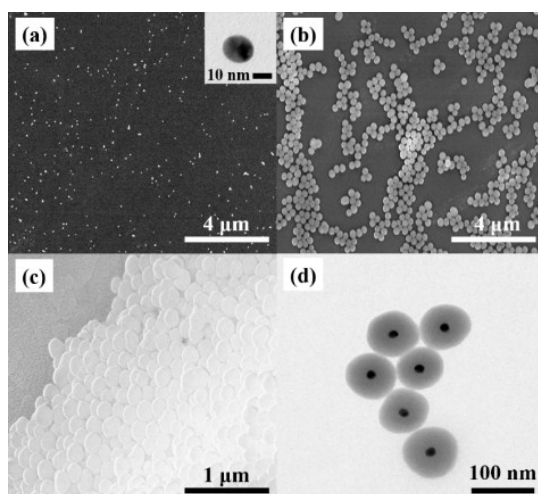


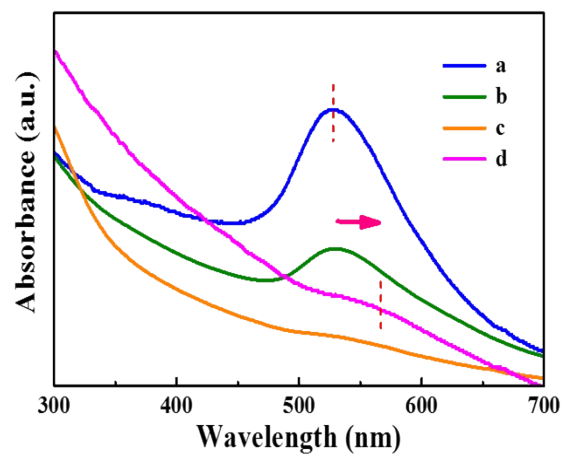
## Supplementary Information

### Preparing Non-volatile Resistive Switching Memories by Tuning the content of Au@air@TiO<sub>2</sub>-*h* Yolk-shell Microspheres in Poly(3- hexylthiophene) Layer

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Qing-Feng Xu<sup>a</sup>, Jian-Mei Lu<sup>a</sup>

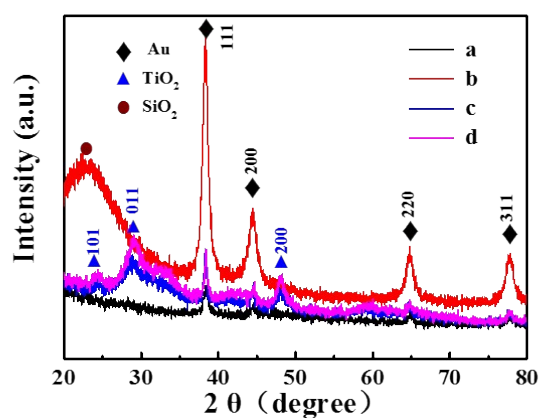


**Figure S1.** TEM and FESEM images of the (a) 16 nm Au nanocores, (b) (c) (d) 67 nm Au@SiO<sub>2</sub> microspheres. The respective scale bars for (a-d) are 4 μm, 4 μm, 1 μm and 1 μm. The insert showed the Au NPs at a scale about 10 nm



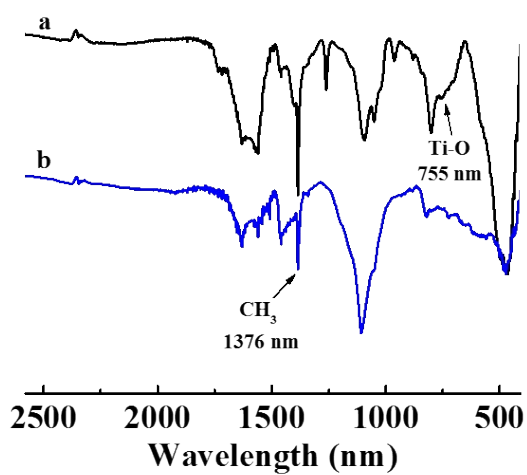
**Figure S2.** UV/Vis absorption spectra of (a) Au nanocores, (b) Au@SiO<sub>2</sub> microspheres, (c) Au@SiO<sub>2</sub>@TiO<sub>2</sub>-*h* microspheres, (d) Au@air@TiO<sub>2</sub>-*h* yolk-shell microspheres dispersed in ethanol.

The UV/Vis absorption spectra of the Au nanocores, the Au@SiO<sub>2</sub> and Au@air@TiO<sub>2</sub>-*h* yolk-shell hybrid microspheres dispersed in ethanol are shown in Fig. S2. The absorption peak of the Au@air@TiO<sub>2</sub>-*h* nanospheres is red shifted from 525 nm to 560 nm and lower intensity compared to the Au NPs. And the red shift is due to an increase in the local refractive index of the medium surrounding the Au NPs<sup>1</sup>.

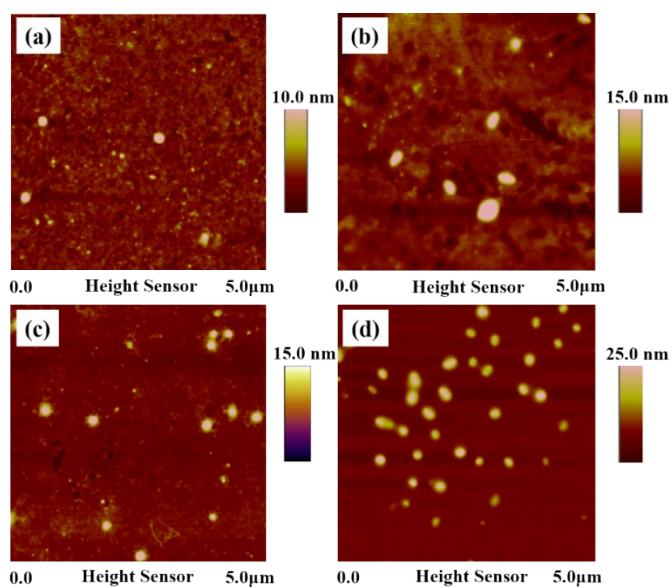


**Figure S3.** XRD patterns of the (a) Au nanocores, (b) Au@SiO<sub>2</sub> microspheres, (c) Au@SiO<sub>2</sub>@TiO<sub>2</sub>-*h* microspheres, (d) Au@air@TiO<sub>2</sub>-*h* yolk-shell microspheres.

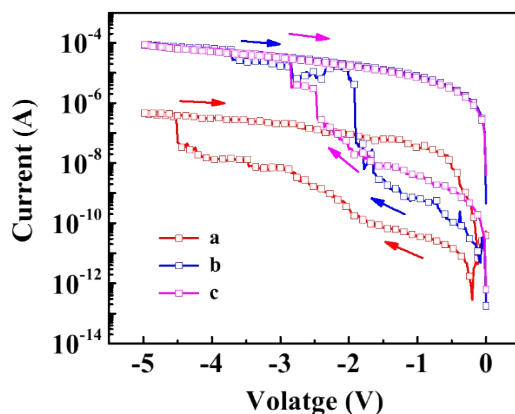
The crystal structures of the nanoparticles in different stages are further discerned by X-ray diffraction (XRD) patterns (Fig. S3). There are three series of peaks, which are respectively attributed to face-centered cubic Au (black rhombics), anatase-type TiO<sub>2</sub> (blue triangles) and amorphous-type SiO<sub>2</sub> (brown dots). Only peaks of Au and TiO<sub>2</sub> can be found in core-shell hollow spheres, indicating the yolk-shell nanoparticles have been successful synthesized.



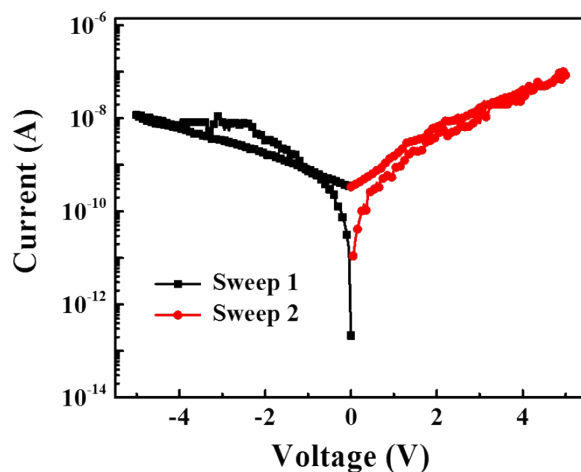
**Figure S4.** FT-IR absorption spectra of the (a) Au@air@TiO<sub>2</sub>-h + P3HT, and (b) pure P3HT.



**Figure S5.** AFM 2D height images of the Au@air@TiO<sub>2</sub>-h + P3HT polymer films containing: (a) 5 wt%, (b) 12 wt%, (c) 20 wt%, (d) 30 wt% Au@air@TiO<sub>2</sub>-h microspheres for the switching device. The surface average roughness is 1.59 nm, 2.92nm, 1.28 nm, 9.96 nm, respectively.



**Figure S6.** Typical current-voltage ( $I$ - $V$ ) characteristics of the (a) Al/[20 wt% Au NPs + P3HT]/ITO; (b) Al/[20 wt% Au@SiO<sub>2</sub> + P3HT] /ITO; (c) Al/[20 wt% Au@SiO<sub>2</sub>@TiO<sub>2</sub>-h + P3HT] /ITO switching device. ( $I_{cc} = 10$  mA).



**Figure S7.** Typical current-voltage ( $I$ - $V$ ) characteristics of the Al/P3HT/ITO switching device. ( $I_{cc}=10$  mA)

## Reference

1. T. Cai, B. Zhang, Y. Chen, C. Wang, C.-X. Zhu, K.-G. Neoh and E.-T. Kang, *Chemistry – A European Journal*, 2014, **20**, 2723-2731.