

Electronic Supplementary Information

Enhanced photoconductive properties on a simple composite coaxial nanostructure of zinc oxide and polypyrrole

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Crystal orientation of the ZnO nanorods

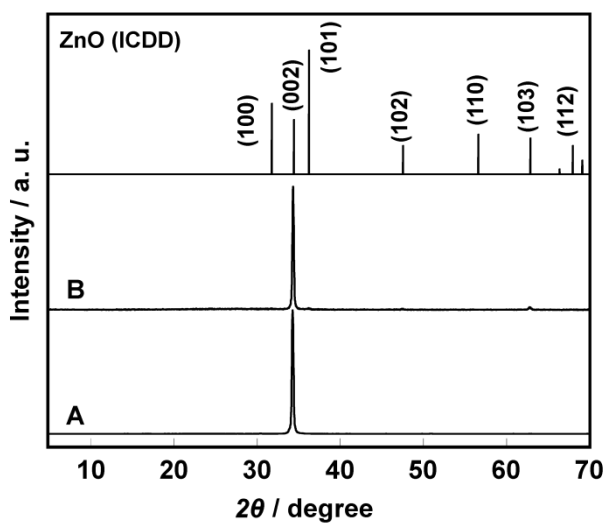


Figure S1. XRD patterns of the ZnO nanorods (A) and the ZnO/PPy coaxial nanostructures after the coating for 24 h (B) on an ITO substrate.

The peak of the (002) plane was intensified rather than that of the other planes. The results suggest that the ZnO nanorods were formed on the substrate with preferential orientation in the *c* axis.

Thickness of the PPy layer with changes of the coating time

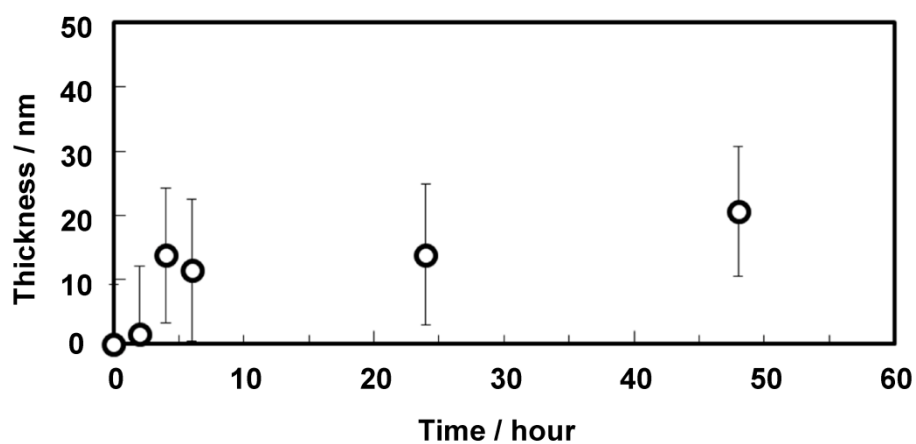


Figure S2. Thickness of the PPy layer around the ZnO nanorods with the changes of the coating time.

The thickness of the PPy layer is not so influenced by the changes of the time to immersion of the ZnO nanorods in the oligomer solution.

EDX and FT-IR spectra of PPy

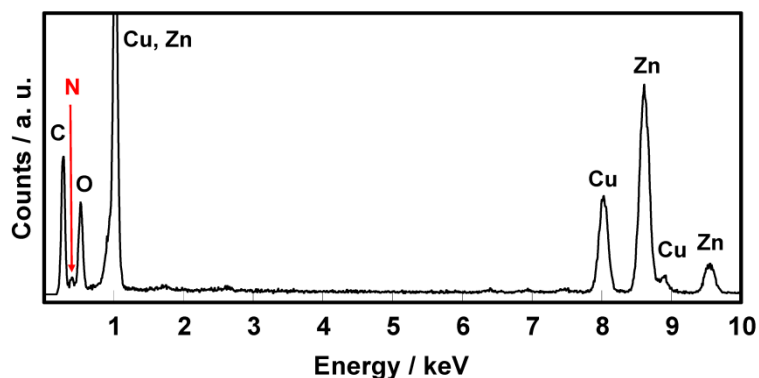


Figure S3. EDX spectrum of the ZnO/PPy coaxial nanocables after the coating for 24 h.

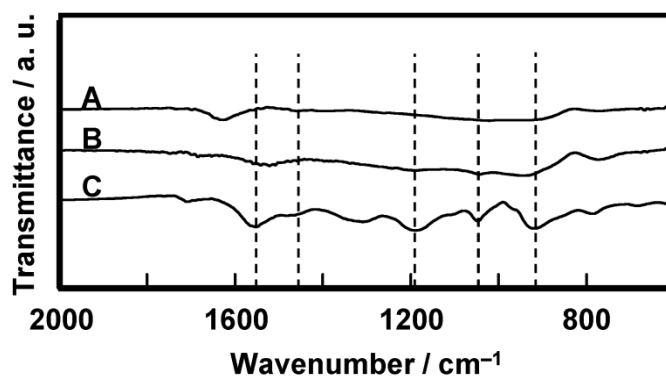


Figure S4. FT-IR spectra of bare ZnO nanorods (A), ZnO/PPy coaxial nanostructures (B), and PPy powder precipitates (C).

The peak resulting from nitrogen in PPy appeared in the EDX spectrum (Figure S3). In the FT-IR spectrum (Figure S4), the absorption band around 1550 cm⁻¹ is assigned to the antisymmetric and symmetric ring-stretching modes of pyrrole rings.^[S1] The stretching vibration of C-N bond was observed around 1050 cm⁻¹ in the spectrum. The absorption bands around 930 cm⁻¹ and 1200 cm⁻¹ implied the formation of doped-type PPy.^[S1] These results support the formation of PPy.

[S1] a) B. Tian, G. Zerbi, *J. Chem. Phys.* **1990**, *92*, 3886; b) B. Tian, G. Zerbi, *J. Chem. Phys.* **1990**, *92*, 3892.

TG analysis of the ZnO/PPy coaxial nanostructure

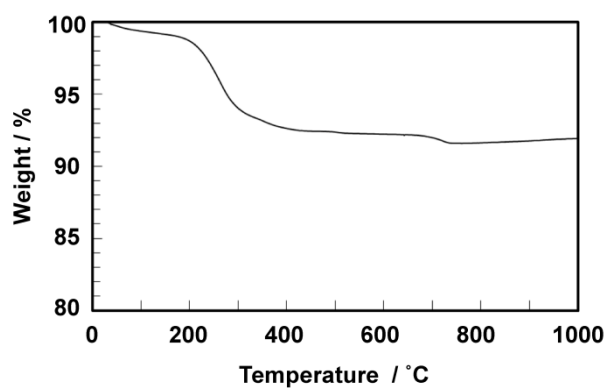


Figure S5. TG curve of the ZnO/PPy coaxial nanostructure after the coating for 24 h.

The weight loss about 7 % around 350 °C corresponds to the removal of PPy from the coaxial nanostructures.

Coating behavior of PPy on substrates

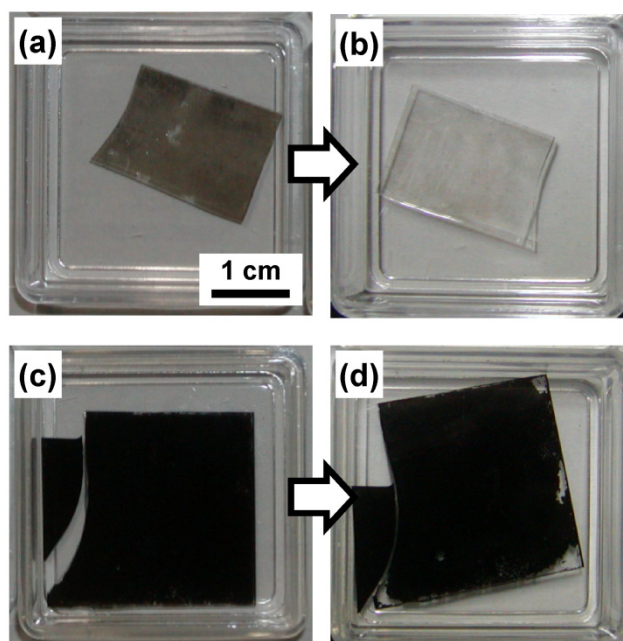


Figure S6. Differences in the coating behavior of PPy on a bare glass substrate (a,b) and on the ZnO nanorods (c,d). The left (a,c) and right (b,d) panels respectively show to the photographs before and after the ultrasound cleaning in a water bath. The coating time for PPy was 24 h on the both substrates.

The PPy coating on a bare glass substrate with the lighter color than was easily removed in an ultrasonic bath. In contrast, the PPy coating on the ZnO nanorods array was not removed by the same treatment. The results imply the interaction between PPy and ZnO.

XPS analysis for the state of nitrogen in PPy

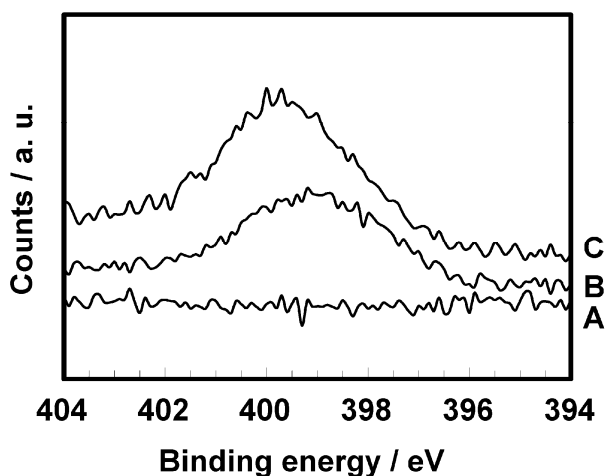


Figure S7. Narrow scan XPS profiles of the ZnO nanorods (A), the ZnO/PPy coaxial nanocable (B), and the PPy precipitates (C). The times for the coating and deposition of PPy were 24 h.

The narrow scan spectra around 400 eV indicate the state of nitrogen species. The nitrogen was not detected from the ZnO nanorods (spectrum A). The peak of nitrogen is slightly shifted to the higher energy region (spectra B and C). The shift indicates that the nitrogen of the PPy coated on the ZnO nanorods was similar to that of the imine state. Therefore, it is inferred that the interaction between PPy and ZnO nanorods leads to the homogeneous coating.

Bulk PPy sample

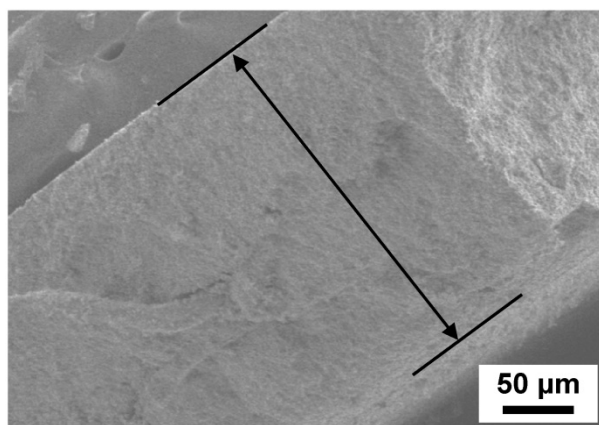


Figure S8. Cross-sectional FESEM image of the bulk PPy sample.

The thickness of the PPy pellet as the reference sample is about 200 μm .

Stacked structure of ZnO and PPy

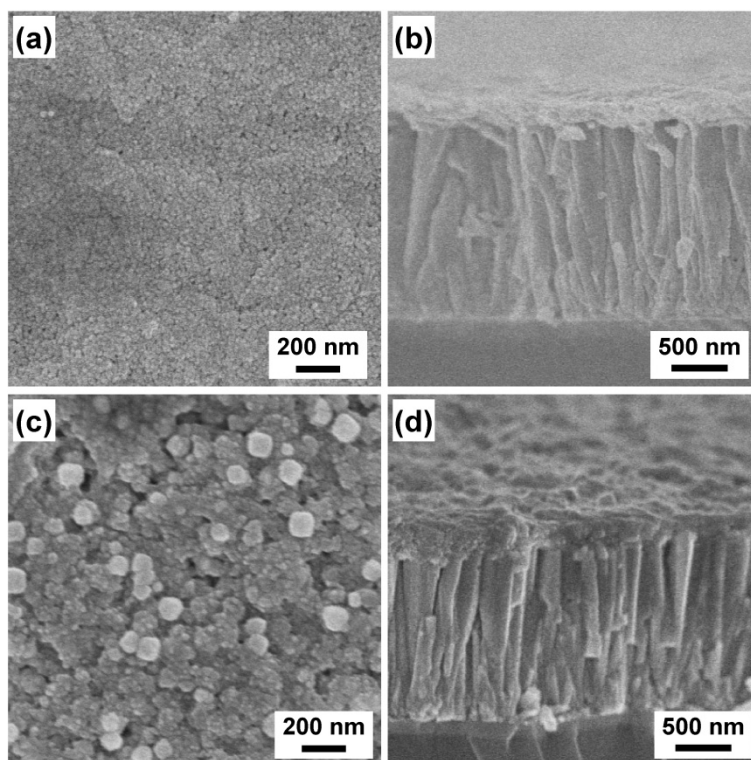


Figure S9. FESEM images of the flat ZnO substrate (a,b) and the stacked structure after the PPy coating (c,d). (a,c) the surface images. (b,d) the cross-sectional views.

The flat ZnO substrate was prepared in the presence of maleic acid. The experimental detail was described in the procedure section of this ESI. Since the growth of ZnO in the *c* axis direction is inhibited by maleic acid, the widened nanorods were closely packed with each other as shown in Figure S11b. In addition, the interspace of the ZnO nanorods was filled by the sol-gel coating. The bulk ZnO with the flat surface was formed (Figure S11b).

Different coaxial nanostructures

Table S1. Photoconductive properties of the coaxial nanostructures with the changes of the thickness and the sorts of polymer for the coating.

coating (time)	$I_{\text{dark}} / \text{mA cm}^{-2}$	$I_{\text{light}} / \text{mA cm}^{-2}$	$I_{\text{light}}/I_{\text{dark}} / -$
PPy (0.5 h)	1.604×10^{-1}	1.693×10^2	1.056×10^3
PPy (1 h)	5.44×10^{-2}	1.264×10^2	2.324×10^3
PPy (2 h)	1.125×10^{-2}	2.099×10^2	1.866×10^4
PPy (5 h)	3.430×10^{-2}	6.966×10	2.028×10^3
PPy (28 h)	1.110×10^{-1}	5.375×10	4.843×10^2
P3HT	3.451×10^{-2}	4.048×10	1.173×10^3

The coating time related to the thickness was changed from 0.5 to 28 h. In the main text, the photoconductive properties at the PPy coating time of 2 h were displayed in Fig. 5 and Table 1. The P3HT was coated on the ZnO nanorods array to study the influence of the polymer. The commercial P3HT (Rieke Metals) was dissolved in chlorobenzene. The P3HT concentration was adjusted to 35 mg cm^{-3} . The P3HT was coated by spin-coating at 600 rpm. for 60 sec. Based on these data, the on-off ratio comparable to 10^4 was not achieved on the different conditions as shown in the main text.

Experimental Procedure

Synthesis of ZnO nanorods: The growth of ZnO nanorods was performed through aqueous solution process according to the previous reports by our group.^[14] Prior to the growth of the ZnO nanorods, ITO substrates (2.5 cm × 2.5 cm) were coated by sol-gel derived ZnO to promote the heterogeneous nucleation in the aqueous solution process.^[16] The stock solutions containing 10 mM ZnSO₄·7H₂O (Kanto, 99.5 %) and 300 mM NH₄Cl (Kanto, 99 %) were prepared using purified water at room temperature. The pH of the stock solution was adjusted to 11 by 5 M NaOH aqueous solution. After the adjustment of pH, the substrate coated with the sol-gel derived ZnO was immersed in the solution for 24 h at 60 °C. The resultant substrates were washed by purified water and then dried at room temperature.

Coating of PPy on the ZnO nanorods: The PPy coating was referred to the previous reports for the nanocoating of PPy on organic substrates.^[15] The stock solution contained 5 vol. % of pyrrole monomer (Kanto, 99.0 %) in 2-propanol (2-PrOH). Then, 10 g dm⁻³ of CuCl₂·2H₂O was added to 2-PrOH under stirring. After stirring for 30 min., the precipitates dispersed in the liquid phase were filtered to obtain the clear solution containing the PPy oligomer. The ZnO nanorods on the ITO substrate were immersed in the clear oligomer solution for the certain period (0.5–24 h). The resultant substrate showing block color was washed by acetone and purified water. Then, the substrates were dried under nitrogen gas flow.

Syntheses of the stacked structure consisting of ZnO and PPy: The ZnO crystals with the flat surface were synthesized with addition of 14 mM maleic acid to the precursor solution containing the zinc source and complexing agent. After the growth of the ZnO crystals, the sol-gel derived ZnO was coated to ensure the filling of the pores on the surface.^[16] After the spin coating of the precursor solutions containing the zinc source, the resultant ZnO substrate was sintered at 400 °C for 20 minutes. This process including the coating and sintering were carried out three times. Then, the PPy coating was performed for 1 hour by the same method

as that of ZnO/PPy coaxial nanostructures (Figure S9 in the ESI).

Syntheses of the bulk PPy: When the PPy coating was performed on the ZnO nanorods, the black precipitates were filtered to obtain the PPy coating solution containing the oligomer. As for the bulk PPy, the black precipitates were collected and then dried. The resultant precipitates were compacted to a pellet 13 mm in diameter and ca. 0.2 mm in thickness (Figure S8 in the ESI).

Characterization: The morphologies were observed by a field-emission scanning electron microscope (FESEM, Hitachi S-4700 and FEI Sirion) operated at 5.0 kV and a field-emission transmission electron microscope (FETEM, FEI Tecnai F20) operated at 200 kV. The electron energy loss spectroscopy (EELS) was performed by using an energy filter for FETEM (Gatan, GIF model 607). The crystallographic orientation of the ZnO nanorods was analyzed by X-ray diffraction (XRD, Rigaku miniFlex II). Fourier-transform infrared absorption spectroscopy (FT-IR, Bruker Alpha), X-ray photoelectron spectroscopy (XPS, JEOL JPS-9000MX), and thermogravimetric analysis (TG, Seiko TG-DTA 6500) were used for the analyses of the PPy layer. The optical absorption spectra were measured by an absorption spectrophotometer (UV-Vis, JASCO V-560).

Photochemical properties: A part of the substrate was immersed in hydrochloric acid to expose the ITO surface through the removal of the ZnO layer by the etching. A silver foil was pressed on the top of the substrate with a glass slide. A potentiostat (Hokuto Denko, HSV-100) was connected to the silver foil and the ITO substrate. The simulated sunlight (AM 1.5) was used as a light source. The current was measured from -2.0 V to 2.0 V (vs. ITO substrate) with a scan rate of 100 mV s⁻¹. The dark current was initially measured. After 3 minutes, the light current was measured with irradiation of the simulated sunlight. The schematic illustration for the experimental setup was displayed in Figure S10.

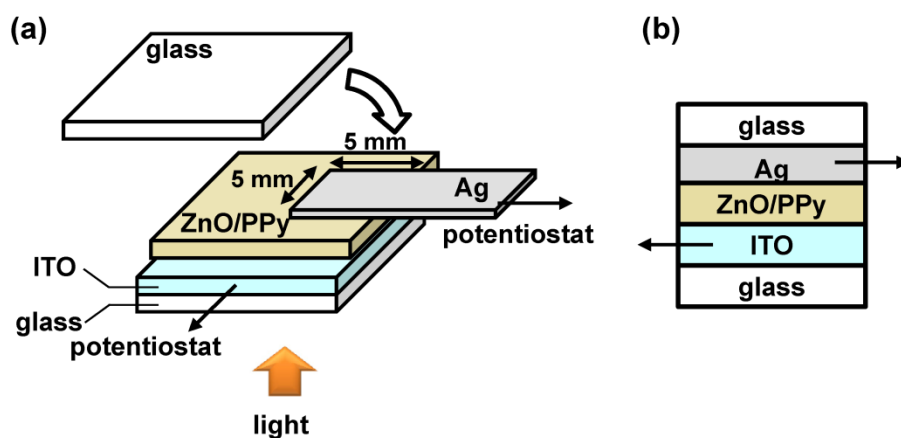


Figure S10. Schematic illustration of the experimental setup for the measurement of the photoconductive properties. (a) the overview of the specimen. (b) cross-sectional illustration of the specimen. The bottom glass is a support for ITO. The top glass plate is attached to ensure the contact between the Ag foil and the ZnO/PPy composite structures.