

Possible Handle for Broadening the Catalysis Regime Towards Low Temperatures : Proof of Concept and Mechanistic Studies with CO oxidation on Surface Modified Pd- TiO₂

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Electronic Supplementary Information (ESI):

ESI-1. Synthesis methodology of Pd NPs and Pd-TiO₂ catalysts:

a. Synthesis of TiO₂ thin film catalyst: TiO₂ thin film catalyst was prepared on a Si (111) wafer (99.9 % pure and 0.625 mm thick - MaTeck, Germany) by a two-step process that combines sol-gel and spin coating methods. Initially, 1 mL of titanium tetra-isopropoxide was added to 10 mL ethanol and kept for continuous stirring for 10 min. After 10 min, 1 mL of acetylacetone was added to the solution and kept under stirring conditions for 30 min. After 30 min, 10 mL ethanol was added to the solution and kept stirring for 3 h. This solution is kept for 48 h for aging. After 48 h, yellowish-coloured sol appears, and the same was utilized for spin coating on the Si wafer. Si wafer was cleaned before spin-coating. 30 μ l of the above solution was spun coated by a micropipette over a rotating Si wafer (1 cm² area) at a spinning speed of 4000 rpm for 60 s. The prepared thin films were dried in an air oven at 373 K for 2 h. Finally, films were heated to 723 K in a muffle furnace at a heating rate of 2 K/min. in static air and calcined at the same temperature for 1 h. These TiO₂ films were further used for the preparation of Pd-TiO₂-supported catalysts.

b. Synthesis of Pd NPs: Pd NPs with different morphologies were prepared by the wet chemical synthesis method. To synthesize Pd_{NC}, initially, 105 mg of poly-vinyl pyrrolidone (PVP), 60 mg of ascorbic acid (AA), and 300 mg of KBr were added into 25 mL 2-neck round bottom flask containing 8 mL de-ionized (DI) water. The resulting solution was kept for 20 min sonication followed by heating to 358 K. At this temperature, the addition of Pd precursor (60 mg K₂PdCl₄ in 3 mL DI water) was carried out to the host solution. After the addition the resultant solution was kept for continuous stirring for 3 h at 358 K. After 3 h, the solution was cooled to ambient temperature, followed by centrifugation to separate the nanoparticle and washed with acetone; this is further washed with a mixture of ethanol-hexane three times. Resulting NPs were dispersed in 15 mL ethanol and preserved in the refrigerator. For the synthesis of Pd_{TO} NPs, instead of KBr, citric acid was used as a capping agent, and the reaction temperature was kept at 363 K. For the synthesis of the Pd_{PC} NPs, a similar procedure was followed as that of Pd_{NC} except for no use of shape control agent.

c. Synthesis of 1 wt. % Pd-TiO₂ impregnated powder catalyst: The wet impregnation method was employed for preparing Pd-TiO₂ catalyst used for the CO oxidation reaction. Initially, 99 mg of TiO₂ (made by sol-gel method) was dispersed in 10 mL of ethanol and sonicated for 10 min. 1 mg of Pd NPs dispersed in ethanol was added gradually to the TiO₂ dispersed solution. The resulting solution was kept for ultra-sonication for 30 min. Finally, this solution was vacuum dried at 323 K. The dried powder was used as such for applications.

For photo deposited Pd-TiO₂ powder catalyst, 99 mg TiO₂ was initially added to the mixture of 1:4 ratio of methanol:DI water, and required amount of K₂PdCl₄ was added to the solution. The solution was nitrogen purged for 20 minutes and then kept for photodeposition under a UV lamp (400 W) for 40 minutes under continuous stirring. After 40 min., the solution was allowed to cool to ambient temperature and centrifuged; the resulting powder was dried in a vacuum oven to get Pd_{photo}-TiO₂ catalyst.

d. 1% Pd-TiO₂ thin film catalyst: Separately synthesized shape-controlled Pd NPs (Pd_{NC}, Pd_{TO}, and Pd_{PC}) dispersed ethanol solution was impregnated over TiO₂ thin films (except for the Pd-photo deposited samples). Similar procedure as that of described for the Pd-TiO₂ powder catalyst is employed. This was followed by vacuum drying at 323 K in a vacuum oven. To prepare Pd_{photo}-TiO₂ thin film catalyst, required amount of K₂PdCl₄ was dissolved in a 5 mL mixture of methanol:DI water (1:4) and purged with N₂ gas for 20 min to remove dissolved oxygen. After N₂ purging, photo deposition was carried out under UV light (400 W) for 40 mins. Further, these films were also dried in an oven at 353 K and used for analysis.

ESI-2. Catalyst Activity Evaluation:

Typically, 0.5 cm³ of pelletized catalyst was loaded in a uniform heating zone of a tubular reactor supported by quartz wool. A K-type thermocouple placed on the thermowell fixed at the center of the catalyst bed was used in the reactor to measure the catalyst bed temperature. The reactant gas flow rate was kept constant at 267 mL/min at NTP with a feed gas ratio of CO: O₂: N₂ = 1:5:19 (GHSV: 30,000 h⁻¹). Carbonyl trap was employed to remove any trace amount of nickel carbonyl. Brooks mass flow controllers were used for controlling the input gas flow. About 30 min was allowed to stabilize the reaction temperature and reach a steady state before carrying out any reaction product analysis by gas chromatography (GC). The gases exiting the reactor were analyzed by Nucon 5700 GC equipped with thermal conductivity detector (TCD) and a Porapak Q column with argon (Ar) as a carrier gas. The percent conversion of CO and/or CO₂ production was calculated using the formula: [(CO_{in}-CO_{out})/CO_{in}] *100 or [(CO_{2out})/CO_{in}] *100, respectively.

ESI-3. KPFM Measurement Method Details

In KPFM, apart from atomic force, electrostatic force between the tip and the sample is determined by the contact potential difference (CPD) by applying an AC voltage to the tip. In this experiment, an AC bias (5 V) was applied to the tip to produce an electric force on the cantilever, which is proportional to CPD between the tip and sample. A titanium iridium tip as a surface probe was used to conduct the analysis. The potential images were recorded for

AC bias for the maximum potential of the Pd-TiO₂ samples. KPM images were obtained using a lift-off mode. In this method, a topographic line scan is recorded at a smaller distance, and the same line is rescanned in the lift mode with the cantilever tip raised to a lift height of 30 nm. In this way, one gets both KPM and AFM information simultaneously from the same spot. In short, KPM was used to image variations in the contact potential difference (CPD) (ϕ) between a conducting cantilever and the sample under investigation. CPD (ϕ) is defined as $(\phi_{\text{tip}} - \phi_{\text{film}})/q$, where ϕ_{tip} and ϕ_{film} are the work functions of the tip and sample, respectively, and q is the magnitude of the charge. In the present experiment, a bias voltage $V_{\text{tip}} = V_{\text{dc}} + V_{\text{ac}} \sin(\omega t)$ was applied directly to the tip, holding the sample at ground potential, where ω is the cantilever resonant frequency. A feedback loop continuously adjusts V_{dc} to maintain a condition that minimizes the force component at a frequency between the cantilever tip and sample surface, and it is recorded as a function of the position, yielding a map of the sample surface potential.

Separate experiment were also carried out for the estimation of surface potential of Pd-TiO₂ NPs, reported in the main manuscript. The surface potential measurements were made on freshly exfoliated HOPG surface. The Pd-NP and Pd-TiO₂-NP Surface potential is estimated with respect to the HOPG surface potential as reported in the manuscript.

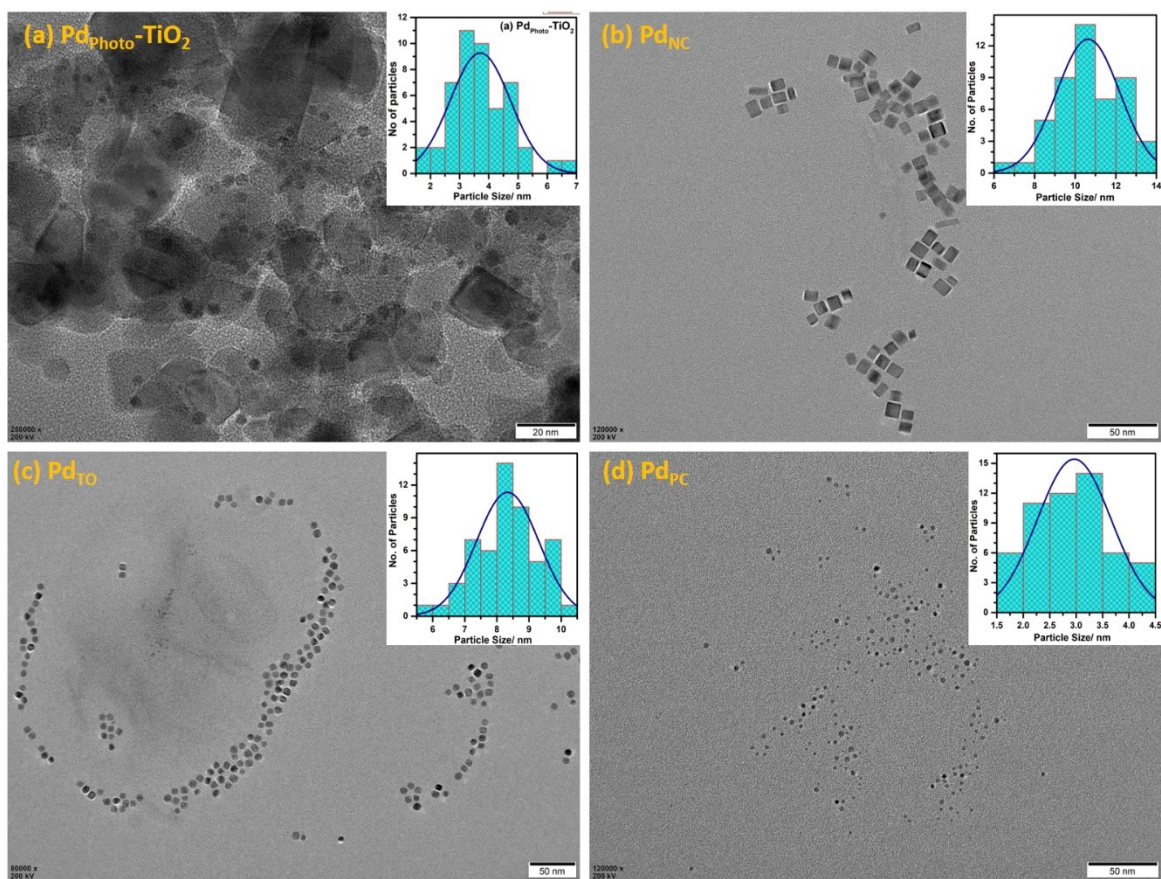


Figure S1: TEM images recorded for prepared (a) $\text{Pd}_{\text{Photo-TiO}_2}$, (b) Pd_{NC} , (c) Pd_{TiO} and (d) Pd_{PC} NPs. The inset of each image shows the distribution of Pd NPs.

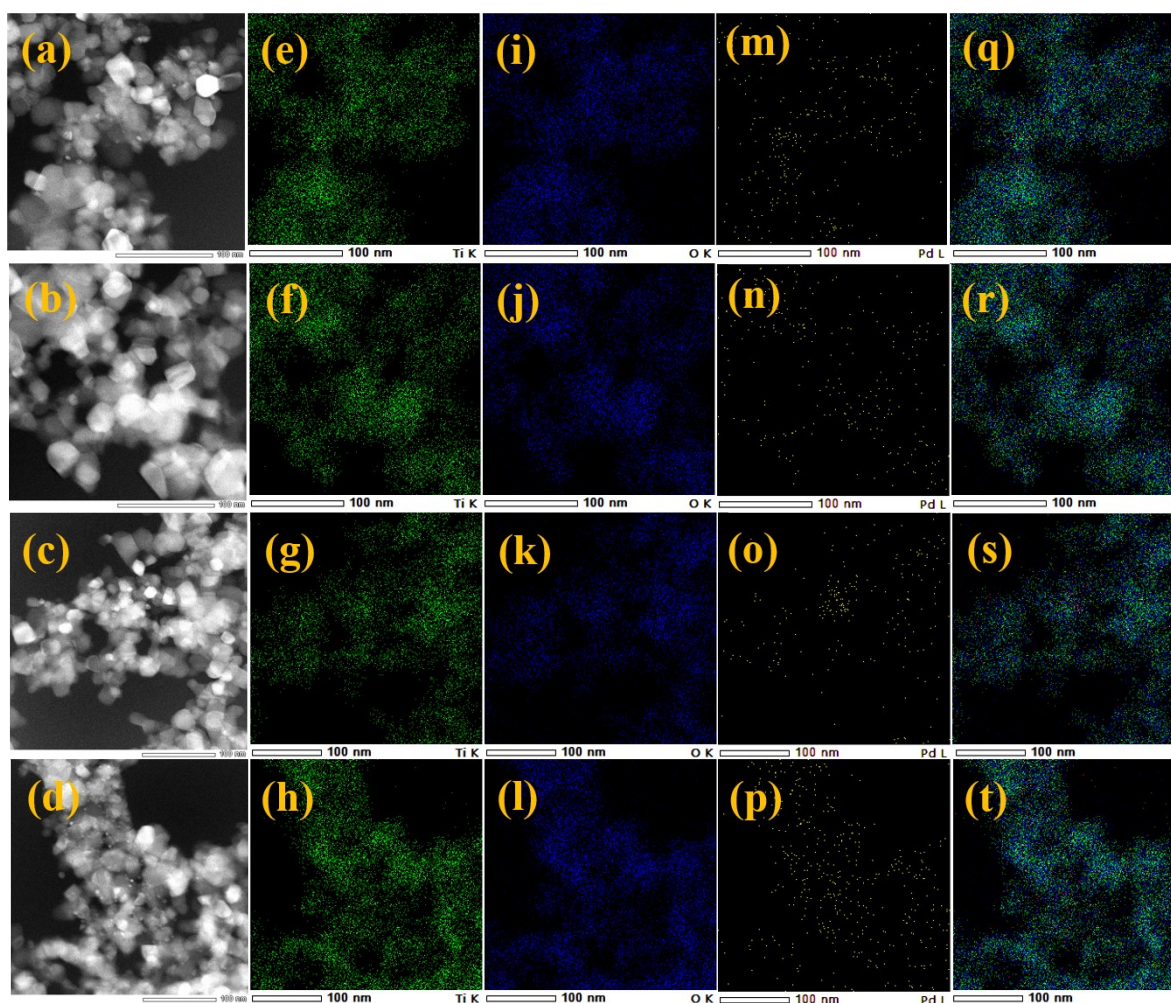


Figure S2: TEM images recorded for (a) Pd_{photo}-TiO₂, (b) Pd_{NC}-TiO₂, (c) Pd_{TO}-TiO₂, and (d) Pd_{PC}-TiO₂ with corresponding elemental distribution for Ti (e,f,g,h - green), O (i,j,k,l - blue), Pd (m,n,o,p - yellow), and the overlay of Ti, O, and Pd (q,r,s,t), respectively. The scalebar for all images is 100 nm. Figure S2a shows the TEM image of a cluster of Pd_{photo}-TiO₂ particles, with uniform distribution of Pd over TiO₂ support. The scattered yellow dots observed for Pd demonstrate the uniform distribution of Pd (Figure S2m, n, o and p) over the TiO₂. Similar to Pd_{photo}-TiO₂, TEM for elemental distribution for other Pd-TiO₂ catalysts as well shows uniform distribution of Pd over TiO₂ support.

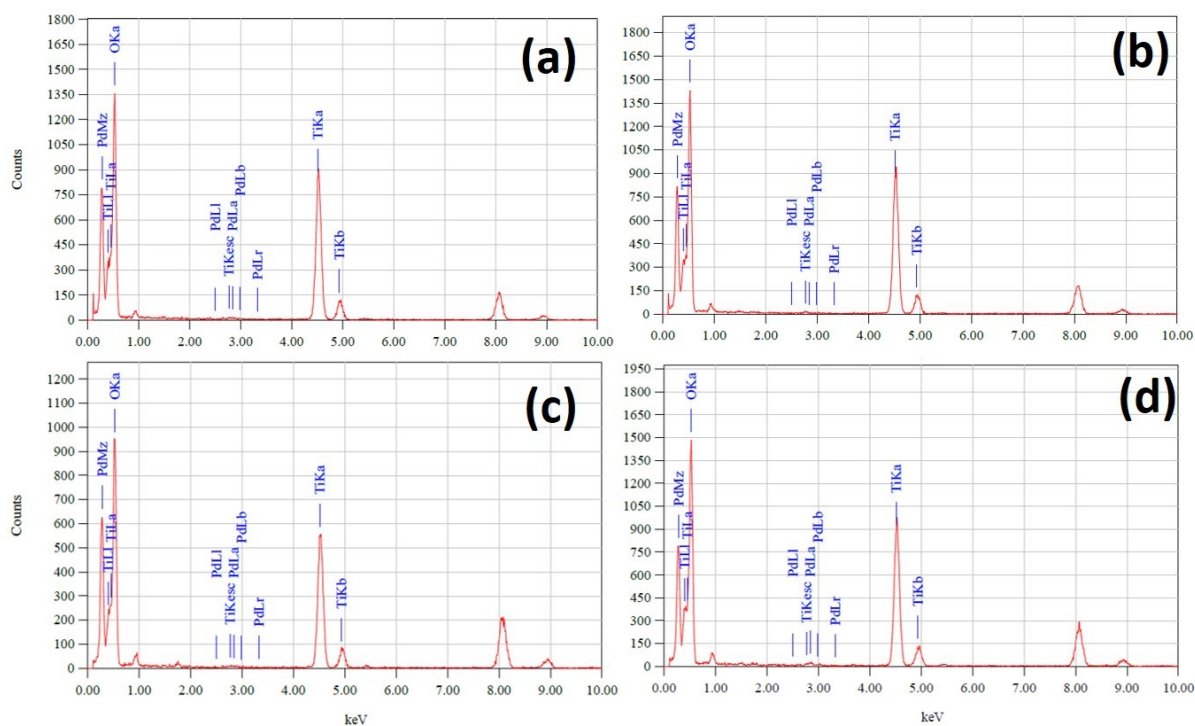


Figure S3: EDS spectra of (a) Pd_{photo}-TiO₂, (b) Pd_{NC}-TiO₂, (c) Pd_{TO}-TiO₂, and (d) Pd_{PC}-TiO₂ catalysts.

Table S1: EDS estimation for elements Pd, Ti, and O in various Pd/TiO₂ catalysts.

Catalyst Name	Pd (mass %)	Ti (mass %)	O (mass %)
Pd _{photo} -TiO ₂	0.97	46.49	52.54
Pd _{NC} -TiO ₂	0.91	47.12	51.97
Pd _{TO} -TiO ₂	0.94	46.34	52.72
Pd _{PC} -TiO ₂	1.14	45.96	52.90

Table S2: Pd-content determined from ICP analysis

Catalyst Name	Pd (mass %)
Pd _{photo} -TiO ₂	0.97
Pd _{NC} -TiO ₂	1.05
Pd _{TO} -TiO ₂	0.91
Pd _{PC} -TiO ₂	1.15

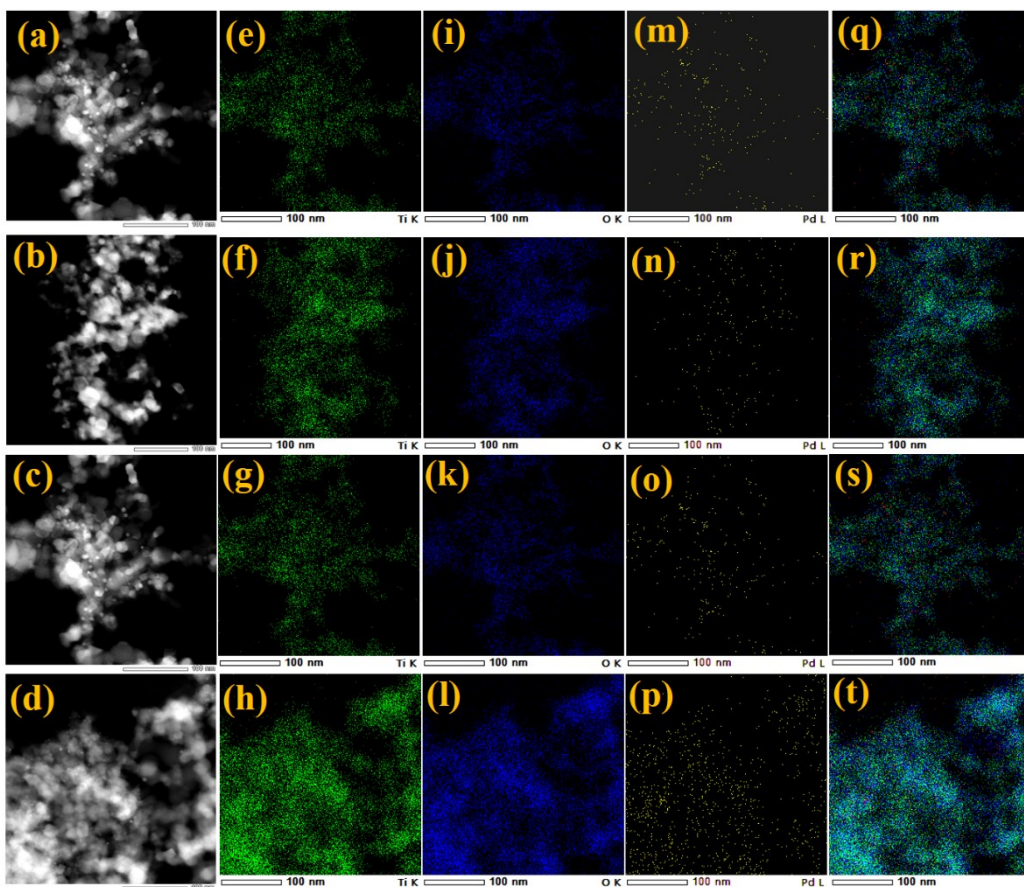


Figure S4: TEM images recorded catalysts surface modified at 523 K for (a) Pd_{photo}-TiO₂, (b) Pd_{NC}-TiO₂, (c) Pd_{TO}-TiO₂, and (d) Pd_{PC}-TiO₂ with corresponding elemental distribution for Ti (e,f,g,h - green), O (i,j,k,l - blue), Pd (m,n,o,p - yellow), and the overlay of Ti, O, and Pd (q,r,s,t), respectively. The scalebar for all images is 100 nm. It shows the uniform distribution of Pd over the TiO₂ support after SM.

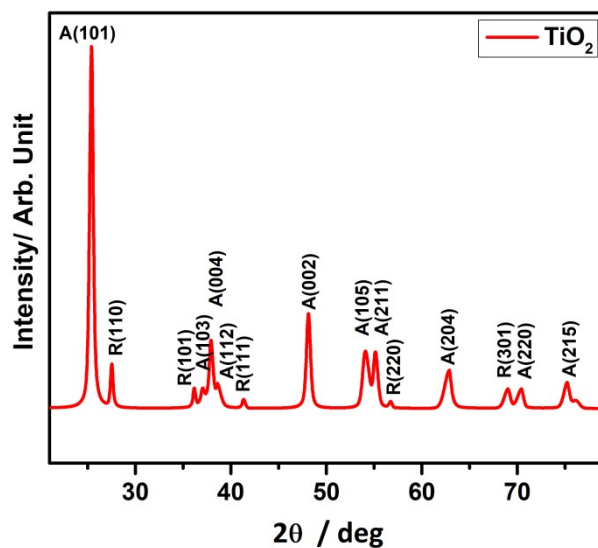


Figure S5: XRD study of TiO_2 . A and R correspond to the anatase and rutile phases of TiO_2 .

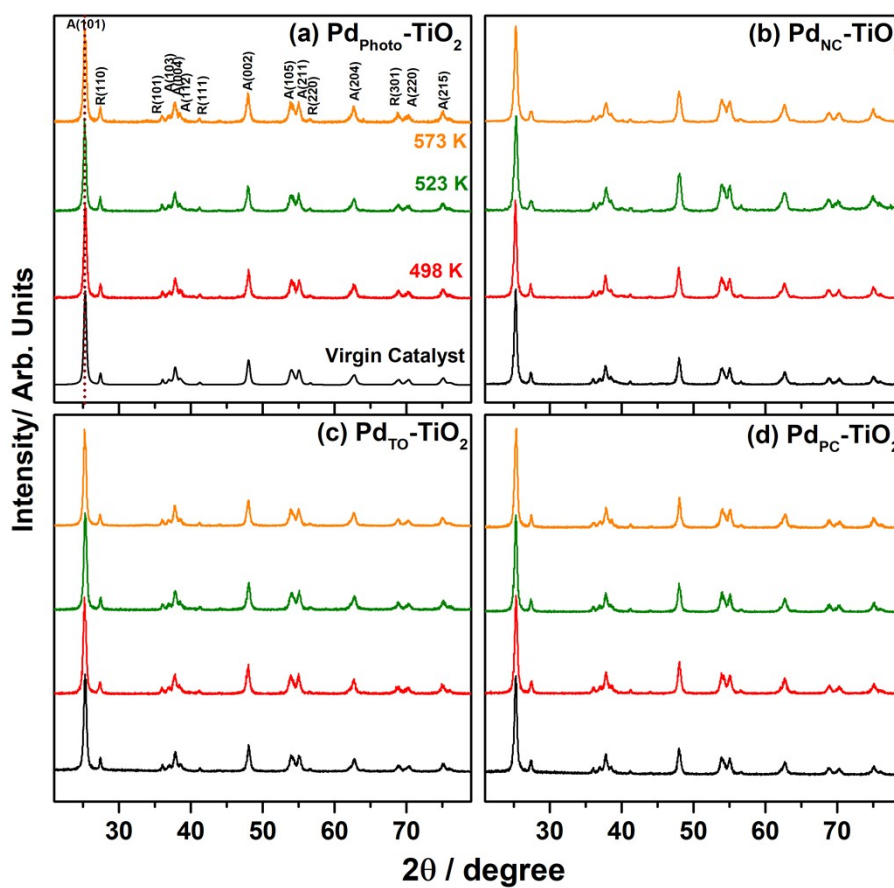


Figure S6: XRD of virgin and SMD Pd- TiO_2 catalysts at 498, 523 and 573 K, namely (a) $\text{Pd}_{\text{Photo}}\text{-TiO}_2$, (b) $\text{Pd}_{\text{NC}}\text{-TiO}_2$, (c) $\text{Pd}_{\text{TO}}\text{-TiO}_2$, and (d) $\text{Pd}_{\text{PC}}\text{-TiO}_2$.

Table S3: Rutile/ Anatase ratio for TiO₂, Pd_{Photo}-TiO₂ and SMd Pd_{Photo}-TiO₂ catalysts at various temperatures.

Sr. No.	Catalyst	Anatase (%)	Rutile (%)	Rutile/Anatase
1.	TiO ₂	88.5	11.5	0.130
2.	Pd _{Photo} -TiO ₂	88.5	11.5	0.130
3.	SMd Pd _{Photo} -TiO ₂ @ 498 K	88.6	11.4	0.129
4.	SMd Pd _{Photo} -TiO ₂ @ 523 K	88.4	11.6	0.131
5.	SMd Pd _{Photo} -TiO ₂ @ 573 K	88.4	11.6	0.131

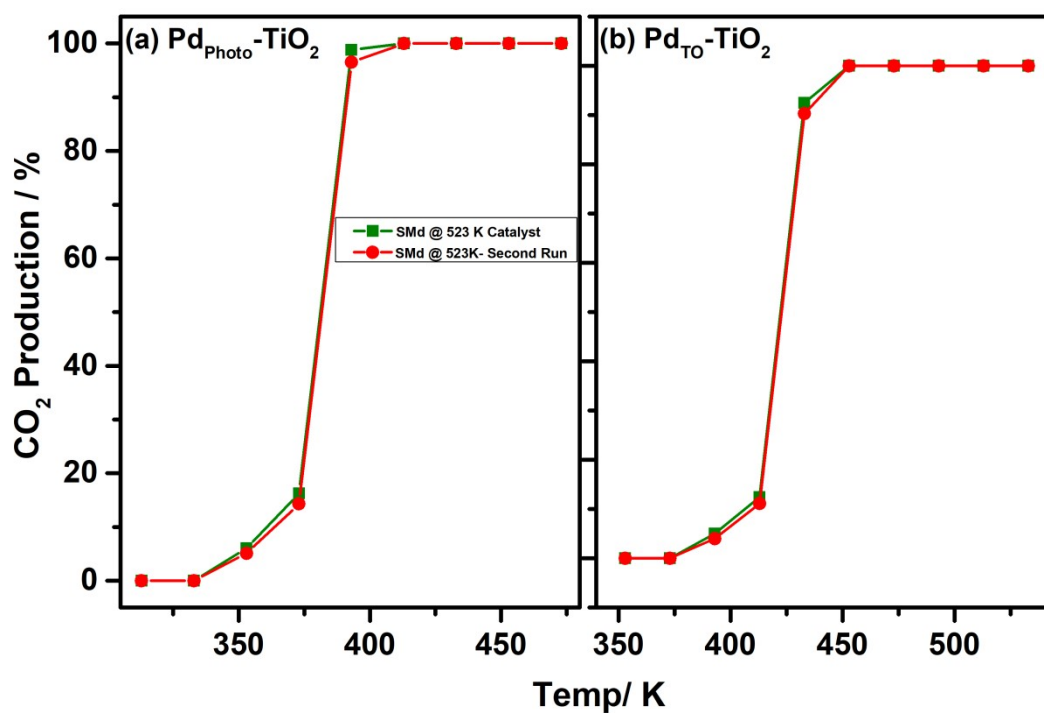


Figure S7: Recyclability of the SMD catalysts for temperature-dependent catalytic CO conversion to CO₂ in the second run for (a) Pd_{Photo}-TiO₂ and (b) Pd_{TO}-TiO₂, are shown. (Reaction conditions: pressure: atmospheric pressure, gas flow: 267 mL/min, GHSV: 30,000 h⁻¹, CO:O₂:N₂ = 1:5:19).

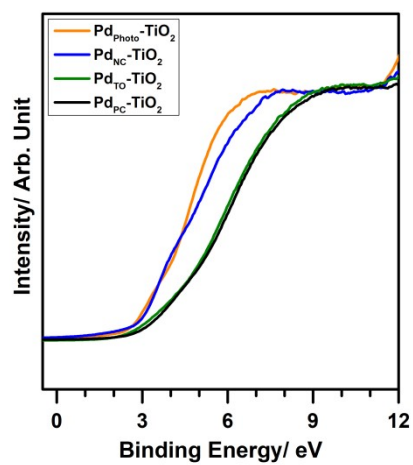


Figure S9: Superimposed UPS VB spectra of as-prepared Pd-TiO₂ samples.

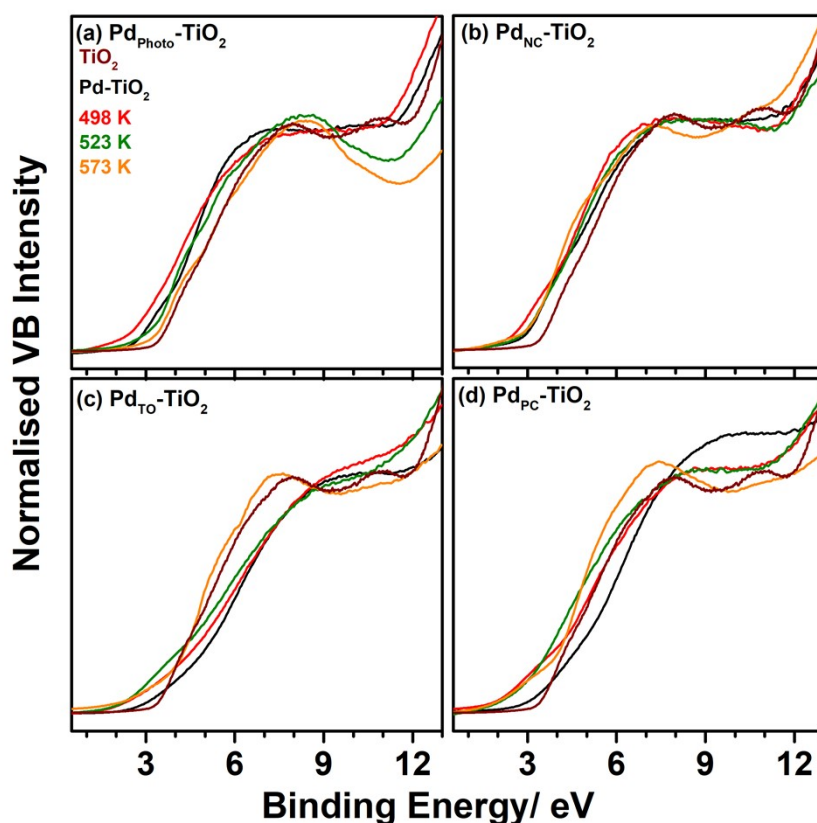


Figure S10: Treatment temperature-dependent superimposed UPS VB spectra for various Pd-TiO₂ samples such as (a) Pd_{Photo}-TiO₂, (b) Pd_{NC}-TiO₂, (c) Pd_{TO}-TiO₂, and (d) Pd_{PC}-TiO₂. The same color codes are followed in all panels. UPS spectrum of TiO₂ (wine trace) is also added for reference. It is to be mentioned that VB intensity was normalized to the main peak of O 2p feature of TiO₂ mainly to investigate the changes observed in the UPS spectra. Pure TiO₂ shows two broad VB O 2p features at between 5 eV to 10 eV with a VB onset at 3.5 eV. On integration with Pd, both the VB features of TiO₂ merge into one broad feature for all Pd-TiO₂ catalysts; irrespective of the method of preparation and SM treatment, this broadening occurs, indicating a similar interaction. With Pd loading, virgin and SM treated Pd_{Photo}-TiO₂ spectra displays a very broad signal with a shift in VB onset to a lower BE side, and the same is shown in an elongated pink oval in panel a (Fig. S10a). Similar shift to lower BE is observed for other three Pd-TiO₂ too (Figs. S10b-d). Nonetheless a contrasting observation noted is the new states created above the O 2p VB of TiO₂ (below 3.5 eV), while the O 2p VB itself moves to higher BE and broadened due to Pd-integration. While the SM treated Pd-TiO₂ VB features are observed at the same BE as that of TiO₂ for Pd_{Photo}-TiO₂ and Pd_{NC}-TiO₂, it is further shifted to higher BE for Pd_{TO}-TiO₂ and Pd_{PC}-TiO₂. This particular observation indicates that Pd interacts relatively strongly with O 2p bands of TiO₂ and integrated electronically in the former (Pd_{Photo}-TiO₂ and Pd_{NC}-TiO₂) cases, while less strongly with latter two (Pd_{TO}-TiO₂ and Pd_{PC}-TiO₂). New states observed around 3.5 eV is attributed to Pd 4d states. Intensity of this new state remains the same for 498 and 523 K SM treated catalysts; however, it decreases after SM treatment at 573 K for all Pd-TiO₂ cases, highlighting a significant change in the state of Pd. It is likely that diffusion of O-atoms into the subsurface of Pd at higher SM temperatures could be the possible reason behind these significant changes.

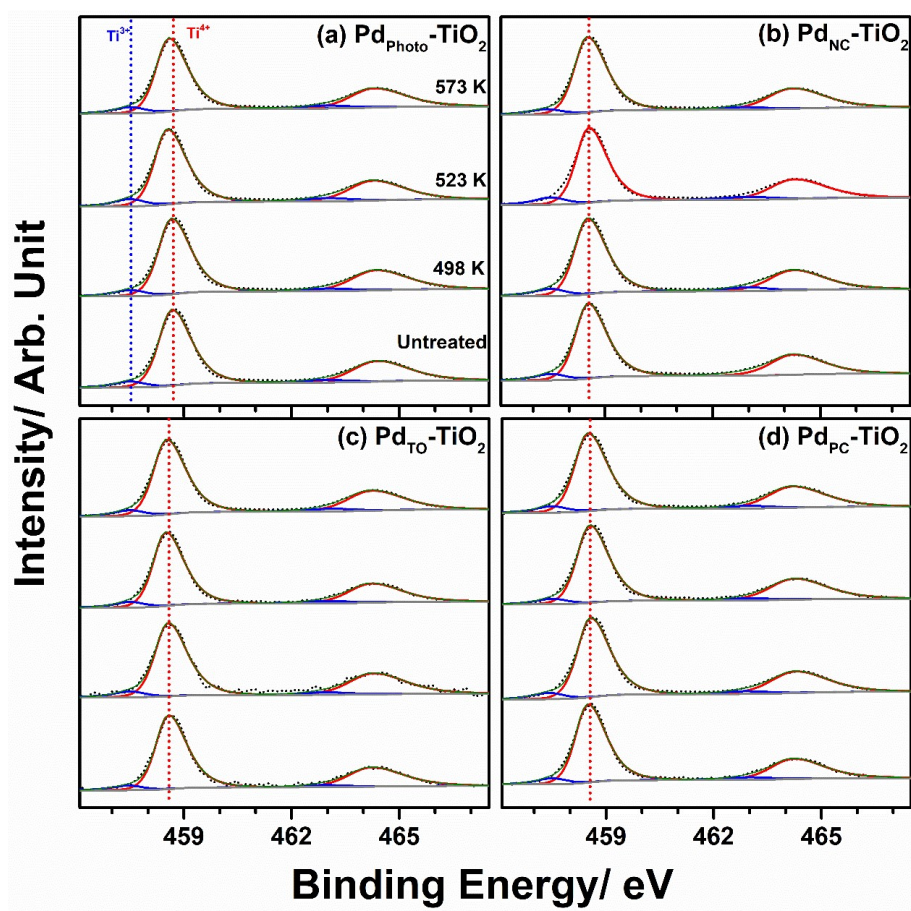


Figure S11: Surface modification temperature treatment dependent Ti 2p XPS spectra for (a) Pd_{Photo}-TiO₂, (b) Pd_{NC}-TiO₂, (c) Pd_{TO}-TiO₂, (d) Pd_{PC}-TiO₂.

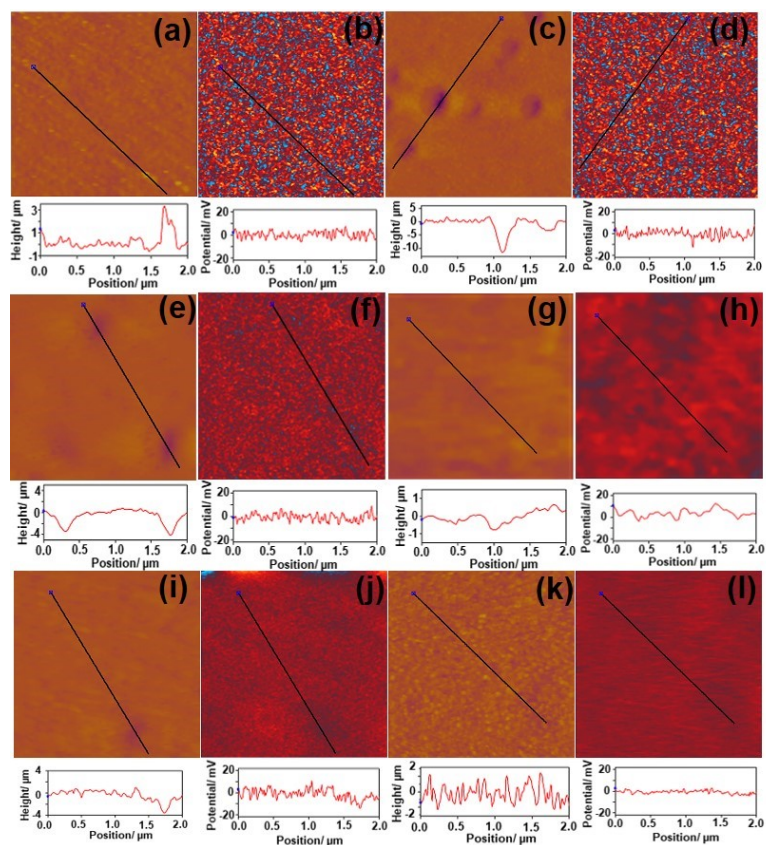


Figure S12: (a) AFM topography image, (b) surface potential image recorded on Pd_{TO}-TiO₂ catalysts. A corresponding line profile is provided at the bottom of each image. Similarly, (c), (e), (g), (i), and (k) are the topography images with corresponding surface potential images (d), (f), (h), (j), and (l) recorded for Pd_{TO}-TiO₂ catalysts modified at temperatures of 448, 473, 498, 523, and 573 K respectively.

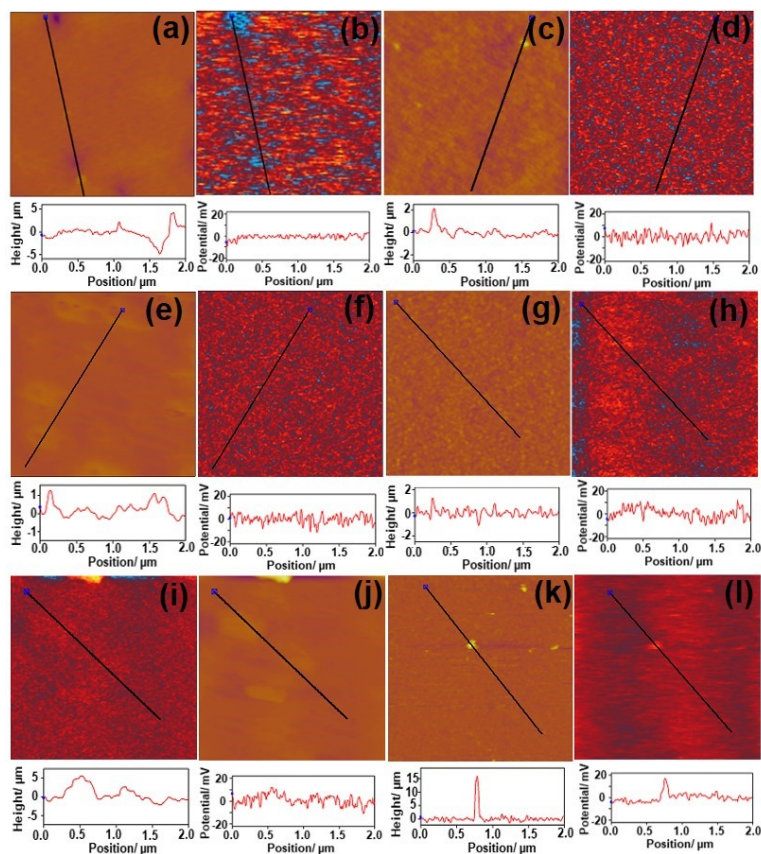


Figure S13: (a) AFM topography image, (b) surface potential image recorded on Pd_{PC}-TiO₂ catalysts. A corresponding line profile is provided at the bottom of each image. Similarly, (c), (e), (g), (i), and (k) are the topography images with corresponding surface potential images (d), (f), (h), (j), and (l) recorded for Pd_{PC}-TiO₂ modified at temperatures of 448, 473, 498, 523, and 573 K respectively.