*Supporting information*

# $WO_X$@PEDOT Core-Shell Nanorods: Hybrid Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells

Ping Liu,[a,b] Chen Wang,[a,b] Dongying Zhou,[a,b] Quan Yuan,[a,b] Yu Wang,[a,b] Yao Hu,[a,b] Dongwei Han,[a,b] Lai Feng[a,b,*]

[a] *Soochow Institute for Energy and Materials Innovations, College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215006, China*

[b] *Jiangsu Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies, Soochow University, Suzhou 215006, China*

**Corresponding author (Tel: +86 512 65223650; E-mail address: fenglai@suda.edu.cn (Lai Feng))*


**Figure S1.** Photos of the samples of $WO_X$ NWs, $WO_X$@PEDOT and PEDOT:PSS.

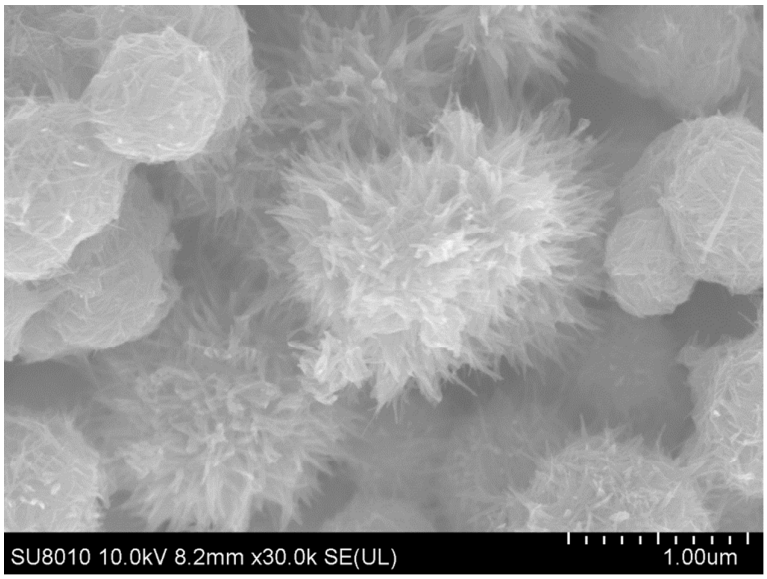


**Figure S2.** SEM image of as-prepared $WO_X$ NWs.

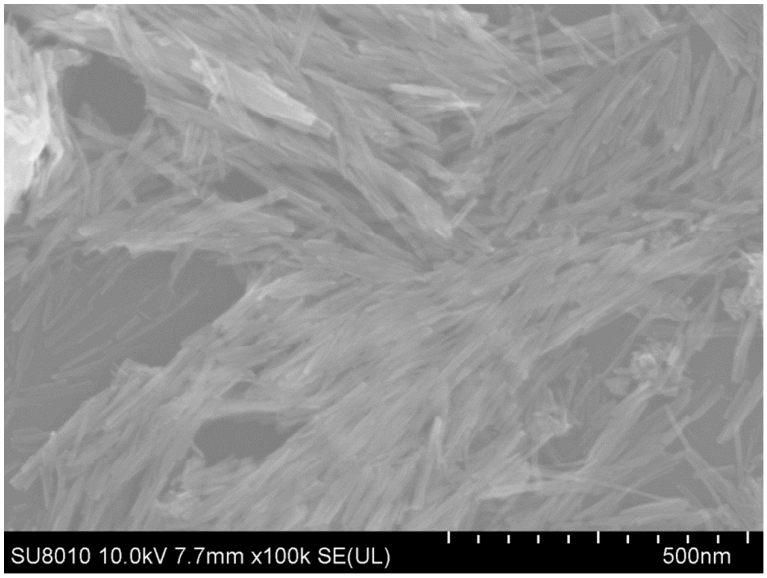


**Figure S3.** SEM image of $WO_X$ NWs obtained after constant stirring in aqueous solution without EDOT.

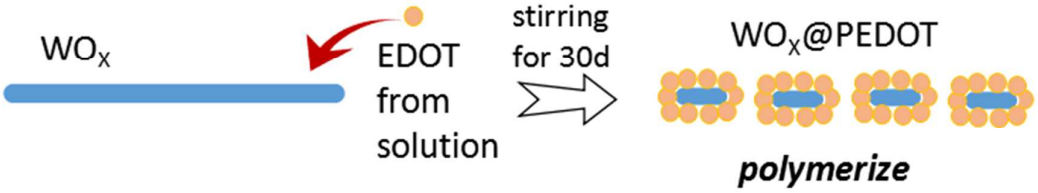


**Figure S4.** Schematic illustration of the truncation process to produce $WO_X$@PEDOT NRs from $WO_X$ NWs.

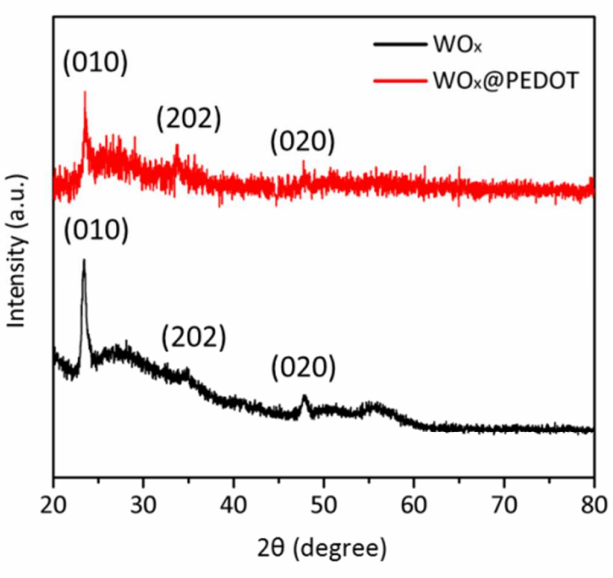


**Figure S5.** XRD patterns of $WO_X$ NWs and $WO_X$@PEDOT NRs.

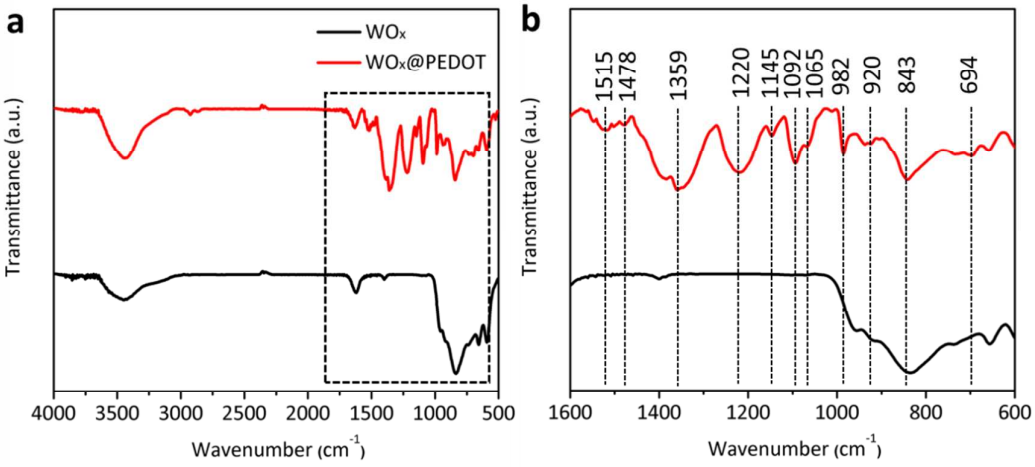


**Figure S6.** (a,b) FT-IR full and highlighted spectra of $WO_X$ NWs and $WO_X$@PEDOT NRs.

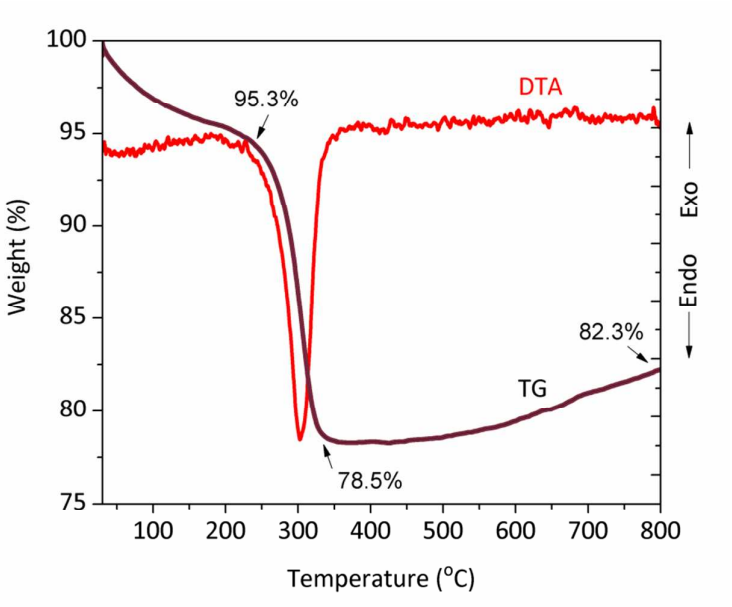


**Figure S7.** TGA profile of $WO_X$@PEDOT NRs measured in air atmosphere.

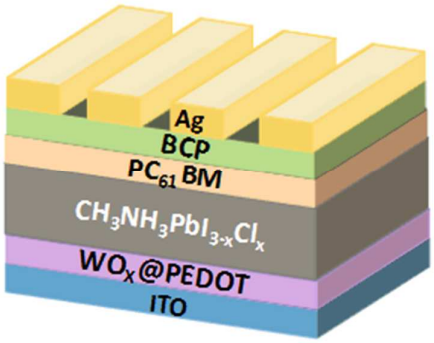


**Figure S8.** Device architecture of solution-processed planar p-i-n PeSC.

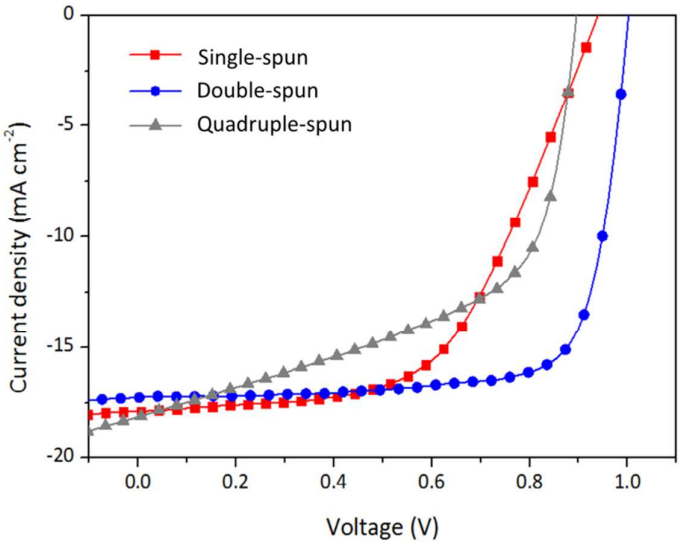


**Figure S9.** $J-V$ curves of PeSCs containing single, double, and quadruple-spun $WO_X$@PEDOT layers.

**Table S1.** Photovoltaic parameters extracted from the devices containing single, double, and quadruple-spun $WO_X$@PEDOT layers.

| HTL | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF(%) | PCE (%) |
|---|---|---|---|---|
| Single-spun $WO_X$@PEDOT layer | 0.94 | 17.88 | 56.0 | 9.40 |
| Double-spun $WO_X$@PEDOT layers | 1.00 | 17.25 | 76.8 | 13.24 |
| Quadruple-spun $WO_X$@PEDOT layers | 0.89 | 18.08 | 56.1 | 9.04 |

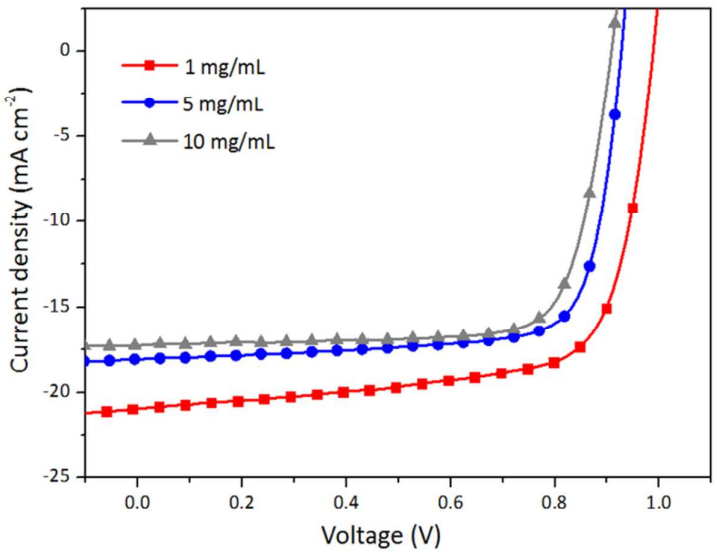


**Figure S10.** *J*−*V* curves of PeSCs with $WO_X$@PEDOT:PEDOT:PSS prepared using the $WO_X$@PEDOT solution with the concentration of 1 mg/mL, 5 mg/mL and 10 mg/mL.

**Table S2.** Photovoltaic parameters extracted from the devices with $WO_X$@PEDOT:PEDOT:PSS prepared using the $WO_X$@PEDOT solution with the concentration of 1 mg/mL, 5 mg/mL and 10 mg/mL.

| $WO_X$@PEDOT solution | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF (%) | PCE (%) |
|---|---|---|---|---|
| 1 mg/mL | 0.99 | 20.93 | 71.3 | 14.73 |
| 5 mg/mL | 0.93 | 18.04 | 76.1 | 12.74 |
| 10 mg/mL | 0.90 | 17.24 | 77.4 | 12.04 |

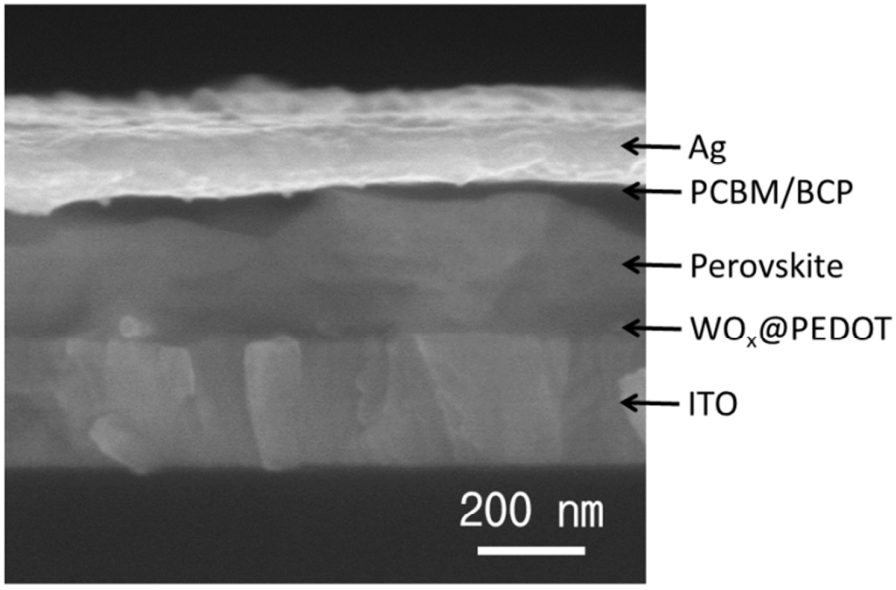


**Figure S11.** Cross-sectional SEM image of typical device with $WO_X$@PEDOT NRs.

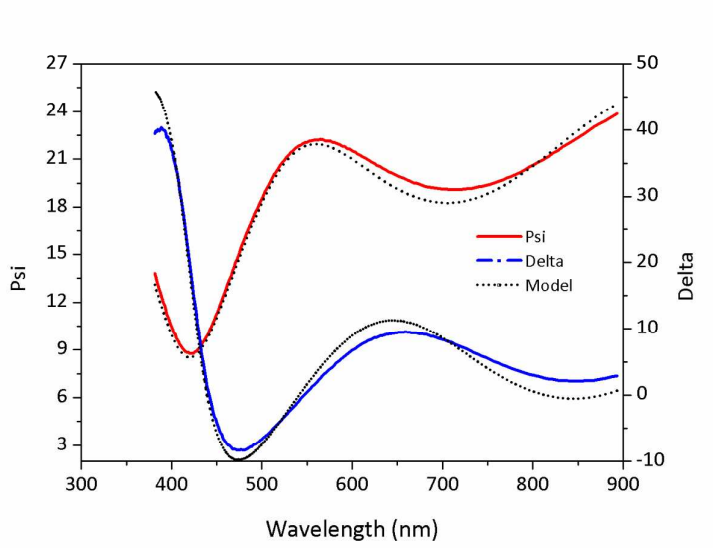


**Figure S12.** Ellipsometric raw data (i.e. Ψ and Δ) as a function of wavelength collected from ITO/$WO_X$@PEDOT film.

The optical models, representing the general structure of the tested samples, were built as "ITO(150 nm)/$WO_X$@PEDOT(Thickness, fit)" for. By fitting, the thickness of the $WO_X$@PEDOT HTL is estimated to be ca. 22 nm.

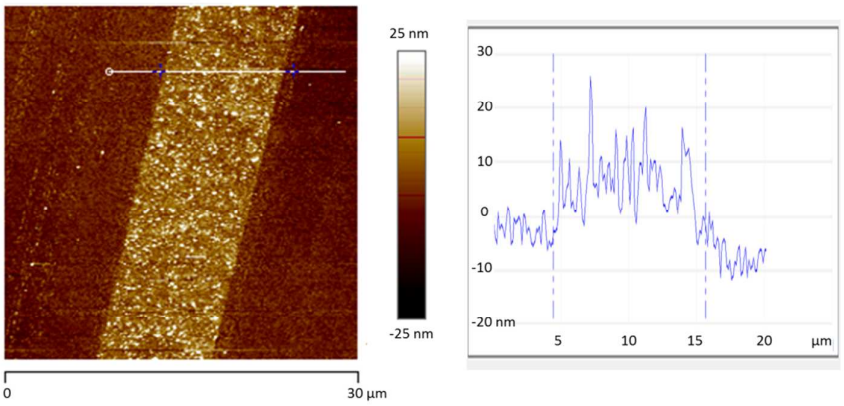


**Figure S13.** Left panel shows AFM height image of the $WO_X$@PEDOT HTL deposited on ITO. The light region indicates the $WO_X$@PEDOT HTL, while the dark region indicates the pristine ITO where the $WO_X$@PEDOT HTL was removed by knife scratching. Right panel displays a height trace, suggesting an average HTL thickness of ca. 20 nm.

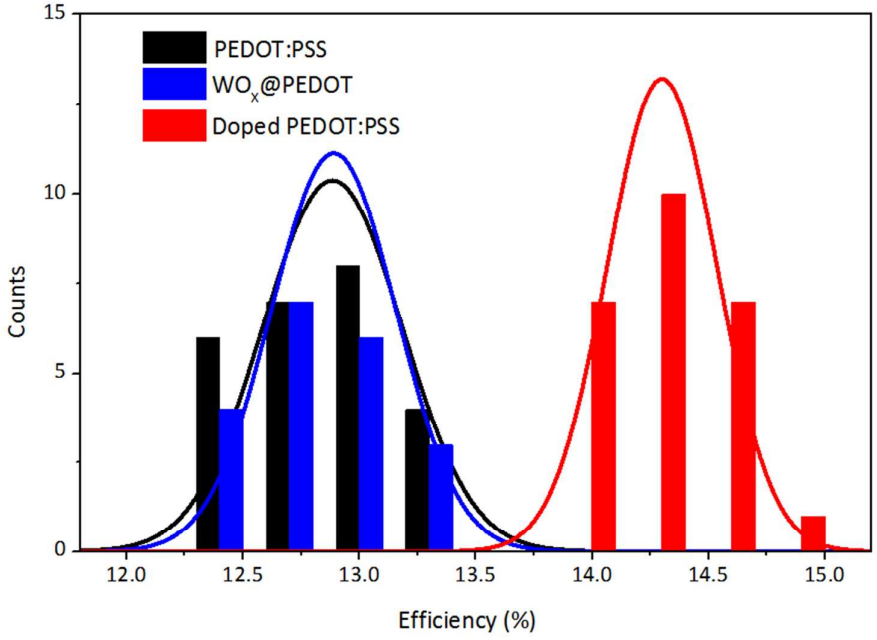


**Figure S14.** PCE distributions for PeSCs with different HTLs.

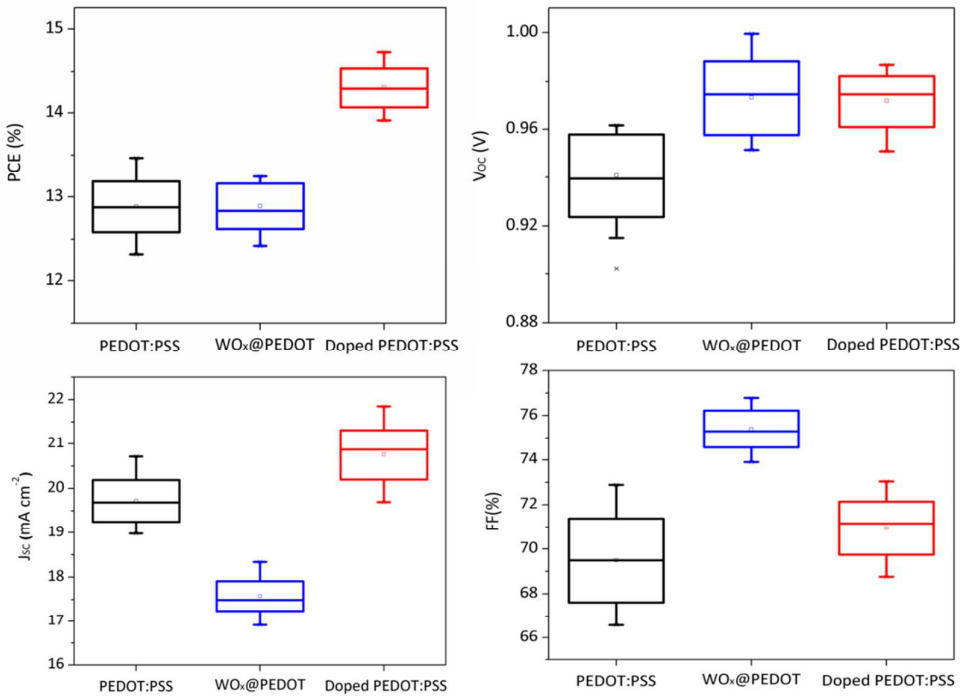


**Figure S15.** Histogram of PCE and $V_{OC}$, $J_{SC}$, FF of 20-25 individual solar cells under 1 sun illumination.

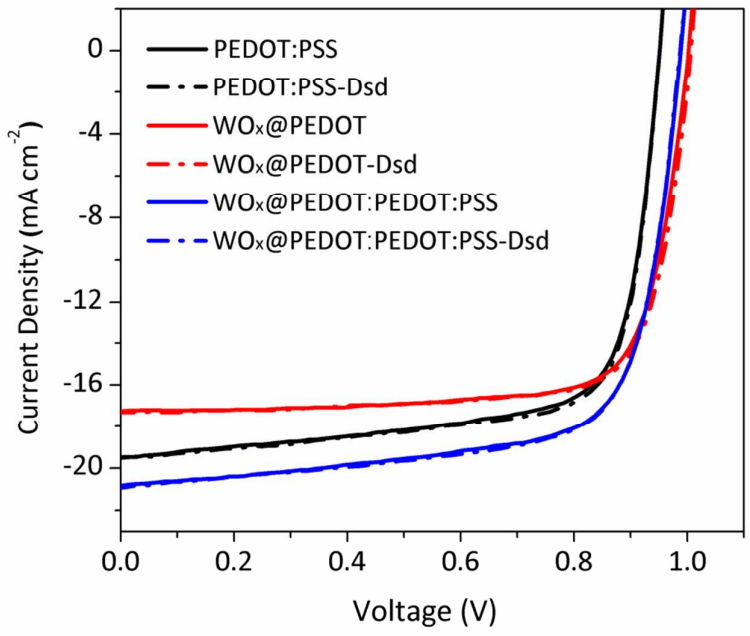


**Figure S16.** *J*−*V* curves of PeSCs with different HTLs with both forward (FS) and reverse (RS) scan modes under 1 sun illumination.

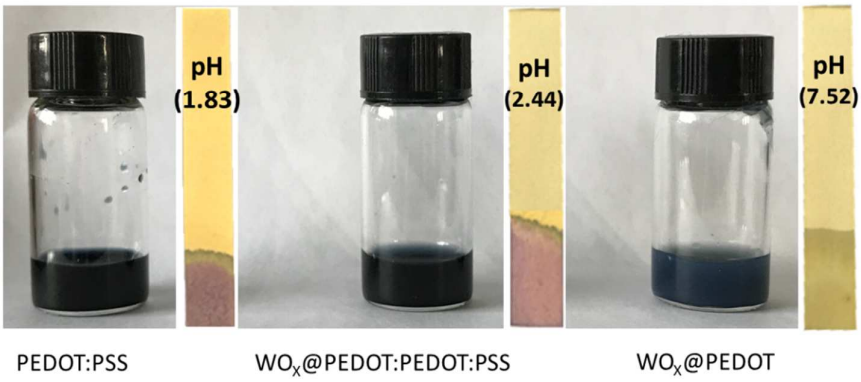


**Figure S17.** Photos of the samples of PEDOT:PSS, $WO_X$@PEDOT and $WO_X$@PEDOT:PEDOT:PSS. The insets show their PH values.