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New insights into the photocatalytic activity of 3-D core-shell P25@silica nanocomposites: impact of mesoporous coating

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Abstract

In this report, three-dimensional (3-D) network of core-shell TiO₂ (P25) - mesoporous SiO₂ (P25@mSiO₂) nanocomposites were prepared via a controllable surfactant-assisted sol-gel method. The nanocomposites were investigated for photocatalytic reactions of organic dye degradation, water splitting, and CO₂ reduction to understand the roles of the mSiO₂ shell in

these photocatalytic reactions. It was found that the mSiO₂ shell accelerates the photodegradation of organic dye, but dramatically reduces the photocatalytic activity of P25 in water splitting and CO₂ reduction. The roles played by the mSiO₂ shell in the photocatalytic reactions are summarized as: (1) effective prevention of agglomeration of P25 nanoparticles, (2) facilitating the transfer of uncharged photo-generated •OH radicals via the abundant –OH groups on the mesoporous surface, (3) provision of increased reaction sites between •OH radicals and dye molecules by its mesoporous nanostructure and large surface area, and (4) prevention of diffusion of the photo-generated charge carriers (photoelectrons and photoholes) because of its insulating nature.

1. Introduction

With the recent advances in nanotechnology and colloidal chemistry, nano-sized catalysts can now be readily synthesized with relative ease. The small size and very active surface of nano-sized catalyst make them prone to deformation and agglomeration during reactions,¹⁻³ leading to the loss of their catalytic activity. Therefore, maintaining the chemical and physical stability of nano-catalysts has become an important topic for researchers. To address this issue, cheap and environmentally friendly materials such as mesoporous silica (mSiO₂) have been widely trialled as supports or protective coatings to stabilize the nano-catalysts.⁴⁻⁸ Among the mSiO₂-based composites, the core-shell configuration, where the catalyst particles are wrapped inside the mSiO₂ shell, has attracted intense research interest especially in the areas of thermal-catalysis and bio-medical applications.^{7, 9-13} The mSiO₂ coating can effectively prevent particle agglomeration, without blocking the diffusion of gaseous reactants and products. In addition, the large surface area of mSiO₂ can significantly enhance the drug loading.¹⁴⁻¹⁷

Compared to the large number of reports available in thermal-catalysis, only a few studies have been reported on mSiO₂ coatings in photocatalysis. It is generally believed that the mSiO₂ outer layer will inhibit charge transfer and shield the activated surface of photocatalysts because of its insulating nature.¹⁸ Nevertheless, some reports have found that photocatalysts coated with SiO₂ possess enhanced photocatalytic activities, especially in the photodegradation of organic dyes. The contributions of mSiO₂ in enhancing the photocatalytic activity reported in the literature so far can be summarized as follows: they (1) stabilize the photocatalyst nanoparticles within the porous shell;¹⁹⁻²¹ (2) enhance the adsorption capacity of certain organic dyes owing to electrostatic interactions, and thus provide a high-concentration environment around the photocatalyst;²² (3) work as a ‘nanoglue’ or binder of the photocatalysts, providing mechanical reinforcement of the substrate;²³ (4) enhance the adsorption of CO₂ molecules and improve the selectivity of gas products in some gas-phase photocatalytic reactions such as CO₂ photo-reduction;^{18, 24} (5) reduce the size of the metal organic frameworks (MOFs) derived photocatalyst particles by a coating of mSiO₂ on the MOF precursor and thus enhance its photocatalytic performance.²⁵ Although continuous progress has been reported in this area, the influence of the mSiO₂ coating on the transport of photo-generated species from the photo-catalyst surface to the reactants still remains unclear.

Herein, we have prepared mSiO₂ coatings on a type of commercially available TiO₂ nanoparticles (P25). The P25@mSiO₂ core-shell network-structured nanocomposites with controllable silica content were synthesized via a surfactant-assisted sol-gel method. The P25@mSiO₂ nanocomposites were used to investigate the effects of mSiO₂ shell on the following photocatalytic processes: (a) photodegradation of methyl orange (MO), (b) photocatalytic water splitting to generate H₂ and O₂, (c) CO₂ reduction. According to our

experimental results, with the exception of the surface adsorption of dye molecules, the mSiO₂ coating efficiently promotes the photodegradation of dye molecules by facilitating the generation and transport of uncharged hydroxyl radicals ($\bullet$ OH), whereas it reduces the activity of P25 in water splitting and CO₂ reduction to different extents mainly because of its insulating property. A possible mechanism is proposed for the enhanced generation and transport of hydroxyl radicals. Our work has demonstrated the selectivity of mSiO₂ for different photo-generated species, which sheds new light on the ongoing research in utilizing mSiO₂ for photocatalytic reactions.

2. Experiment

(1) Sol-gel coating of mesoporous SiO₂ onto P25 nanoparticles: In a typical procedure, 0.050 g of P25 nanoparticles were added to a mixed solvent of ethanol (20 mL) and DI water (5 mL) with pre-dissolved surfactant of hexadecyltrimethyl ammonium bromide (CTAB) (0.25 g). The P25 suspension was sonicated for 5 minutes, after which 25 to 100 μ L tetraethyl orthosilicate (TEOS) was added to the suspension. The samples prepared using 25, 50, and 100 μ L TEOS are denoted as P25@mSiO₂-25, P25@mSiO₂-50, P25@mSiO₂-100, respectively. The sample prepared from 100 μ L TEOS without surfactant is named as P25@SiO₂-100 (nonporous). After sonication for another 5 minutes, 0.50 mL of ammonium hydroxide solution (28% NH₃ in H₂O) was added into the mixture to catalyze the hydrolysis of TEOS. The reaction was carried out at room temperature under continuous stirring for 12 h. The resulting core-shell P25@mSiO₂ nanocomposites were harvested by centrifugation and washed thoroughly by ethanol before 60 °C oven drying. The P25@mSiO₂ samples were further heat treated at 500 °C with a ramping rate of 1 °C/min for 2 h in air. In addition, nonporous SiO₂ was also coated onto P25 as a control

sample following the same procedure but without the addition of CTAB, and the amount of TEOS was 100 μ L.

(2) Photocatalytic reactions

Photodegradation of methyl orange (MO): In each experiment, 20 mg of the catalyst powder was dispersed into 20 mL aqueous solution of methyl orange (MO, $C_{14}H_{14}N_3SO_3^-Na^+$, 10 mg/L) by sonication for 10 minutes, and then it was stored in the dark for 2 h to achieve adsorption equilibrium. The solution was exposed to UV-visible irradiation from a 300 W xenon lamp (HAL-320, Asahi Spectra Co. Ltd.) for the MO degradation study. The distance between the light source and the surface of the MO solution was 15 cm with 500 rpm magnetic stirring at room temperature. Aliquots were removed from solution and centrifuged for UV-vis spectroscopy (Shimadzu UV-2501) during the course of irradiation to quantify the degradation. Chemical scavengers were also employed to investigate the major contributor of the photocatalysis process.²⁶

Photocatalytic hydrogen evolution: In a typical run, 20 mg of the catalyst powder was suspended in 100 mL of aqueous methanol solution (20 vol %) and stirred in a Pyrex glass vessel with a top quartz window to facilitate vertical illumination.²⁷ The temperature of the reactor was maintained at 25 °C by external water circulation. The reactor was then sealed and repeatedly subjected to vacuum degasification by a rotary pump and purged with argon gas to remove any residual air. Subsequently, the photoreactor was irradiated with a 300 W Xe-Hg lamp (Newport, USA) from the top. The average light intensity at the surface of the solution was measured to be 230 mW/cm². The infrared (IR) component in the radiation was removed by the circulating water filter. The generated H₂ gas was quantitatively analyzed every 1 h by a gas chromatograph (Shimadzu GC-2014; Molecular sieve 5A, TCD detector, Ar carrier gas).

Photocatalytic oxygen evolution: This photocatalytic reaction was conducted in a top window Pyrex cell connected to a closed gas circulation and evacuation system.²⁵ A 300 W Xe lamp (Newport) was applied as the light source. In a typical run, 30 mg of the photocatalyst powder was well dispersed with constant stirring in 100 mL of DI water, in which 0.050 M of silver nitrate (AgNO_3) was added. Before the reaction, the system was evacuated and refilled with argon gas three times to remove any traces of air inside and finally filled with argon to approximately 30 Torr. The temperature of the photo reaction cell was kept at about 20 °C by a cooling water jacket. The generated oxygen gas was analysed using an online gas chromatography (Agilent 6890N, TCD detector, argon as carrier gas, 5 Å molecular sieve column).

Photocatalytic CO_2 reduction: The photocatalytic CO_2 reduction was performed in a 100 mL gastight reactor with a quartz window and two side-sampling ports.²⁸ In a typical process, 20 mg of the photocatalyst was suspended in ethanol and the suspension was dispersed on a $2.5 \times 2.5 \text{ cm}^2$ glass slide. Upon drying, the glass slide was loaded with the photocatalyst which was then put into the gastight reactor. Prior to the irradiation, the reactor was purged with high purity CO_2 for 30 min to remove any residual air and then 0.1 mL ultrapure water was injected into the reactor. A xenon lamp (MAX-302, Asahi Spectra Co. Ltd., Tokyo, Japan) was used as the light source for the photocatalytic reaction. During the reaction, the gas product was analyzed periodically through a gas chromatograph (GC-7890A, Agilent Technologies Inc., Santa Clara, CA, USA) with a TCD detector.

Qualitative and quantitative analysis of photo-generated hydroxyl radicals: The $\text{TiO}_2@\text{mSiO}_2\text{-100}$ powder was dispersed in DI water with the concentration of 1 mg/mL. Since •OH radicals are short-lived species, a spin-trapping agent DMPO (5,5-dimethyl-1-pyrroline N-

oxide) was added to the $\text{TiO}_2@\text{mSiO}_2$ suspension to trap $\bullet\text{OH}$ radicals and convert them to stable nitroxides, $\bullet\text{DMPO-OH}$.²⁹ The suspension was first irradiated under UV-vis light for 30 s and around 250 μL solution was withdrawn into a quartz tube (4 mm Outside Diameter), and tested in an X-band EPR spectrometer (Bruker ELEXSYS E500) for the detection of photo-generated hydroxyl groups.

The semi-quantitative analysis of $\bullet\text{OH}$ radicals was carried out with the use of sodium terephthalate as a fluorescence probe, which forms 2-hydroxyterephthalate (2-HTA) with $\bullet\text{OH}$ radicals.²⁶ The experiment followed the same procedures as the photodegradation of methyl orange (MO), except that the dye solution was replaced by sodium terephthalate (10 mg/L) solution. The photoluminescence measurements were conducted using a fluorescence spectrophotometer (Varian Cary Eclipse) on samples after different radiation times.

(3) Material characterization: Crystallographic and phase analysis were performed on a X-ray powder diffractometer (Shimadzu XRD-6000) with $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). The morphology and structural studies, including high-angle annular dark-field scanning (HAADF-STEM), and elemental mapping were conducted on a transmission electron microscope (TEM, JEOL JEM-2100F) attached with an energy-dispersive X-ray spectroscopy (EDS). The BET specific surface areas of products were obtained by N_2 physisorption at 77 K using an ASAP2000 adsorption apparatus from Micromeritics. The average atomic ratio of Si/Ti of the bulk powder sample was determined via an EDS detector (Oxford instruments) installed on a field-emission scanning electron microscope (FESEM, JEOL JSM-7600F).

3. Results and Discussion

Figure 1 schematically illustrates the synthesis scheme of our $\text{P25}@\text{mSiO}_2$ nanocomposites. TEOS hydrolyzes around the TiO_2 nanoparticles with the assistance of CTAB and forms a 3-D

network of core-shell composite particles with TiO_2 nanoparticles at the core. CTAB micelles also templates the mesopores in the SiO_2 shell, but gets removed later during heat treatment. The phase composition of the products was characterized by powder XRD and their diffraction data is illustrated in Figure 2a which shows a mixture of anatase and rutile phases of TiO_2 . In addition, the weight ratios of TiO_2 and SiO_2 in the bulk powders were obtained by EDS and are given in Figure S1 and Table S1. There are no detectable impurity phases in the P25@mSiO_2 samples as compared with bare P25 suggesting that the heat treatment of the $\text{TiO}_2@m\text{SiO}_2$ nanocomposites did not change the TiO_2 phase composition.¹⁸ Since XRD cannot detect amorphous phases, FTIR investigations were done on the samples as this technique detects chemical bonds irrespective of their crystallinity. FTIR spectrum for a P25@mSiO_2 sample is compared with its P25 counterpart in Figure 2b. Two bands located at 1250 cm^{-1} and 1095 cm^{-1} in the spectrum of P25@mSiO_2 -100 (red line) belong to the asymmetric vibration of the Si–O–Si mode. The peak located at 930 cm^{-1} belongs to the as the characteristic stretching vibration of Ti–O–Si bonds. The broad peak at 3450 cm^{-1} is the stretching mode of water and hydroxyl groups.^{18, 30} The UV-Vis absorption spectra of all the samples show similar behavior in Figure 2c which suggests that the SiO_2 coating does not significantly affect the light absorption properties of the P25 nanoparticles. Further, photoluminescence measurement was used to assess the charge carrier recombination behavior as done commonly done by other investigators.^{18, 31-32} The PL intensities of all samples are similar in Figure 2d, indicating that the introduction of silica does not affect the recombination rate of photo-excited electron–hole pairs.

Figure 3 shows the TEM micrographs and EDS elemental mapping of P25@mSiO_2 -100. TEM micrographs of P25@mSiO_2 -25, P25@mSiO_2 -50 and P25@SiO_2 -100 (nonporous) are given in Figure S2. The overall structure of P25@mSiO_2 -100 displays a 3-D network of core-shell

composite particles. The TiO_2 nanoparticles are individually contained within the compartments formed by mesoporous silica shells with an estimated shell thickness of 10 nm. As evident in Figures S2(a)-(c), the thickness of the SiO_2 shell increases with increase of TEOS content. Figure S2(d) displays the morphology of P25@SiO_2 (nonporous) sample, which was prepared as a control sample to study the effect of the mesoporosity. The HAADF-STEM image in Figure 3b reveals the 3-D network structure with clear contrast between the mSiO_2 and TiO_2 components (the heavier element Ti has a brighter contrast than the lighter element Si). The EDS elemental mappings for Ti, Si and Si + Ti over the same location with the HAADF-STEM image in Figures 3c-e confirm that each the thickness of silica shell around TiO_2 cores is nearly uniform. Hence, it is clear that the 3-D core-shell network structure of P25@mSiO_2 has effectively prevented P25 nanoparticles from agglomerating. This could help with the recycling of catalysts because of the enlarged size of the nanocomposite networks.

The BET surface area shown in Figure S3 and Table S2 for bare P25, P25@mSiO_2 -25, P25@mSiO_2 -50, P25@mSiO_2 -100, and P25@SiO_2 -100 (nonporous) are 59.6, 79.9, 135.5, 415.7, and $36.1 \text{ m}^2/\text{g}$, respectively. The pore size for P25 and P25@mSiO_2 -100 peaks at 5.9 nm and 2.4 nm, respectively (Figure S4). The zeta-potential was measured for all the P25@mSiO_2 samples and is listed in Table S3. It can be seen that SiO_2 shifts the surface charge from positive for bare P25 to negative for the P25@mSiO_2 nanocomposites possibly because silica is slightly more acidic than TiO_2 and the surface Si-OH groups have lower pKa values.³³⁻³⁴ In the past, positively charged dyes (such as MB and R-6G) were often selected to demonstrate the photocatalytic activity of TiO_2 - SiO_2 composites where the silica component often acts as an efficient adsorbent of the dyes via electrostatic attractive force.^{19-20, 22-23, 35} The adsorption process for MB or R-6G dyes is even more prominent on mesoporous SiO_2 due to its large surface area. Therefore, to

minimize the adsorption effect to the negatively charged particle surface, we chose the negatively charged dye molecules, methyl orange (MO).³⁶

The photocatalytic activities of bare P25, P25@mSiO₂ (with different SiO₂ content), and P25@SiO₂-100 (nonporous) nanocomposites in photocatalytic reactions were evaluated to understand the role of mesoporous SiO₂ coating in different photocatalytic reactions. The photodegradation of MO carried out under the UV-vis irradiation is given in Figure 4a. From the first two hours in the dark, the P25@mSiO₂ samples as well as mSiO₂ powder show negligible adsorption of MO in comparison with bare P25, which validates the selection of MO as the dye for this investigation based on the zeta-potential results. Therefore, it ensures that the concentration drop of MO will be entirely from photocatalytic reactions with negligible contribution from adsorption. The MO photo-degradation for bare P25 was also conducted with 420 nm filter, as shown in Supporting Information Figure S5. We can see that with the 420 nm filter, the MO only degraded a little in comparison to the photo-degradation without filter. This has eliminated the possibility of self-degradation of dye molecules. All the P25@mSiO₂ samples demonstrated accelerated rates of MO photodegradation compared with bare P25, while the nonporous P25@SiO₂-100 showed dramatically reduced reaction rates. However, the P25@SiO₂-200 demonstrated a dramatic drop of the reaction rate compared to the sample of TiO₂@mSiO₂-100. This could be due to the much-increased composition of inert SiO₂, in the same weight of catalyst powder. Therefore, the enhancement of photocatalytic activity of P25 by mSiO₂ is only within a certain ratio of these two components. In addition, the pure mSiO₂ powder did not show any activity toward MO degradation. Interestingly, as shown in Figure S6, the physical mixture of mesoporous SiO₂ powder with P25 powder following the weight ratio of P25@mSiO₂-100 also demonstrated a noticeable increment of photocatalytic activity compared

to bare P25. The physical mixtures of P25 and mSiO₂ has also confirmed that the Ti-O-Si bonding which forms during heat treatment, does not play a major role in MO photo-degradation. At the thought that mesoporous SiO₂ can increase the acidity of the solution, photo-degradation of MO with also carried out at pH value adjusted to 2. In Figure S6, it is clearly shown that the acidity remarkable decreased the photocatalytic activity of bare P25. Hereby, we can exclude the factors of adsorption, acidity and Ti-O-Si bonding in our study from the drop of MO concentration.

We further used bare P25 and P25@mSiO₂-100 samples for photocatalytic water splitting in solid-liquid phase and CO₂ photoreduction in solid-gas phase reactions. The water splitting results are shown in Figures 4b-c. Surprisingly, in contrast to the trend exhibited in MO photodegradation, the P25@mSiO₂-100 sample shows almost negligible H₂ production (only 0.5% of that produced by bare P25 in the first 6 hours). In order to confirm our findings, we tested the H₂ evolution using P25@mSiO₂-25, P25@mSiO₂-50, and P25@SiO₂-100 (nonporous) samples, and they all generated little or negligible amounts of H₂ as shown in Figure S7. The reproducibility of the minute amount of H₂ generated by all the mSiO₂ coated samples implies that H₂O molecules are prevented from contacting the photo-generated charge carriers, even though the mSiO₂ shell is thin and contains numerous mesopores. In addition, when the results of P25@mSiO₂ samples are plotted in expanded y-scale as in Figure S7b, there is not much difference between mesoporous and nonporous SiO₂ coatings with respect to H₂ evolution. This is possible if the mSiO₂ coating almost completely passivates the surface of P25 nanoparticles for H⁺ reduction reaction, despite the presence of the numerous mesopores. Further, the sample P25@mSiO₂-100 showed very little oxygen evolution activity when compared to bare P25 as evident in Figure 4c. The reasons for the subdued activity in H₂ evolution could be attributed to

the following reasons. Firstly, the outward diffusion of photo-generated charge carriers from P25 surface could be mostly blocked by mSiO₂ due to its insulating property. Secondly, the mesopores on the shell may cause a capillary effect³⁷ that might limit the inward penetration of water molecules to the surface of P25 nanoparticles. Therefore, with the diffusion paths of the reactants being blocked in both directions by the mSiO₂ shell, few H₂O molecules could be split to produce hydrogen or oxygen. These results show that mSiO₂ coatings are damaging for photocatalytic water splitting. Figure 4d illustrates the scenario of CO₂ photo-reduction by bare P25 and P25@mSiO₂-100 in solid-gas reactions. The CH₄ and CO production by bare P25 is almost twice that by the P25@mSiO₂-100 nanocomposite indicating that the mSiO₂ shell has an adverse effect on the reaction. Nevertheless, this adverse effect on P25 is not as marked as in the water splitting reactions. This might be because CO₂, unlike H₂O, is a non-polar gas molecule, therefore the mSiO₂ may allow non-polar gas molecules to permeate through the pores. Yet, the effect of the mSiO₂ shell on the performance of P25 nanoparticles in CO₂ photoreduction is still negative.

In order to identify the major contributor to the MO photodegradation processes, the three representative photo-generated active species of •OOH/•O₂⁻, holes (h⁺) and hydroxyl radicals (•OH) were examined by testing the photocatalytic performance of P25@mSiO₂-100 with chemical scavengers for each active species (Figure 5a). The introduction of 1,4-benzoquinone (1,4-BQ, •OOH/•O₂⁻ scavenger) had little influence on the photodegradation of MO, which indicates that the photo-generated electrons and their downstream species do not contribute to the dye degradation. This could be due to the blocked charge carrier diffusion by the insulating mSiO₂ shell. The addition of scavengers for h⁺ and the hole derived •OH, however, showed negative effects on the photo-degradation rate of P25@mSiO₂, with •OH scavengers displaying

the greatest influence on the photocatalytic performance. Therefore, $\bullet\text{OH}$ radicals are believed to be the major contributor for the degradation of MO when using the $\text{P25@mSiO}_2\text{-100}$ as the photocatalyst. Results of qualitative and semi-quantitative analyses of detecting the $\bullet\text{OH}$ radicals are shown in Figures 5b-c. The EPR spectrum in Figure 5b was taken from a suspension of $\text{P25@mSiO}_2\text{-100}$ after UV-vis irradiation, which has a characteristic 1:2:2:1 hyperfine splitting pattern of $\bullet\text{DMPO-OH}$, confirming the presence of $\bullet\text{OH}$ radicals. A semi-quantitative analysis of the $\bullet\text{OH}$ radicals shown in Figure 5c was conducted by measuring the fluorescence intensity of the 2-hydroxyterephthalic (2-HTA) acid at 420 nm (also see Supporting Information Figure S8 for original fluorescence spectrum), which is the product of sodium terephthalate after reaction with $\bullet\text{OH}$ radicals. The $\text{P25@mSiO}_2\text{-100}$ shows a higher fluorescence intensity of 2-HTA as compared to bare P25, indicating that the introduction of mSiO_2 increases the yield of $\bullet\text{OH}$ radicals. Since P25 is the sole photocatalyst in the nanocomposites, all the $\bullet\text{OH}$ radicals originate from the holes generated on the surface of P25. The higher yield of $\bullet\text{OH}$ radicals in the presence of mSiO_2 shells can be attributed to the reduced agglomeration of P25 nanoparticles, which offers increased exposed surface area of P25. The fluorescence intensity of 2-HTA for bare P25 declines with increase of irradiation, which may be due to certain competitive reaction(s) stopping the 2-HTA from further increment. The $\bullet\text{OH}$ radicals generated from $\text{P25@mSiO}_2\text{-100}$ demonstrate a relatively stable concentration plateau, indicating that the $\bullet\text{OH}$ radicals remain at a higher concentration for a longer time when mSiO_2 shell is present. This could be one of the possible reasons for the enhanced MO photodegradation performance by the P25@mSiO_2 samples.

Since, the inward diffusion of H_2O molecules appears to be hindered by the mSiO_2 shell as evidenced by the water splitting results, we may expect the dye (MO) molecules also to be

blocked due to their much larger molecular size than H_2O . Therefore, the enhanced photo-degradation of MO in Figure 4a can only be attributed to the enhanced outward diffusion of photo-generated active species, which are mainly the uncharged $\bullet\text{OH}$ radicals. However, the direct contact between H_2O molecules and P25 nanoparticles are limited as explained previously, the $\bullet\text{OH}$ radicals should be generated and delivered via some other path(s). Nosaka *et al.* proposed the formation of $\text{Ti-O}\bullet$ on anatase TiO_2 and Ti-peroxo (Ti-OO-Ti) on rutile TiO_2 by photo-generated holes, which can oxidize H_2O molecules to generate $\bullet\text{OH}$ radicals.³⁸ Inspired by their proposal, we believe that the abundant hydroxyl groups usually bonded on the surface of mesoporous SiO_2 undergoes similar a oxidation processes to form intermediate radicals,³⁹ which further form the $\bullet\text{OH}$ radicals from H_2O near the shell surface and thus serve as the ‘relay batons’ to deliver the ‘oxidative power’ of holes to the MO molecules in solution. Especially, just by simple physical mixing of bare P25 and mesoporous SiO_2 powders, the photocatalytic activity increased compared to P25 if the m SiO_2 has sufficient contacts with P25 surface. This has also confirmed that the Ti-O-Si bonding formed during heat treatment does not play a major role here. The mechanism of photodegradation of MO by P25@m SiO_2 is schematically proposed in Figure 6. There are two possible routes for the photodegradation. First, a minor portion of photo-induced holes from exposed TiO_2 surface directly react with adsorbed H_2O molecules to form $\bullet\text{OH}$ radicals, and degrade the dyes within the silica shell or in the surrounding solution (process 1). Secondly, the majority of the photo-induced holes react with the numerous hydroxyl groups on the m SiO_2 surface to form intermediate radicals like $\equiv\text{SiO}\bullet$ (Eq. 1),³⁸ which continue to react with H_2O to release $\bullet\text{OH}$ radicals (process 2, Eq. 2). In summary, m SiO_2 not only acts as catalyst protectors to stabilize the catalyst nanoparticles from agglomeration, but also serves as effective

‘relay baton’ of the uncharged $\bullet\text{OH}$ radicals due to its abundant presence of surface $-\text{OH}$ groups, resulting in higher yields of $\bullet\text{OH}$ and enhanced photodegradation activities.

Conclusion

3-D network of core-shell P25@mSiO_2 nanocomposites have been successfully prepared by a simple surfactant assisted sol-gel method. The P25@mSiO_2 nanocomposites and physical mixture of P25 and mSiO_2 have shown enhanced photodegradation performance on methyl orange (MO) but their performances in photocatalytic water splitting and CO_2 reduction were adversely affected compared with bare P25, despite the provision of large catalyst surface area by avoiding agglomeration of P25. In the photodegradation of MO, hydroxyl radicals ($\bullet\text{OH}$) have been found to play a major role to enhance the performance of P25@mSiO_2 compared to bare P25, as shown in photocatalytic performance tests with chemical scavengers for photo-generated species. Charged photoactive species are mostly blocked by the shell due to the insulating properties of SiO_2 which is probably the reason for the adverse effects on water splitting and CO_2 reduction. Furthermore, P25@mSiO_2 core-shell nanocomposites can increase the production of $\bullet\text{OH}$ radicals, and maintain the higher concentrations for a longer time than with bare P25 nanoparticles. A possible mechanism for the $\bullet\text{OH}$ radical generation and transport in the P25@mSiO_2 nanocomposite has been proposed, in which the mSiO_2 shell produces certain radical intermediates using the photo-generated holes from P25, which then turn into $\bullet\text{OH}$ radicals after reaction with H_2O at the surface of the shell. Thus, the mSiO_2 shell not only serves to protect the P25 nanoparticles from agglomeration, but also acts as a fast ‘relay batons’ to deliver the ‘oxidative power’ of the photocatalyst in the photodegradation of the organic dye.

Associated Content**Supporting Information**

EDS analysis of the content of TiO_2 and SiO_2 in P25@mSiO_2 samples. TEM images of P25@mSiO_2 with 25 to 100 μL TEOS amount prepared with and without CTAB. BET analysis of the specific surface area of all the samples. Surface charge (zeta-potential) of all the samples. Photocatalytic H_2 evolution by all the samples. Fluorescence spectra of 2-HTA concentration change by the bare P25 and P25@mSiO_2 -100 samples, recorded every 5 min. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all the authors. The authors declare no competing financial interest.

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Legends

Figure 1 Schematic illustration of the preparation process of the 3-D P25@mSiO₂ network.

Figure 2 (a) XRD patterns and (b) FTIR spectra of samples. (c) UV-vis diffuse reflectance spectra and (d) PL spectra of P25, P25@mSiO₂ (with different silica content), and P25@SiO₂ (nonporous) samples.

Figure 3 (a) TEM image, and (b) HAADF-STEM images of the P25@mSiO₂-100 and corresponding compositional maps for (c) Ti; (d) Si; (e) Si and Ti overlaid as obtained by EDS.

Figure 4 (a) Photocatalytic degradation of MO using bare P25, P25@mSiO₂ (with different SiO₂ content), and P25@SiO₂-100 (nonporous) as the photocatalyst under the UV-vis irradiation. (b) Photocatalytic hydrogen evolution, (c) oxygen evolution, and (d) CO₂ photoreduction by bare P25 and P25@mSiO₂-100.

Figure 5 (a) Photocatalytic degradation of MO using P25@mSiO₂-100 without scavengers (black), and with the scavengers of h⁺ (blue), •OH (red), and •O₂⁻ / •OOH (green). (b) EPR spectra showing the hyperfine splitting pattern of •DMPO-OH to confirm the presence of •OH radicals generated by P25@mSiO₂-100, (c) Fluorescence intensity at 420 nm arising from the 2-hydroxyterephthalic acid against the light illumination time, as a probe for the semi-quantitative analysis of hydroxyl radicals.

Figure 6 Proposed mechanisms of $\bullet\text{OH}$ generation in $\text{TiO}_2@\text{mSiO}_2$.