Synthesis of TiO$_2$–x/W$_{18}$O$_{49}$ hollow double-shell and core–shell microspheres for CO$_2$ photoreduction under visible light†

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TiO$_2$–x/W$_{18}$O$_{49}$ with core–shell or double-shelled hollow microspheres were synthesized through a facile multi-step solvothermal method. The formation of the hollow microspheres with a double-shell was a result of the Kirkendall effect during the solvothermal treatment with concentrated NaOH. The advanced architecture significantly enhanced the electronic properties of TiO$_2$–x/W$_{18}$O$_{49}$, improving by more than 30 times the CO$_2$ photoreduction efficiency compared to the pristine W$_{18}$O$_{49}$. Operando DRIFTS measurements revealed that the yellow TiO$_2$–x was a preferable CO$_2$ adsorption and conversion site.

Over recent years, a great deal of effort has been dedicated to reducing anthropogenic CO$_2$ concentrations. Amongst the many strategies considered for this purpose, photocatalytic conversion of CO$_2$ and H$_2$O is regarded as one of the most promising solutions, since it not only utilises CO$_2$, but also generates value added chemicals, such as CO and other hydrocarbons. However, the low selectivity and conversion efficiency of CO$_2$ photoreduction renders the process currently unviable for commercialisation. Perhaps the most promising way to further improve the efficiency of CO$_2$ photoreduction, is to fabricate more efficient photocatalysts. Recently, the synthesis of metal oxides with oxygen vacancies has received increasing attention. Compared with vacancy-free counterparts, such metal oxides possess improved optical properties and electrical conductivity, which leads to enhanced separation of photogenerated electron–hole pairs, resulting in overall improvement of the photocatalytic efficiency.

A variety of approaches have been employed to introduce oxygen vacancies into TiO$_2$, among which high temperature calcination in an inert gas environment has proven particularly successful. For example, the reduction of TiO$_2$ anatase was achieved through hydrogenation in a 5% H$_2$/95% Ar environment heated at 450 °C for 7 h. The resultant ‘vacancy-rich’ titania possessed a yellow colour, revealing an extension of the frequency of absorption into the visible region when compared with P25 TiO$_2$, which is white in colour.

In addition, the use of advanced architectures, including core–shell, and multi-shelled hollow micro/nanostructures, has been shown to have a positive effect, enhancing the photocatalytic efficiency. For example, Hong et al. fabricated an Ag core with TiO$_2$ shells (14.8 μmol g$^{-1}$), which revealed a higher gas–solid CO$_2$ photoreduction under a solar simulator when compared to the as-prepared TiO$_2$ nanoparticles (3.9 μmol g$^{-1}$) and Ag deposited on TiO$_2$ (4.4 μmol g$^{-1}$) after 3 h. Another recent study demonstrated the fabrication of metal–organic framework (MOF) encapsulated Au@PtAg co-catalysts. The advanced nanostructure of the assembled noble metals and MOF shell promoted the separation of photogenerated electron–hole pairs and CO$_2$ adsorption, respectively, leading to enhanced CO production from CO$_2$, improved selectivity towards CO and stability for the gas phase CO$_2$ photoreduction.

To incorporate the optical properties (i.e., enhancement in visible light absorption through oxygen vacancies) into a photocatalyst with advanced architecture, we have proposed and developed both core–shell nanoparticles and hollow microspheres with a double-shell. The novelty of this method is the fabrication of both a core and the shell comprising oxygen deficient materials (i.e., TiO$_2$–x/W$_{18}$O$_{49}$) without the use of a co-catalyst. Since nanostructured W$_{18}$O$_{49}$ had been demonstrated to photoreduce CO$_2$ effectively, a similar synthesis approach was adopted to fabricate the shell layer of the nanoparticles.

The core–shell TiO$_2$–x/W$_{18}$O$_{49}$ was fabricated by a combination of solvothermal and calcination methods. Briefly, TiO$_2$ microspheres were synthesized by a solvothermal method (Step 1).
The resultant TiO₂ microspheres were calcined, producing a yellowish orange powder, denoted as TiO₂-x (Step 2). Next, a thin SiO₂ layer was coated onto the TiO₂-x microspheres as a protective layer for the core material (Step 3). Subsequently, a layer of W₁₈O₄₉ was coated onto the SiO₂ layer by solvothermal treatment (Step 4). Finally, the SiO₂ was removed by hydrothermal etching in concentrated aqueous NaOH solution (Step 5). The resulting samples were denoted as TW6h, TW12h and TW24h, where the number indicated the time (hours) taken in Step 4. A detailed description of the synthesis procedure can be found in the ESI†.

The fabricated TiO₂-x consisted of highly crystallised anatase phase (JCPDS card no. 21-1272, Fig. S1A(a), ESI†). The TiO₂-x had a spherical shape and possessed a rough surface (Fig. S2a and b, ESI†). Taking a closer look under TEM, the TiO₂-x (diameter ~ 120 nm, Fig. S2c, ESI†) was self-assembled from many bean-like TiO₂-x nanoparticles (~20 nm, Fig. S2d, ESI†). The selected-area electron diffraction pattern (SAED, inset of Fig. S2d, ESI†) revealed that each bean-like nanoparticle was highly crystallised with an interlayer spacing of ~1.9 nm, matching the interplanar distance of the (200) plane of anatase.

In Step 4, the solvothermal treatment time was manipulated. The crystallinity of the W₁₈O₄₉ layer was observed to initially increase and subsequently decreased with the solvothermal treatment time (Fig. S1A(b–e), ESI†). No W₁₈O₄₉ peak was observed after 6 h of solvothermal treatment; this was probably due to the small amount of W₁₈O₄₉ crystallised on the core nanoparticles (Fig. 1c). When the hydrothermal treatment was extended to 12 h, a weak W₁₈O₄₉ peak at 23.7° started to emerge (Fig. S1A(c), ESI†). Meanwhile, the characteristic peaks of WO₃ were also observed in the TW12h sample (JCPDS card no.: 3-1035, discussed in next paragraph). Prolonging the solvothermal treatment time to 24 h resulted in a further decrease of the intensity of TiO₂-x as well as the WO₃ peaks (Fig. S1A(d), ESI†).

Raman spectroscopy was used to further investigate the effect of solvothermal time towards the formation of W₁₈O₄₉ and/or WO₃ on the TiO₂-x nanoparticles. The characteristic bands of the anatase polymorph of TiO₂-x were revealed in the Raman spectrum (Fig. S1B(a), ESI†). When W₁₈O₄₉ was incorporated via solvothermal treatment for 6 h, the Raman feature of the anatase phase was maintained (Fig. S1B(b), ESI†). Further increasing the solvothermal time to 12 h, the anatase band centred at 141 cm⁻¹ was reduced dramatically compared to sample TW6h (Fig. S1B(c), ESI†). This observation was paralleled with the observations made with the laboratory-based PXRD (Fig. S1A(c), ESI†). In addition, the characteristic bands of WO₃, centred at 397, 517, 637, 691 and 886 cm⁻¹ were also observed. When the solvothermal time was extended to 24 h, the intensity of the anatase peak (141 cm⁻¹) increased again (Fig. S1B(d), ESI†). This observation was in contradiction with the laboratory-based PXRD results, as shown in Fig. S1A(d) (ESI†). This discrepancy was very likely attributed to the increase of the WO₃ crystallinity with the solvothermal time. Furthermore, the co-existence of W₁₈O₄₉ and WO₃ phases led to an indistinguishable Raman pattern after 200 cm⁻¹ in sample TW24h (Fig. S1B(e), ESI†).

The synthesis process of Step 4 was characterised using in situ and time resolved synchrotron-based PXRD. The crystallised TiO₂ coated with SiO₂ was mixed with the precursor solution of W₁₈O₄₉ prior to the time resolved PXRD (Fig. S3a, ESI†). A broad peak of a poorly crystalline precursor centred at ~8° was observed initially (Fig. S3a, ESI†). When the sample was heated, the broad peak lost its intensity over time, suggesting that the W precursor was consumed (Fig. S3b, ESI†). Meanwhile, peaks corresponding to W₁₈O₄₉ started to emerge, indicating the occurrence of nucleation and crystallisation of W₁₈O₄₉ at the expense of the W precursor. When the temperature reached 180 °C, the intensity of the W₁₈O₄₉ peaks increased and was maintained throughout the experiment. Similar observation was obtained in the small angle region (q = 0.12 Å⁻¹, Fig. S3c, ESI†). The emergence of this peak was attributed to the scattering of the nanocrystals from the newly formed tungstate, in agreement with the observation under TEM-EDX (Fig. 1).

When the TiO₂-x was treated in the WCl₆ solution for 6 h using solvothermal treatment, the rough surface in the TiO₂ could still be seen under SEM (Fig. S4a, ESI†). When prolonging the solvothermal time to 12 h, the surface of the particles became smooth and a layered structure within each nanoparticle was seen (Fig. S4b, ESI†). The micromotmed TW12h exhibited a core–shell structure. The core possessed a similar structure as observed in the TiO₂-x and a visibly porous shell layer of ~30 nm thick was observed (Fig. S4e, ESI†). Further extending to 24 h, the size of the nanoparticles increased to ~300 nm (Fig. S4c, ESI†). Although the thickness of the shell layer was maintained at ~30 nm, the diameter of the core with a hollow void increased to ~200 nm (Fig. S4f, ESI†).

The micromotmed TW6h nanoparticle was dominated by Ti while W was scarcely distributed on the surface as shown in TEM-EDX (Fig. 1b). This observation supported the result obtained in Raman, in which the weak shoulder peak centred at 115.6 cm⁻¹ was assigned to the characteristic band of W₁₈O₄₉. When TiO₂-x was treated in WCl₆ solution for 12 h, the TW12h sample revealed a core–shell structure consisting of self-assembled spherical TiO₂-x nanoparticles as the core and a visibly porous W₁₈O₄₉ shell (Fig. 1f–j). Further increasing the

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**Fig. 1** TEM images of TW6h (a), TW12h (f) and TW24h (k) nanoparticles and the corresponding TEM-EDX mapping of the nanospheres (b–e, g–j and k–o, respectively).
solvothermal time to 24 h, the TiO$_2$-x nanospheres exhibited a hollow structure (diameter ~ 80 nm), resulting in a double layered shell (Fig. 1k-o). The outer layer of the nanosphere consisted of ~ 30 nm of W; whereas the thickness of the second layer was ~ 60 nm of Ti. From the results obtained, a growth mechanism was proposed. When the time for solvothermal treatment in Step 4 increased, the time for the crystallisation of W$_{18}$O$_{49}$ was prolonged, and thus, more pores were created (Fig. 1k). Consequently, the strong alkaline NaOH used in Step 5 could enter the core of the nanospheres. The highly concentrated NaOH aqueous solution then broke some of the Ti–O bonds of the TiO$_2$-x under the autogeneous pressure in the autoclave.$^{18}$ Hence, the influx of concentrated NaOH into the TW12h and TW24h particles was speculated to lead to the dissolution of TiO$_2$-x. However, the outflow of dissolved titania was probably restricted by the W$_{18}$O$_{49}$ shell layer. As a result, the re-crystallisation of titania occurred within the nanosphere at the edges of the core TiO$_2$-x nanoparticle. As a result, a hollow structure in the TiO$_2$-x core was formed due to imbalanced mass transport, which is known as the Kirkendall effect, leading to an increase in the diameter of the core TiO$_2$ nanosphere.$^{19}$

The yellowish orange TiO$_2$-x exhibited an enhanced absorbance between 400 and 600 nm when compared to P25 (Fig. S5A, ESI†). The enhancement of absorbance in the TiO$_2$-x sample was due to the presence of Ti$^{3+}$ and Ti$^{2+}$ moieties, as evidenced by the XPS studies (Fig. S6a, ESI†). When the W shell was incorporated onto the as-prepared TiO$_2$, the high resolution Ti spectrum of TW6h did not show significant change compared to the as-prepared TiO$_2$-x (Fig. S6b, ESI†). However, the high resolution Ti spectrum of TW12h exhibited only four deconvoluted peaks, which centred at 462.1, 457.3 (attributed to the 2p$_{3/2}$ of Ti$^{3+}$), 458.8 and 464.0 eV (attributed to the 2p$_{1/2}$ and 2p$_{3/2}$ of Ti$^{4+}$, Fig. S5B, ESI†). The disappearance of Ti$^{2+}$ was very likely due to the dissolution and re-crystallisation reaction that occurred in Step 5. As a result, the absorbance at 400–500 nm for the TW12h and TW24h samples was slightly lower than that of the pristine TiO$_2$-x and TW6h (Fig. S5A, ESI†).

The enhancement of light absorbance at 500–600 nm in the TWxh and W$_{18}$O$_{49}$ samples was attributed to the oxygen vacancies contributed by W$_{18}$O$_{49}$. The presence of oxygen vacancies within the TWxh samples was evidenced in the high resolution O 1s spectrum (Fig. S5C, ESI†). The O 1s spectrum was deconvoluted into three peaks, which centred at 529.1, 530.1 and 531.0 eV. The peak centred at 531.0 eV was attributed to the O related defects, such as oxygen vacancies and oxygen interstitials, and was probably contributed by TiO$_2$-x and W$_{18}$O$_{49}$.20,21 Whereas the peaks centred at 529.1 and 530.1 eV were attributed to the lattice O of Ti–O and W–O, respectively.22 The high resolution W 4d$_{5/2}$ and 4d$_{3/2}$ peaks centred at 247.2 and 259.7 eV revealed typical W$^6+$ spectra; while the peaks centred at 243.3 and 256.9 eV corresponded to the W$^5+$ moiety (Fig. S5D, ESI†).

The synthesized samples revealed outstanding performance in CO$_2$ photoreduction under visible light (Table 1). After irradiation for 2 h, sample TW6h produced the highest amount of CO. Prolonged solvothermal treatment significantly reduced the performance of TW12h and TW24h. However, they are still performing better than pristine TiO$_2$-x and no product was observed from P25 under the same conditions. Without using expensive co-catalyst (e.g., Pt, Ru), the photoproduction of CO using TiO$_2$-x/W$_{18}$O$_{49}$ was higher than the photocatalyst with co-catalyst (i.e., 0.8% Pt on TiO$_2$–SiO$_2$ produced 1.3 μmol g$_{\text{catalyst}}^{-1}$ h$^{-1}$ of CO.23 mononuclear C$_3$H$_2$–RuH complex oxo-bridged TiO$_2$ hybrid produced ~ 5 μmol g$_{\text{catalyst}}^{-1}$ h$^{-1}$ of CH$_4$,24 as reported in the literature.

The presence of oxygen vacancies revealed enhanced electronic properties. The superior performance of TW6h was further evidenced in the high current density response under solar irradiation (Fig. S7, ESI†). However, the responded current density decreased when the solvothermal time was increased from 6 to 24 h. This was probably due to the reduction in the amount of oxygen vacancies as a result of dissolution and re-crystallisation reactions occurring in the TW12h and TW24h samples (Fig. 1, Fig. S5C, F and G, ESI†) as well as the formation of WO$_3$ (Fig. S1, ESI†).

The superior photocatalytic performance of the TiO$_2$-x compared to P25 could be correlated with the amount and chemical states of CO$_2$ adsorbed as evidenced in operando DRIFTS results (Fig. S8, ESI†). Operando DRIFTS results indicated that P25 had insignificant adsorption throughout the experiment. Therefore, no product was expected from P25 which is in line with the results obtained in the CO$_2$ photoreduction under visible light irradiation.

The pristine TiO$_2$-x revealed a strong band at around 2342 cm$^{-1}$, which corresponds to gas phase CO$_2$, when CO$_2$ was fed into the reactor at 24 °C in the dark (Fig. S8b, ESI†). Since the surface of TiO$_2$-x also provided active sites for water splitting, a large amount of adsorbed species will suppress H$_2$ production from water splitting, thus providing high selectivity towards CO formation.26 The bands at around 1620, 1420 and 1296 cm$^{-1}$ were assigned to the asymmetric CO$_3$ stretching vibration [$v_{\text{as}}$(CO$_2$)], symmetric CO$_3$ stretching vibration [$v_{\text{s}}$(CO$_2$)], and O–H deformation vibration [$\delta$(O–H)], of monodentate bicarbonate species (m-HCO$_3^-$), respectively.29–31 The intensity of these bands (i.e., TiO$_2$-x sample) was much higher than that of P25 in the dark. However, the intensity of these bands in sample TiO$_2$-x decreased immediately upon light irradiation. At the same time, the bands at around 1577 and 1396 cm$^{-1}$, which were assigned to the $v_{\text{as}}$(CO$_2$) and $v_{\text{s}}$(CO$_2$) of the bidentate formate species (b-HCO$_3^-$), grew in intensity (Fig. S8d, ESI†).20–32 This indicated that CO$_2$ molecules adsorbed on the
surface of TiO$_2$-$x$ mainly as m-HCO$_3^-$ and converted into b-HCO$_3^-$, which plays a key role in providing high photocatalytic activity as the intermediate species for CO photoreduction with water upon light irradiation.$^{31,33}$ When the reaction temperature was increased to 80 °C, the intensity of the b-HCO$_3^-$ bands continued to increase (Fig. S8f, ESI†). This indicated that the conversion of m-HCO$_3^-$ into the b-HCO$_3^-$ was enhanced at increased temperature. In other words, the operando DRIFT suggested that the desorption of CO was effective, allowing the subsequent adsorption of CO$_2$ in the configuration of m-HCO$_3^-$ on the surface of the photocatalyst as illustrated in the proposed reaction scheme (Scheme S1, ESI†). The pristine TiO$_2$-$x$, and TW$x$h samples also exhibited higher CO production when compared to the pristine W$_{18}$O$_{49}$. Hence, the synergistic effect of a core–shell structure in TiO$_2$-$x$/W$_{18}$O$_{49}$ and the presence of Ti$^{3+}$ and Ti$^{4+}$ in the pristine TiO$_2$-$x$ and TW6h samples had enhanced the electronic properties of the TW$x$h samples (Fig. S7, ESI†), resulting in an enhancement in the photocatalytic reduction of CO$_2$ under visible light irradiation (Scheme S2, ESI†).

In conclusion, core–shell and double-shelled hollow microspheres of TiO$_2$-$x$/W$_{18}$O$_{49}$ were synthesized with different durations of solvothermal treatment. The TiO$_2$-$x$ extended the light absorption up to 500 nm when compared to commercial titania (P25), whereas W$_{18}$O$_{49}$ further enhanced the absorption to 500–650 nm. TiO$_2$-$x$ and TW6h samples exhibited superior photocatalytic reduction of CO$_2$ compared to P25 and pristine W$_{18}$O$_{49}$. Overall, the microstructure of TiO$_2$-$x$/W$_{18}$O$_{49}$ revealed a positive effect on CO$_2$ photoreduction efficiency.

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Conflicts of interest
There are no conflicts to declare.

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