**Supplementary Information**

**Enhanced Photocatalytic CO2 Reduction with Defective TiO2 Nanotubes Modified with Single-Atom Binary Metal Components.**

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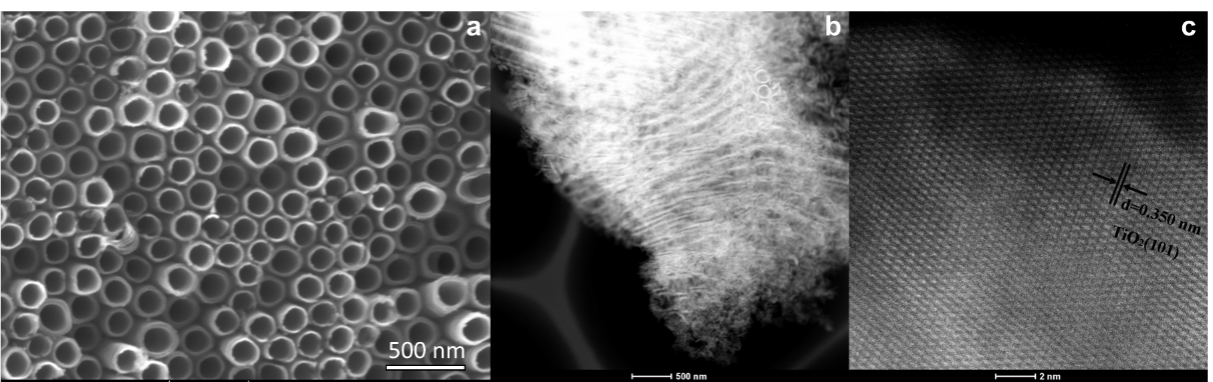
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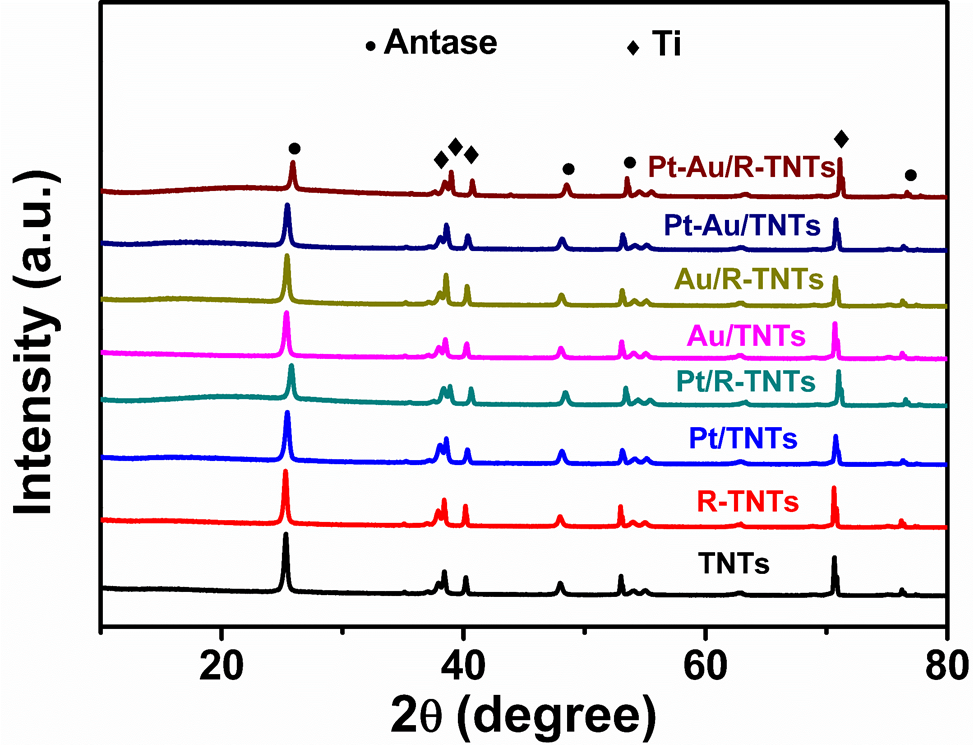
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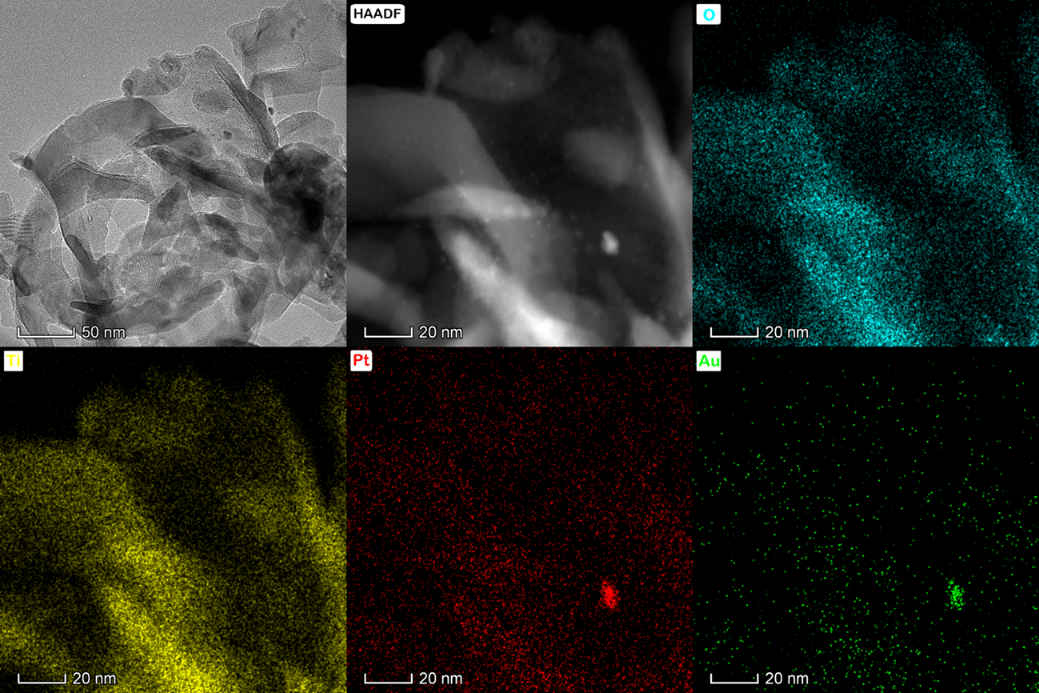
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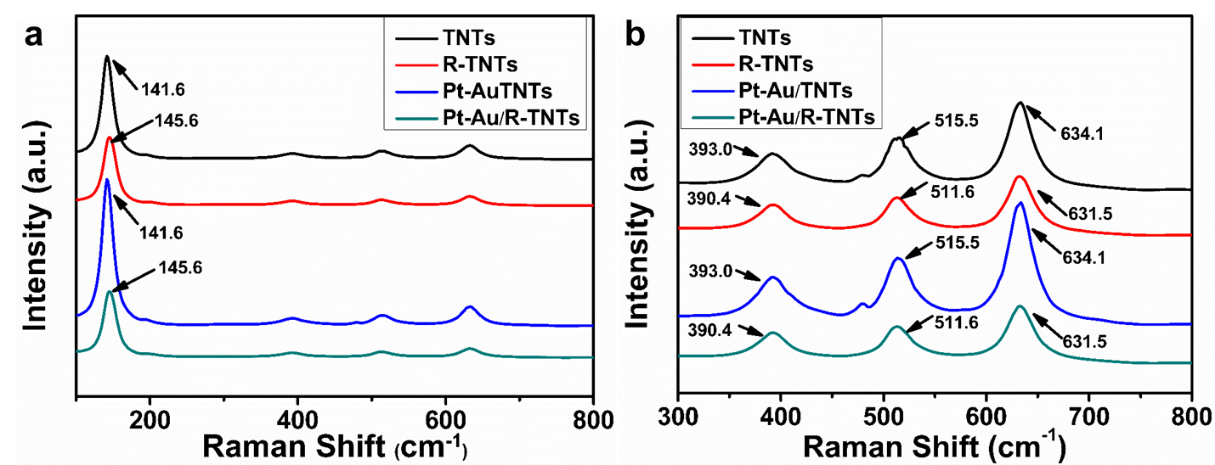
**Supplementary Figure 1.** (**a**) SEM image, (**b**) TEM image, and (**c**) high-resolution TEM images of the TNTs support.



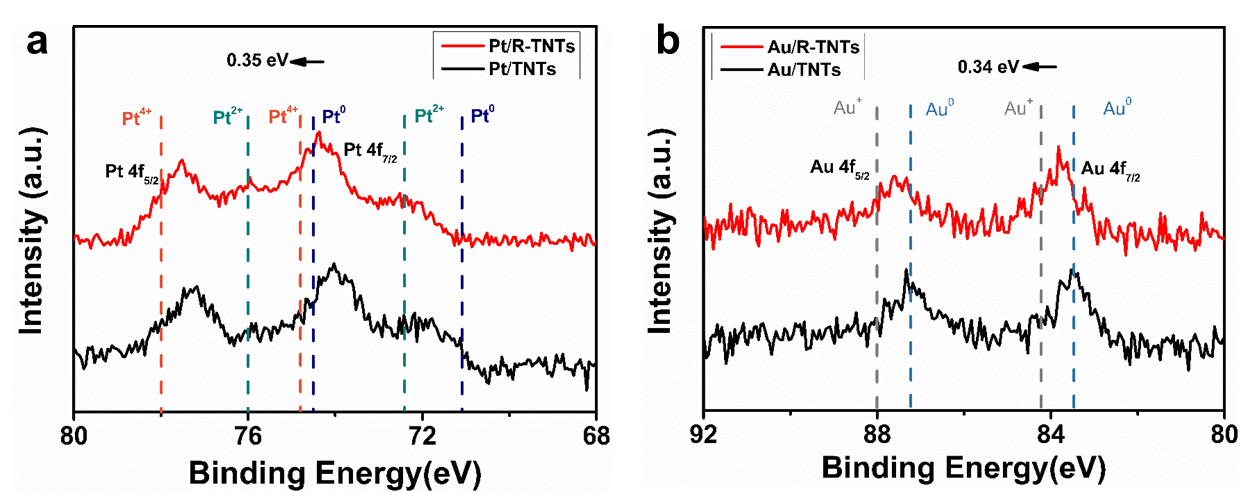
**Supplementary Figure 2.** XRD patterns of the fabricated catalysts.



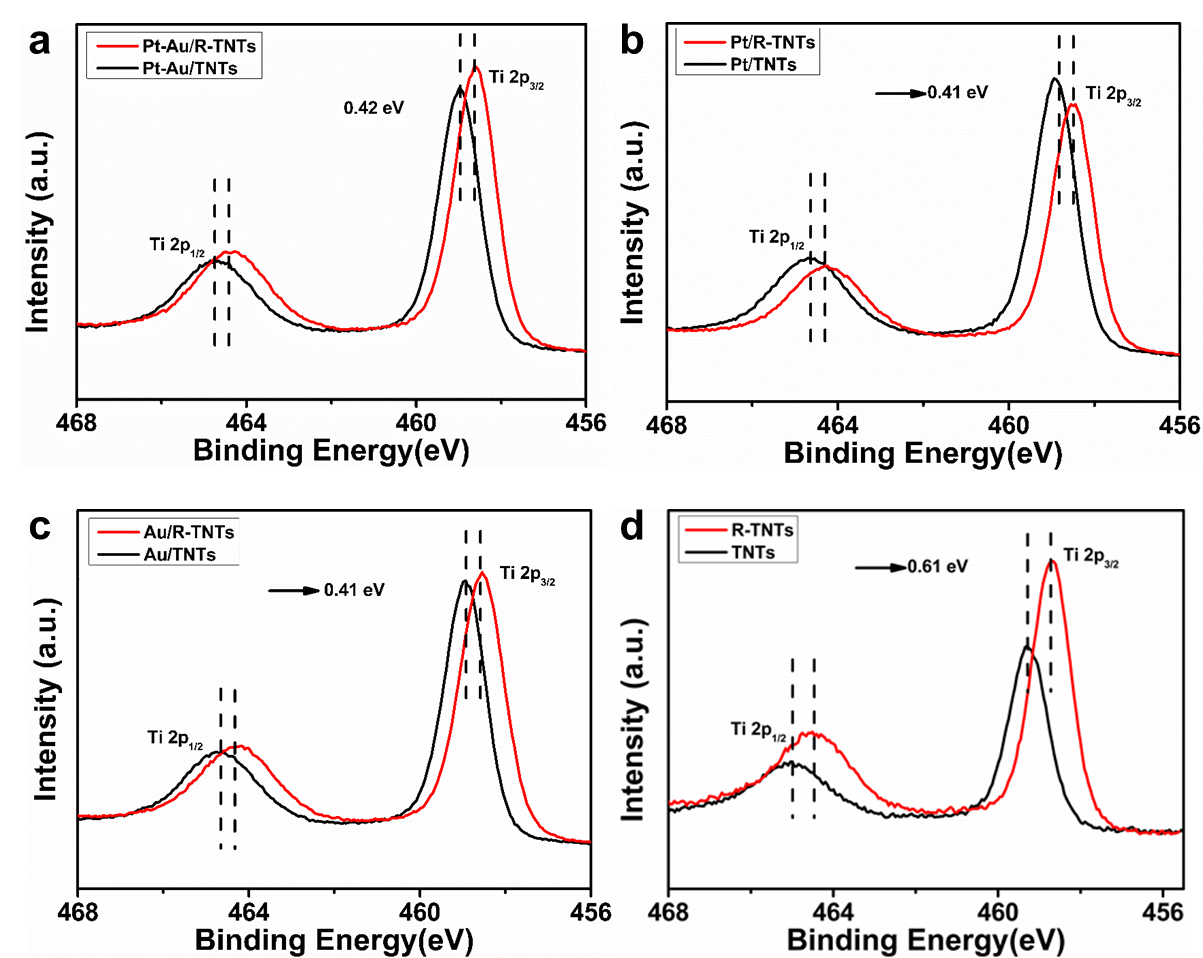
**Supplementary Figure 3.** Elemental mappings of Pt-Au/TNTs show the distribution of O (cyan), Ti (yellow) Pt (red), and Au (green).

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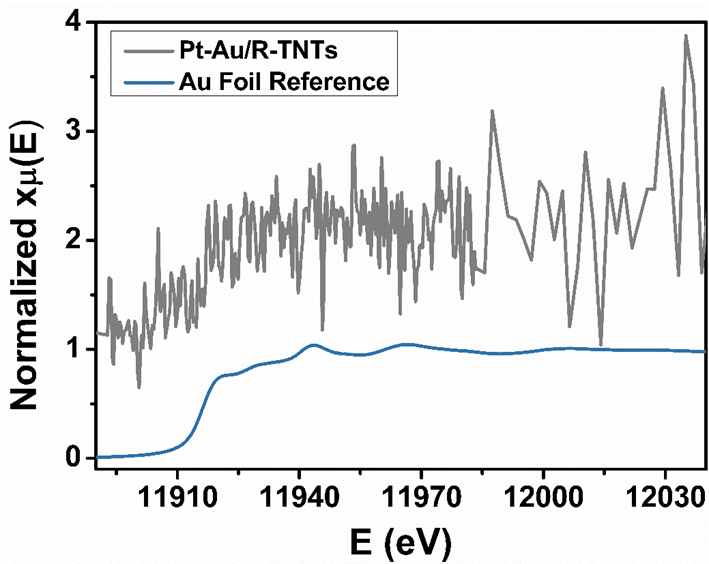
**Supplementary Figure 4.** (**a**) Raman spectra of catalysts, (**b**) the amplifying spectra between 300 and 800 nm.

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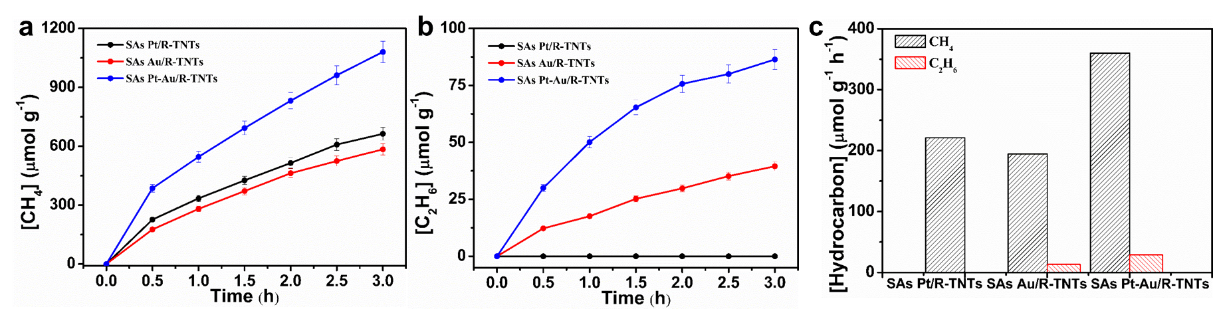
**Supplementary Figure 5.** High resolution XPS: (**a**) Pt 4f spectra of Pt/R-TNTs and Pt/TNTs; (**b**) Au 4f spectra of Au/R-TNTs and Au/TNTs.

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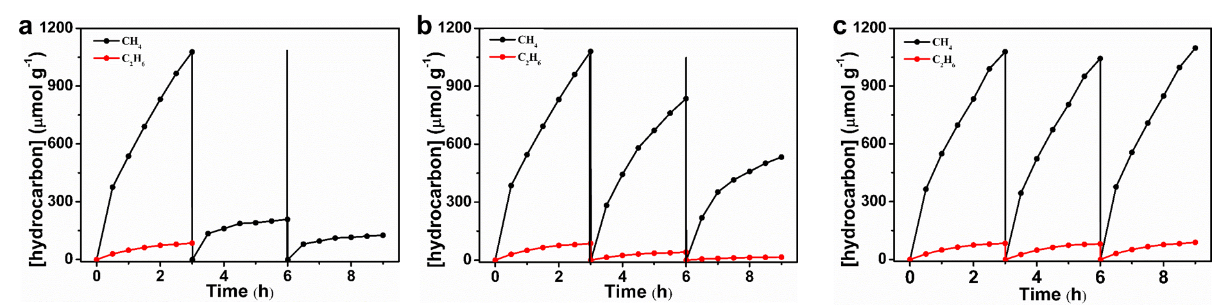
**Supplementary Figure 6.** High resolution XPS Ti 2p spectra of catalysts.



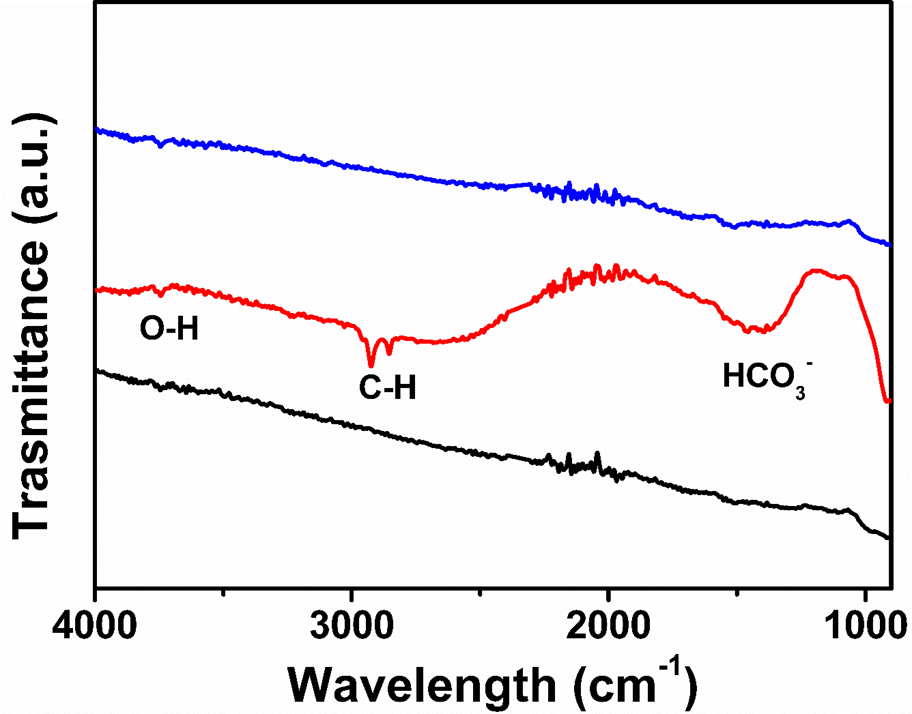
**Supplementary Figure 7.** XANES spectra of Au L3-edge. No characteristic signals for Au was observed due to trace quantity of the Au and high disturbance of Pt.

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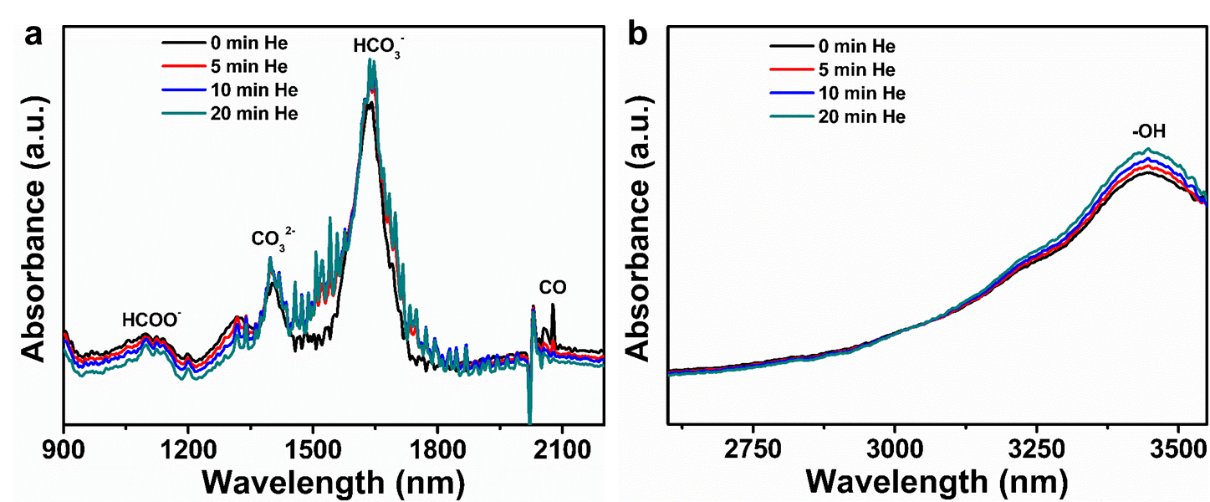
**Supplementary Figure 8.** Cumulative (**a**) CH4 and (**b**) C2H6 evolution for SAs Pt-Au/R-TNTs, Pt/R-TNTs, and Au/R-TNTs catalysts. (**c**) The average yield of CH4 and C2H6 for per hour.

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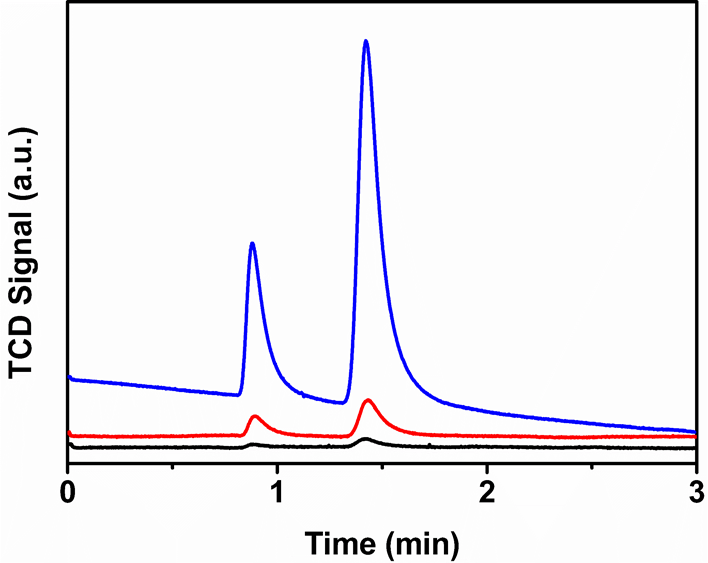
**Supplementary Figure 9.** Photocatalytic stability test of the SAs Pt-Au/R-TNTs catalysts under: (**a)** no treatment of the catalyst, (**b**) the surface of the catalyst refreshed with deionized water for repeated test, and (**c**) replaced water vapor with 10 vol % CH3OH/H2O as the proton source.



**Supplementary Figure 10.** FIRT spectrum of SAs Pt-Au/R-TNTs catalysts: before reaction (black), after photocatalysis for 3 h (red), after photocatalysis for 3 h and scouring off the surface with deionized water (blue).



**Supplementary Figure 11.** *In situ* DRIFT spectra of SAs Pt-Au/R-TNTs in CO2 atmosphere under dark condition.



**Supplementary Figure 12.** TCD signals of measured gas: before reaction (black), after photocatalysis of SAs Pt-Au/R-TNTs catalysts for 3 h (red, the volume ratio of O2/N2 viz. 0.42), air atmosphere (blue, the volume ratio of O2/N2 viz. 0.27).

**Supplementary Table 1.** Summary of catalytic performance and metals mass percentage in the catalysts.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| catalyst | CH4 yield  (µmol g-1 h-1) | C2H6 yield  (µmol g-1 h-1) | Pt wt % | Au wt % |
| SAs Pt-Au/R-TNTs | 360.0 | 28.8 | 0.16 | 0.17 |
| Pt-Au/TNTs | 75.5 | -- | 0.18 | 0.15 |
| SAs Pt /R-TNTs | 221.5 | -- | 0.31 | -- |
| SAs Au/R-TNTs | 194.7 | 13.2 | -- | 0.29 |
| R-TNTs | 2.8 | -- | -- | -- |