Supplementary Information (SI) for Nanoscale.
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Supporting Information

Facile Engineering of TiO_2@Pd Based Hybrid Heterogeneous Nanostructures for Enhanced NO_2 Gas Sensing at Room Temperature under UV Activation

Thi Minh Thu Pham[a#], Kedhareswara Sairam Pasupuleti[b#], Tae Hyeon Jeong[a,c], Seung Min Lee[a], Thi Hong Men Nguyen[a], Moon-Deock Kim[b,d*], Young Heon Kim[a*]

[a]*Graduate School of Analytical Science and Technology (GRAST), Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 34134, Republic of Korea.*

[b]*Institute of Quantum Systems (IQS), Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon, 34134, Republic of Korea.*

[c]*Center for Research Facilities, Pukyong National University, 45 Yongso-ro, Nam-gu, Busan 48513, Republic of Korea.*

[d]*Department of Physics, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 34134, Republic of Korea.*

[#]These authors contributed equally to this work.

*Corresponding author. E-mail: y.h.kim@cnu.ac.kr

Synthesis mechanism of porous TiO_2@Pd Hybrid HNs formation

The formation of porous TiO_2 Ns through mesocrystals involved several steps, as follows. Initially, TBT and AA react, resulting in AA coordination to titanium centers and the formation of uncertain titanium acetate complexes ($(CH_3COO)_xTi(OC_4H_9)_{4-x}$) through a ligand exchange. As a byproduct of this reaction process, C_4H_9OH (butanol) was released, and the produced C_4H_9OH can react via a slow esterification reaction, resulting in water molecules. Further, when the hydrolysis-condensation and nonhydrolytic condensation processes occur, TiO_2 Ns are formed in the form of crystallized round spherical beads with soft silky fibers running along their surface with Ti-O-Ti surficial bonds. Further, the organic residuals in the as-obtained product were removed by calcination at 450 °C for 3 hours to obtain nanoporous TiO_2 Ns. This step can effectively remove any other remaining organic components and facilitate the development of a porous structure in the TiO_2 Ns.

The growth of Pd NPs on the porous TiO_2 Ns surfaces to form porous TiO_2@Pd HNs was readily achieved in aqueous medium at 90 °C using H_2PdCl_4 and LAA as the Pd precursor and mild reducing reagent, respectively. CTAB is a highly well-liked and commonly utilized stabilizing chemical for the production of hybrid structures as well as during the reduction of Pd^{2+}. The use of CTAB results in the formation of single-crystalline Pd NPs encapsulating over the TiO_2 Ns surface. Further, the in-situ growth of Pd NPs on the TiO_2 Ns may cause the lattice mismatch between the two materials, resulting in more defect states that may reduce the sensing capabilities of the TiO_2@Pd HNs. To overcome this lattice mismatch and promote the growth of uniform Pd NPs, a CTAB wetting film must be established at the TiO_2 and Pd interface. Typically, this wetting film is formed by the formation of a molecular bilayer of surfactants on the surface of the seed material. Moreover, the CTAB can be used as a critical strategy for the successful growth of Pd NPs to avoid the effect of lattice mismatch between the Pd NPs and TiO_2 Ns by carefully controlling the reduction process of the metal precursors.

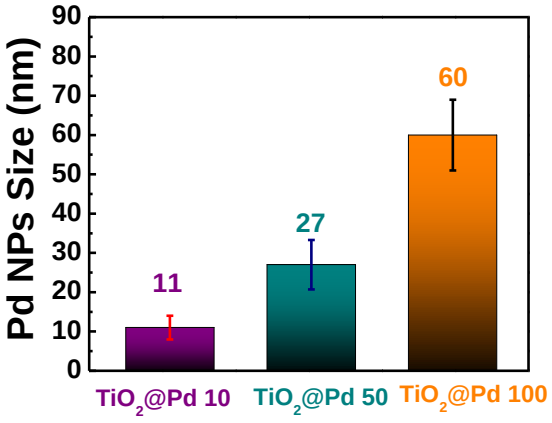

Figure S1. (a) The bar chart shows the Pd NPs size distribution over the TiO_2@Pd 10, 50, and 100 HNs samples.

Table S1. BET surface area and pore size of the as-prepared samples.

Sample	Surface area (m^2/g)	Pore diameter (nm)
Bare TiO_2	86.54	13.6
TiO_2@Pd 10 HNs	129.36	15.4
TiO_2@Pd 50 HNs	164.91	21.4
TiO_2@Pd 100 HNs	156.68	20.1

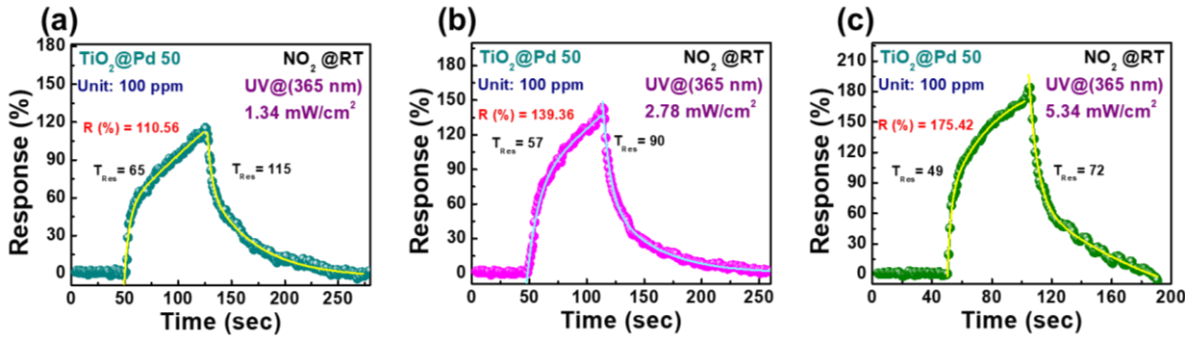

Figure S2. (a-c) The dynamic transient sensing response curves of the optimized TiO_2@Pd 50 HNs towards NO_2 (100 ppm) gas measured under different power densities (1.34, 2.78, and 5.34 mW/cm^2) of UV light (365 nm) at RT.

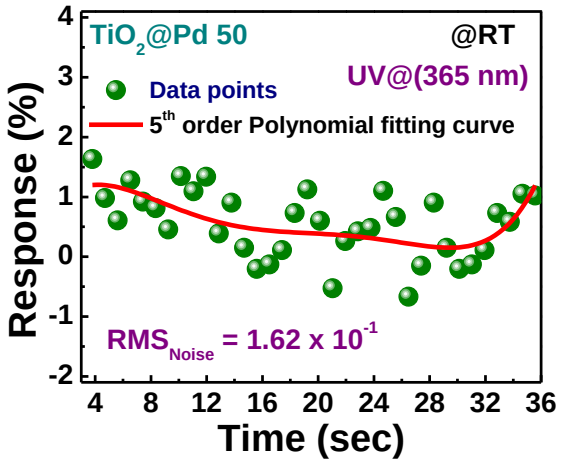

Figure S3. (a) 5th order polynomial fitting curves of the TiO_2@Pd 50 HNs sensor measured under UV@365 nm at RT (Note: the data point which we had used only the point when the sensor was in the air).

Determination of the theoretical detection limit

As per the IUPAC calcifications, the theoretical detection limit (DL) of the as-prepared sensors was estimated using a well-documented formula (Eq. S1) as given below.

$$DL\ (ppb) = 3\left(\frac{\mathrm{RMS_{noise}}}{\mathrm{Slope}}\right) - - - -(S1)$$

Where the $\mathrm{RMS_{noise}}$ is the root mean square noise, which is estimated from the base noise level of the sensor's response/resistance points under air ambient. By using 5th-order polynomial fitting curves to the set of points displayed in Figure S2, the $\mathrm{RMS_{noise}}$ was calculated.

$$\mathrm{RMS_{noise}} = \sqrt{\mathrm{R^2\ /\ N}} - - - -(S2)$$

Here R and N were denoted as $R = \sum_{t=4}^{36}\left(R_i + R_f\right)^2 - - - -(S3)$, and several points to be considered from the graph (N=32).

The slope was calculated from the linear fitting curves for the sensor's responses measured against different ppm concentration levels of the target gas. Upon substituting the slope and $\mathrm{RMS_{noise}}$ values in the above-mentioned equations, the calculated DL of the hybrid TiO_2@Pd 50 HNs sensor was found to be 82 ppb under UV light activation. Similarly, calculations have been used to estimate the DL of the hybrid TiO_2@Pd 50 HNs (DL~302 ppb) and pristine TiO_2 Ns (DL~946 ppb) sensors under dark conditions as presented in Table S2.

Table S2. Estimated detection limit TiO_2@Pd 50 hybrid HNs sensor measured under dark and UV@365 nm light illumination at RT.

S.NO	Samples	Detection limit (DL~ppb)
1.	**TiO_2@Pd 50 HNs (UV (365 nm)**	**~82 ppb**
2.	**TiO_2@Pd 50 HNs (dark)**	**~302 ppb**
3.	**TiO_2 Ns**	**~946 ppb**

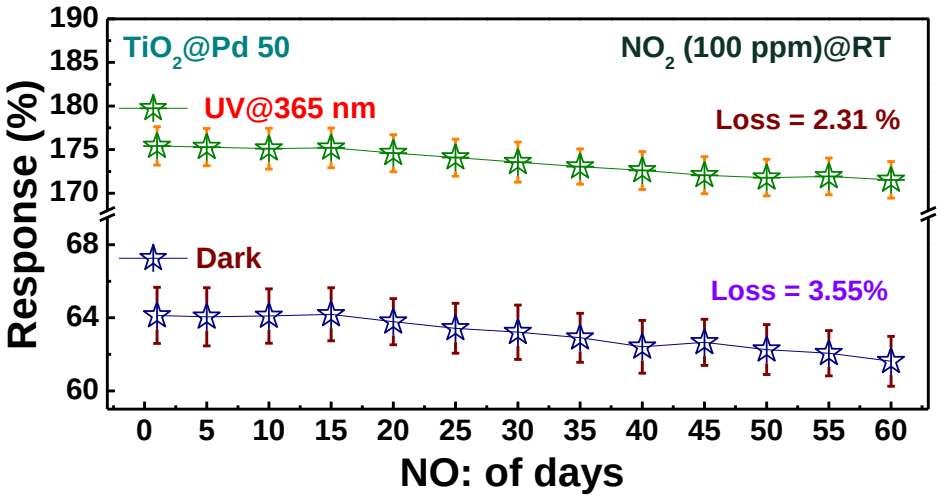

Figure S4. (a) Long-term reproducibility test results of TiO_2@Pd 50 HNs sensor measured under dark and UV@365 nm light illumination towards 100 ppm of NO_2 gas at RT.