

Ruthenium Decorated Polypyrrole Nanoparticles for Highly Sensitive Hydrogen Gas Sensors Using Component Ratio and Protonation Control

Jungkyun Oh¹, Jun Seop Lee^{2*}, and Jyongsik Jang^{1*}

¹ School of Chemical and Biological Engineering, Seoul National University, 1

Gwanangro, Sillim-dong, Gwanak-gu, Seoul 08862, Republic of Korea

² Department of Materials Science and Engineering, Gachon University, 1342 Seongnam-

Daero, Sujeong-Gu, Seongnam-Si, Gyeonggi-Do 13120, Republic of Korea

*Corresponding authors: jsjang@plaza.snu.ac.kr (J. Jang) and junseop@gachon.ac.kr (J. S. Lee)

1_Synthesis of Ru_CPPy

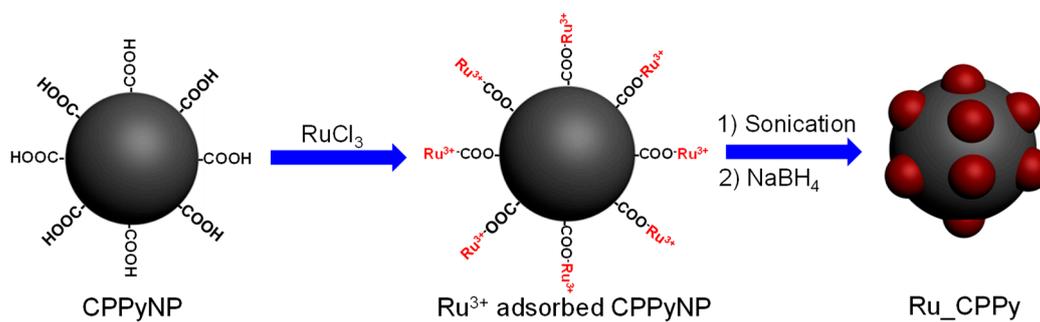


Figure S1. Schematic illustration for the fabrication process of ruthenium nanoclusters decorated carboxylated polypyrrole nanoparticles (Ru_CPPy).

2_Images of CPPyNP

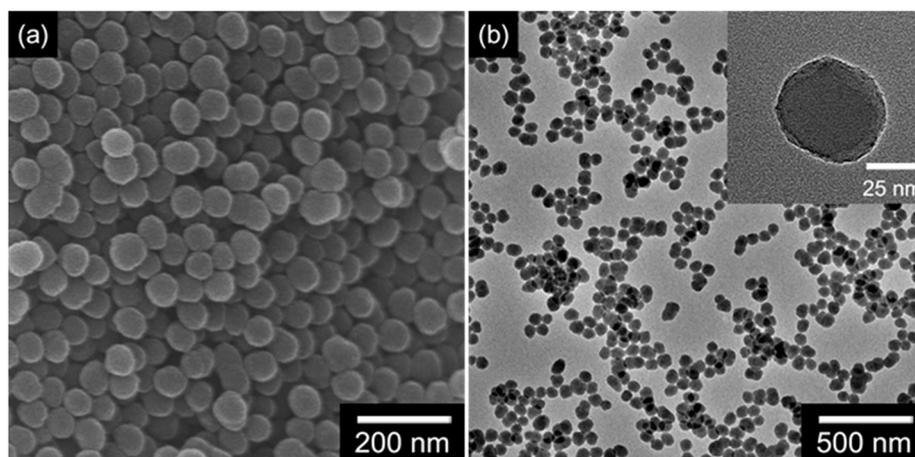


Figure S2. (a) FE-SEM and (b) TEM images of pristine CPPy NPs.

3. Ru particles without CPPyNP

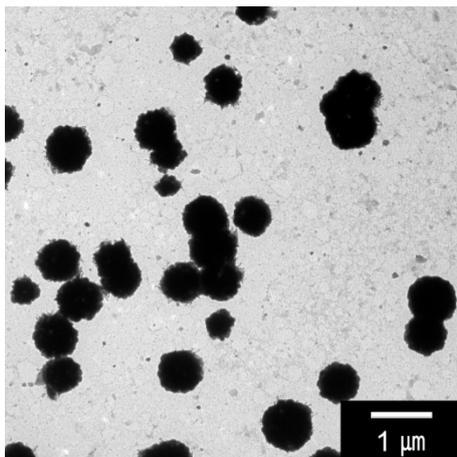


Figure S3. TEM image of Ru particles without CPPyNPs.

4_Size of Ru nanoclusters

Table S1. Average sizes of Ru nanoparticles on the surface of Ru/CPPyNPs with different concentrations of Ru precursor aqueous solution.

| Material | Ru nanoparticle size (nm) |
|-------------|---------------------------|
| Ru_CPPy_0.5 | 2.0 (\pm 0.15) |
| Ru_CPPy_1.5 | 3.5 (\pm 0.20) |
| Ru_CPPy_3.0 | 6.0 (\pm 0.32) |
| Ru_CPPy_4.0 | 10.0 (\pm 4.0) |
| Ru_CPPy_5.0 | 13.1 (\pm 7.0) |

5_XRD spectra of particles

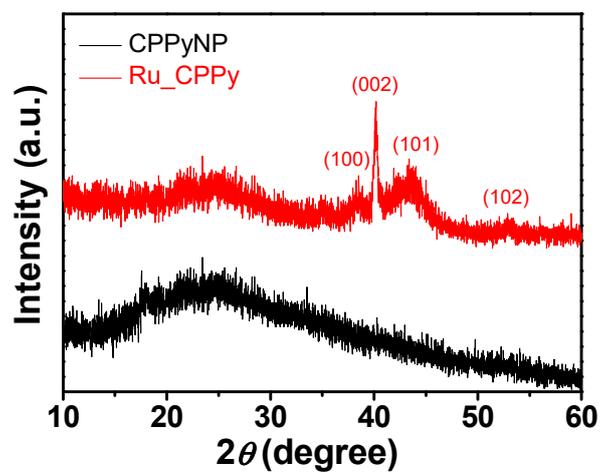


Figure S4. X-ray diffraction (XRD) patterns of CPPyNP (black) and Ru_CPPy (red).

6_Lattice structure of Ru component

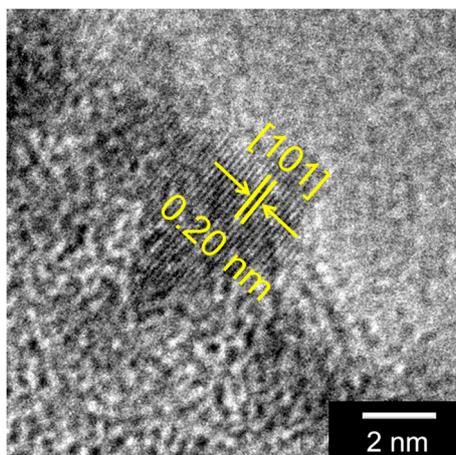


Figure S5. High-resolution transmission electron microscopy (HR-TEM) image of Ru nanocluster on the particle surface

7_ Raman and FT-IR spectra of protonated nanoparticles

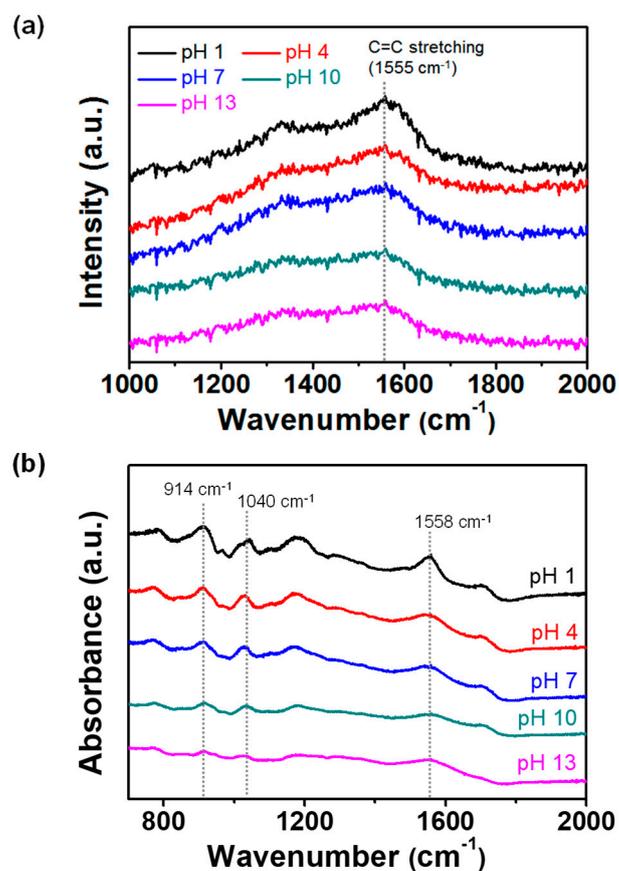


Figure S6. (a) Raman spectra and (b) Fourier-transform infrared spectroscopy (FT-IR) of Ru_CPPy with different pH treatments (black: pH 1; red: pH 4; blue: pH 7; pink: pH 10; green: pH 13).

8_ XRD spectra of particles at different pHs

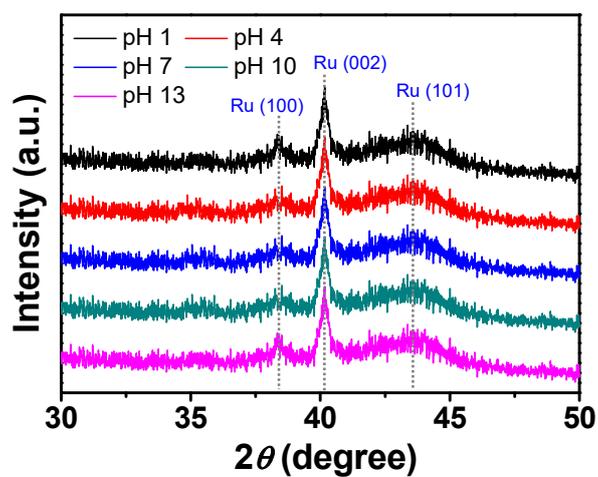


Figure S7. X-ray diffraction (XRD) of Ru_CPPy with different pH treatments (black: pH 1; red: pH 4; blue: pH 7; pink: pH 10; green: pH 13).

9_ FE-SEM images of sensor electrodes

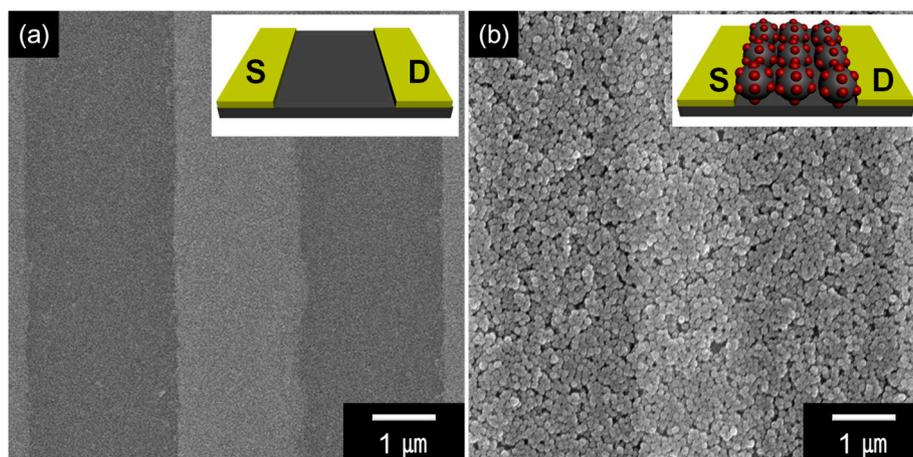


Figure S8. FE-SEM images of (a) bare interdigitated micro array (IDA) electrode and (b) Ru_CPPy decorated on the IDA substrate.

10_ Sensing performance of other nanoparticles

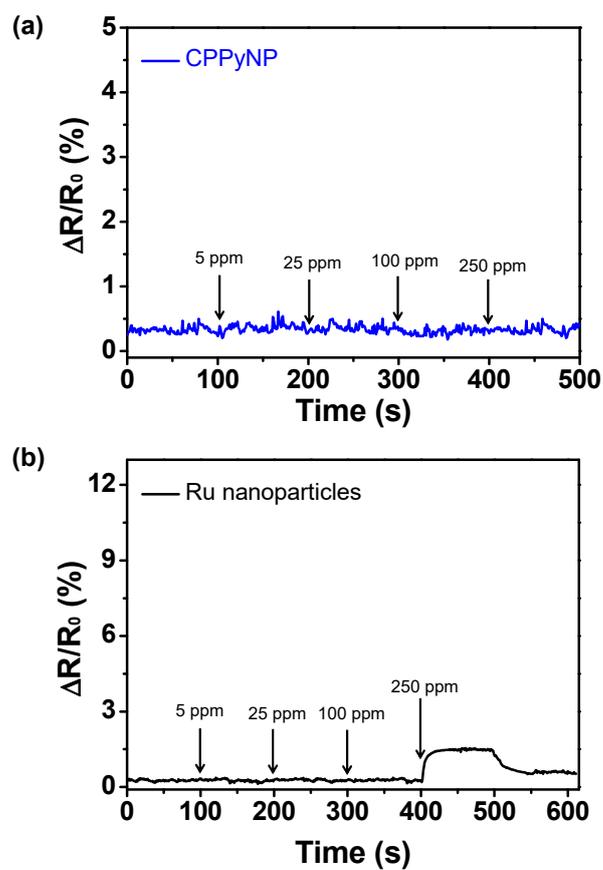


Figure S9. Normalized resistance changes upon sequential exposure to various concentrations of hydrogen gas to (a) pristine CPPyNPs and (b) Ru particles.

11_ H₂ Sensing performance comparison of electrodes

Table S2. Hydrogen gas sensing ability of different nanomaterials based sensing electrodes.

| Configuration | Working temperature | MDL ^{a)} | Response time | Recovery time | Reference |
|----------------------------------|---------------------|-------------------|---------------|---------------|-----------|
| Pd NPs ^{b)} on graphene | 25°C | 20 ppm | ≥15 min | ≥30 min | [S1] |
| Pd NPs on graphene nanoribbons | 25°C | 30 ppm | ≥60 s | ≥300 s | [S2] |
| Pd NCs ^{c)} on graphene | 25°C | 6 ppm | 20 min | 54 min | [S3] |
| Pd-NiO particle | 150°C | 30 ppm | 131 s | 151 s | [S4] |
| Ru_CPPy_3.0 | 25°C | 0.5 ppm | 31 s | 58 s | This work |

^{a)} Minimum detectable level, ^{b)} nanoparticles, ^{c)} nanocubes

12_ Sensing performance with temperature difference

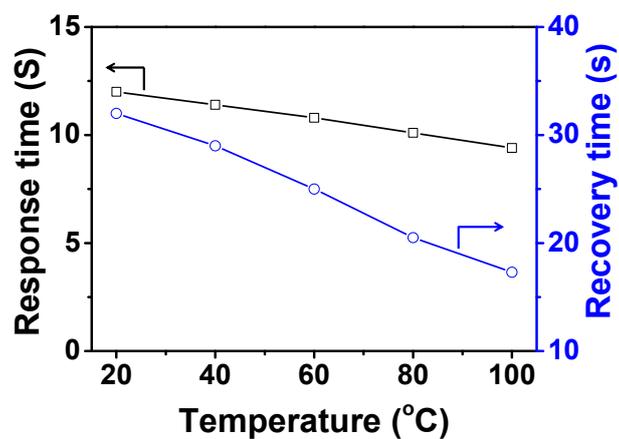


Figure S10. Response and recovery time changes of the pH 1 electrode with working temperature variation.

13_ Morphology images of nanoparticles before and after H₂ detection

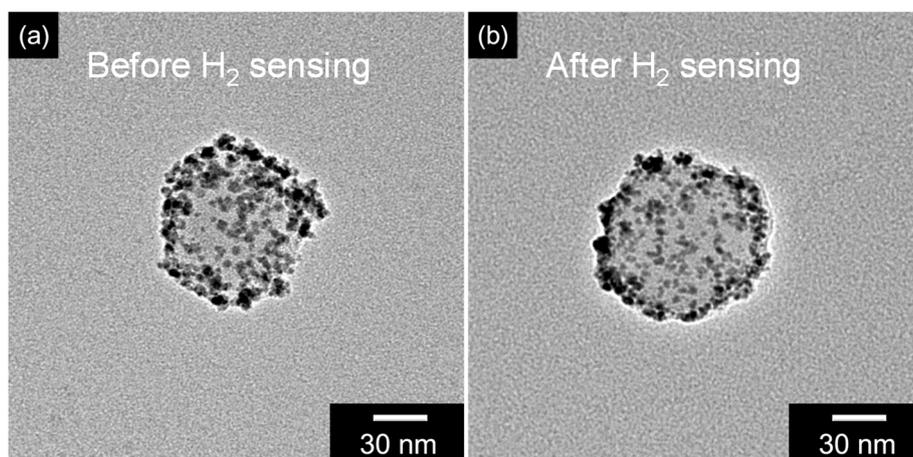


Figure S11. Transmission electron microscopy (TEM) images of Ru_CPPy (a) before and (b) after hydrogen sensing.

14_ Selectivity of the sensor electrode

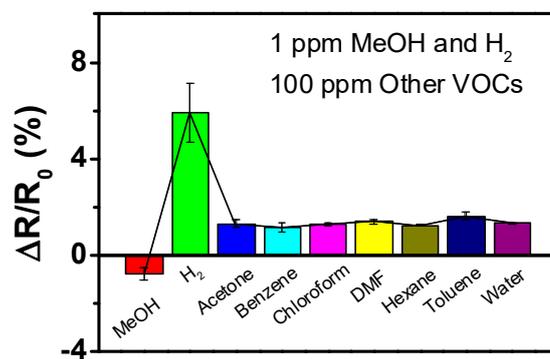


Figure S12. Normalized resistance changes of the electrode do different analytes.