering from the Nanjing University of Technology (2005) and studied as a PHD candidate in Zhejiang University. His work has mainly focused on the development of inorganic-organic hybrid photoconductive materials.