# Supporting Information

Hollow $TiO_2$ Microsphere/Graphene Composite Photocatalyst for $CO_2$ Photoreduction

Yi-Chen Chung[a,#], Pei-Jie Xie[a,#], Yi-Wei Lai[a], An-Ya Lo*[,a]

[a] Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung, Taiwan

No.57, Sec. 2, Zhongshan Rd., Taiping Dist., Taichung 41170, Taiwan (R.O.C.)

* Corresponding author.

E-mail: a.y.lo1125@gmail.com

# Both authors contributed equally to this work.

Table S1 Processing parameters and diameter ranges of silica microspheres.

| $SiO_2$ microsphere | EtOH (mL) | $H_2O$ (mL) | $NH_4OH$ (mL) | TEOS (mL) | Diameter range (nm) |
|---|---|---|---|---|---|
| $SS_{100}$ | 100 | 10 | 2.5 | 1.5 | 100~120 |
| $SS_{200}$ | 100 | 5 | 4.5 | 2.4 | 210~230 |
| $SS_{300}$ | 100 | 10 | 4.5 | 2.4 | 290~310 |
| $SS_{400}$ | 100 | 10 | 4.5 | 5 | 390~410 |

Table S2. Analysis of the Pore Properties of Silica Balls with Different Particle Sizes.

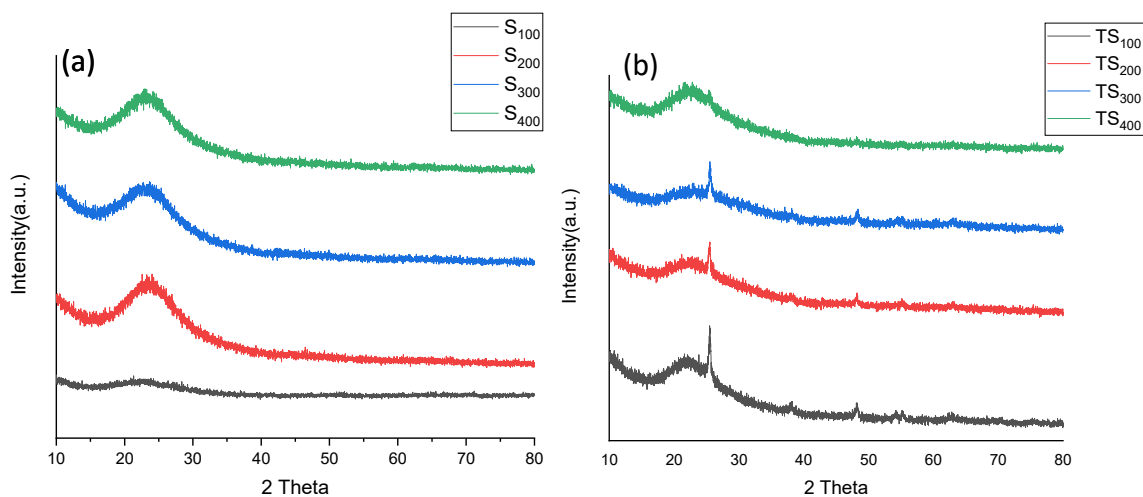| Samples | $SiO_2$ wt % | Surface Area ($m^2$/g) |
|---|---|---|
| $SS_{100}$ | 100 | 25.02 |
| $SS_{200}$ | 100 | 12.98 |
| $SS_{300}$ | 100 | 10.12 |
| $SS_{400}$ | 100 | 7.297 |
| $TS_{100}$ | -- | 25.20 |
| $TS_{200}$ | -- | 68.75 |
| $TS_{300}$ | -- | 45.23 |
| $TS_{400}$ | -- | 43.80 |
| $hTS_{200-8}$ | 64.7 | 37.92 |
| $hTS_{200-10}$ | 51.6 | 41.64 |
| $hTS_{200-12}$ | 4.1 | 141.88 |
| $h TS_{200-14}$ | 3.7 | 64.93 |



Figure S1 XRD patterns of (**a**) $SS_x$ and (**b**) $TS_x$.
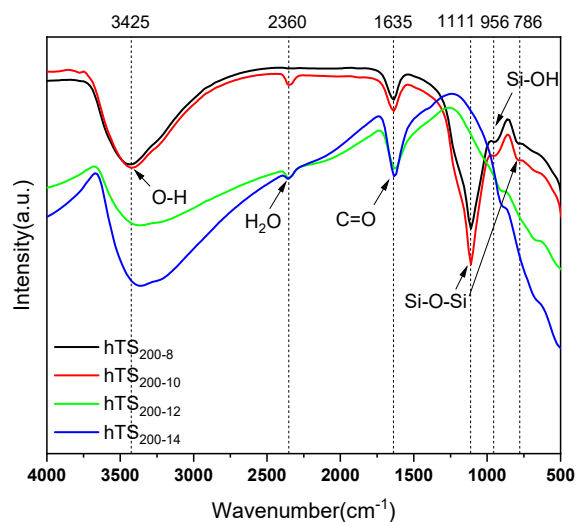
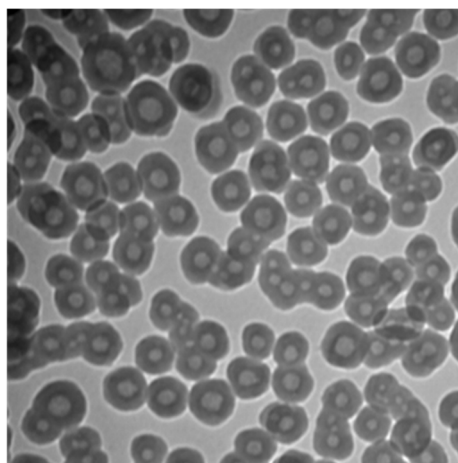Figure S2 FTIR spectra of hTS$_{200-y}$ samples.
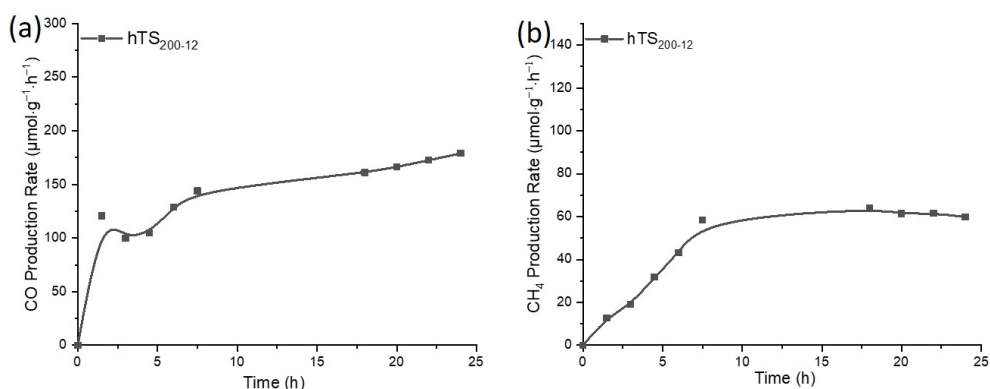


Figure S3. TEM image of hTS$_{x-y}$.



Figure S4. Long-term stability test of hTS$_{200-12}$ photocatalyst for the production rates of (a) CO and (b) CH$_4$. The long-term irradiation was conducted in a commercial photocatalytic system (PCX50BDiscover, PerfectLight) with wavelength of 365 nm, and 50 ml quartz reactor.
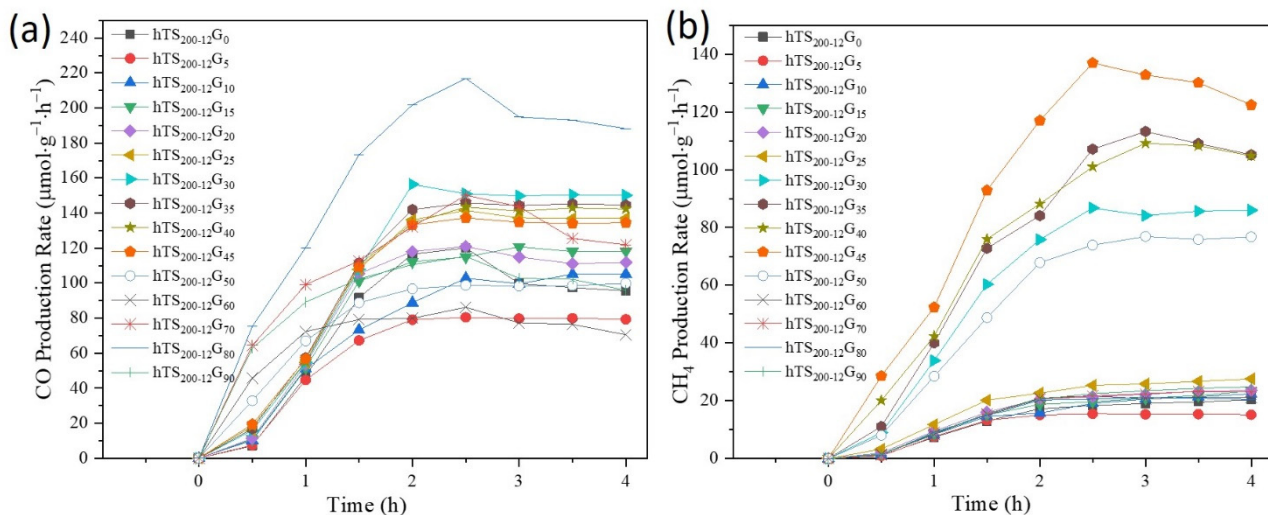
Figure S5 Effect of $CO_2PR$ reaction time over $hTS_{200\text{-}12}G_z$ on (a) CO and (b) $CH_4$ yields. The photoreduction experiments were conducted in a homemade photoreaction system, where the volume of the reaction chamber was 240 mL with a quartz cover serving as the window for light irradiation from a 100 W Hg lamp.
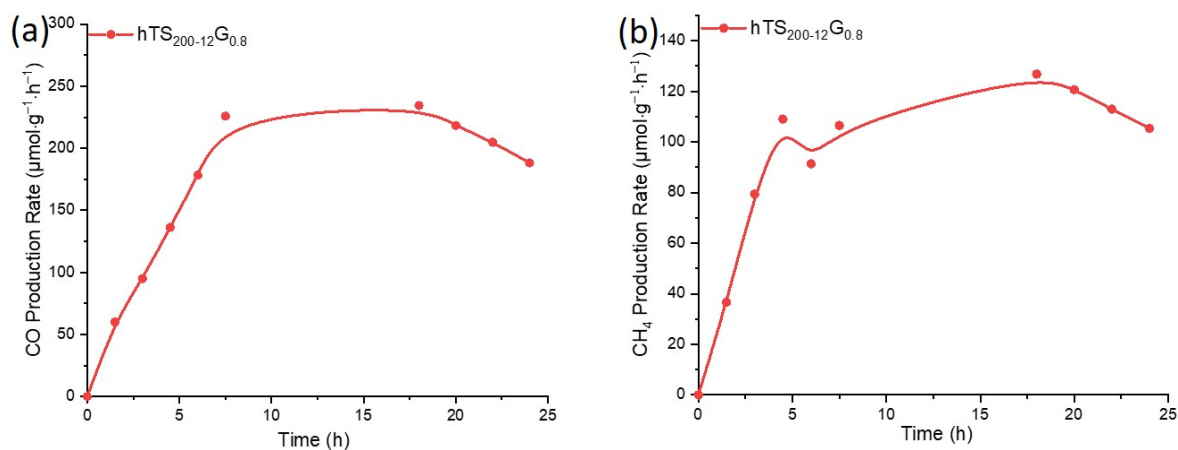


Figure S6 Long-term stability test of $hTS_{200\text{-}12}G_{80}$ photocatalyst for the production rates of (a) CO and (b) $CH_4$. The long-term irradiation was conducted in a commercial photocatalytic system (PCX50BDiscover, PerfectLight) with wavelength of 365 nm, and 50 ml quartz reactor.
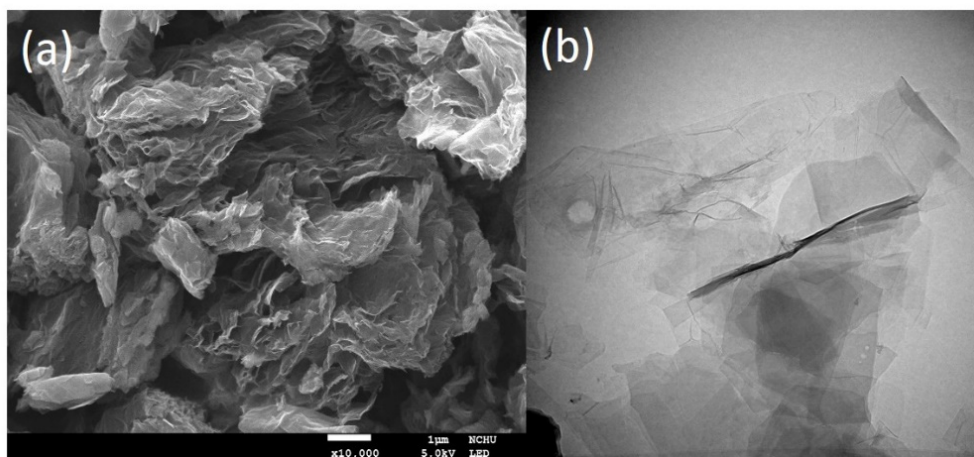
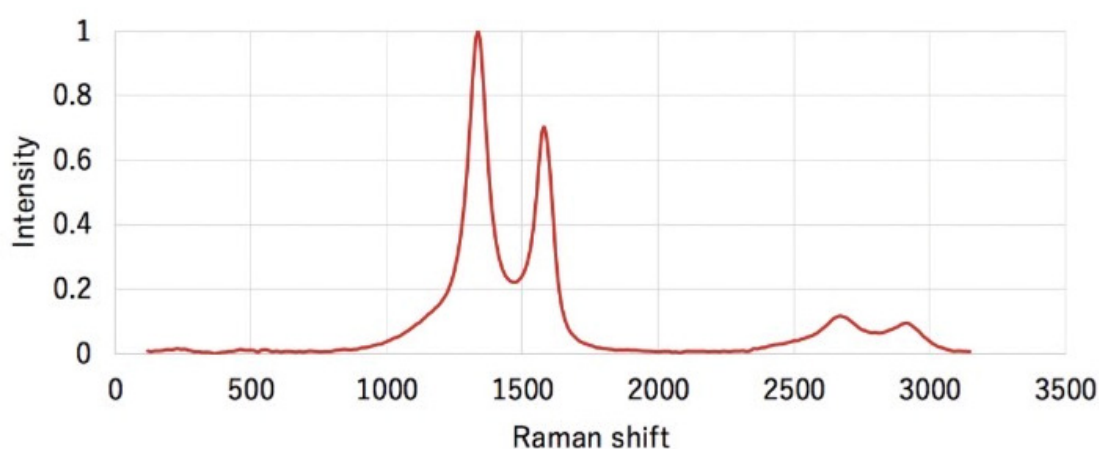Figure S7. (a) SEM and (b) TEM image of graphene. (SSA=411.1 m$^2$/g)



Figure S8. Raman spectrum of N002-PDR graphene powder provided from Angstron Materials Inc. (AMI). N002-PDR powder contains graphene with less than three graphene layers and has maximum x-y dimensions of 10 μm. This commercially available graphene product has been used in several studies [1-4], and the 2D band has also been discussed in the literature [3]. This indicates the good quality of the commercial graphene sheets. In short, as the graphene (N002-PDR) has been widely used and its Raman spectrum and 2D band investigated and reported in the literature.Considering the procedure used for the preparation of the hTS$_{x-y}$/graphene composites involved the use of only pure ethanol as solvent to disperse hTS$_{x-y}$ on graphene; ethanol is generally considered a weak reducing agent. Furthermore, both TiO$_2$ and graphene are generally considered to be chemically stable. Therefore, it is believed that the chemical state of graphene did not change during preparation of the composites.
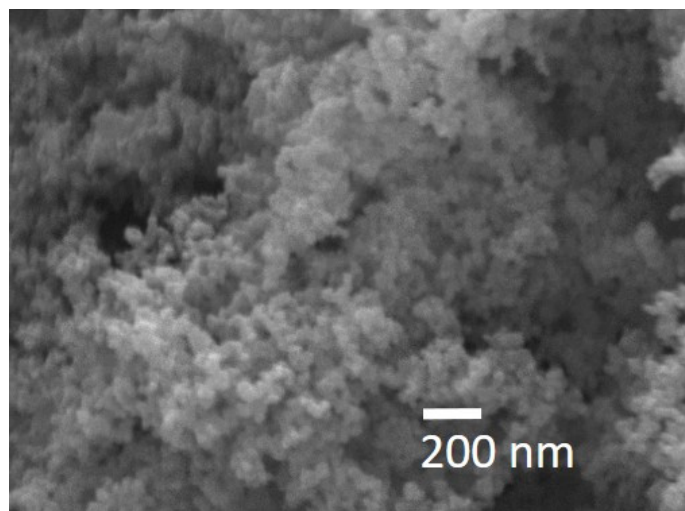
Figure S9 SEM image of P25.

1.  Castelaín, M., et al., *Comparative study of the covalent diazotization of graphene and carbon nanotubes using thermogravimetric and spectroscopic techniques.* Physical Chemistry Chemical Physics, 2013. **15**(39): p. 16806-16811.
2.  Karbalaei-Bagher, M., Z. Ahmadi, and H. Nazockdast, *A mechanistic approach on the curing kinetics of benzoxazine-filled oxygen plasma treated graphene nanosheets.* Materials Research Express, 2019. **6**(9): p. 095332.
3.  Bourdo, S.E., et al., *Physicochemical characteristics of pristine and functionalized graphene.* Journal of Applied Toxicology, 2017. **37**(11): p. 1288-1296.
4.  Lo, A.-Y., et al., *Effect of Composition Ratios on the Performance of Graphene/Carbon Nanotube/Manganese Oxide Composites toward Supercapacitor Applications.* ACS Omega, 2020. **5**(1): p. 578-587.