Supporting Information

Fabrication of Heterogeneous Exposed Core/Shell Catalyst Arrays Using the Space Specificity of an Embodied Micelle and Their Application to a High Performance Photocatalyst

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Fabrication Method: The diblock copolymer polystyrene-*block*-poly (4-vinyl-pyridine) (PS-b-P4VP) was purchased from Polymer Source Inc. The average molecular weights of the PS and P4VP blocks were 47600 and 20600 g/mol, respectively. Iron chloride, chloroplatinic acid hexahydrate, tetraethyl orthosilicate (TEOS), and titanium (IV) isopropoxide (TTIP) were purchased from Sigma Aldrich Chemical Co. The microwave plasma-enhanced chemical vapor deposition (MPECVD) system was purchased from Woosin Cryovac Ltd.

To obtain a monolayer film of diblock copolymer micelles, a micellar solution was prepared by dissolving monodisperse PS-b-P4VP in toluene (HPLC grade, 99.9%) to yield a 0.5 wt% solution. A monolayer film of the resulting hexagonal micelles was coated on the silicon substrate using a spin-coater at 2000 rpm for 60 s. The substrate was immersed in methanol for 10 h to produce the embodied micelles. Then, the solution-immersion method was conducted for 10 min using a 0.1M solution of the metal precursor in methanol. Next, the oxide material was deposited by vaporization process. The substrate was put in a sealed chamber with two vials glass, one contained 5 ml of the oxide precursor and the other contained 5 ml of deionized water, at 60 ℃ for 5 h. The substrate was finally treated with hydrogen plasma (800 W; approximately 21 Torr) at 180 ℃ for 75 s to remove the embodied micelles and to reduce the metal ions.

Evaluation of Photocatalytic Ability: At first, we prepared the heterogeneous exposed core/shell catalysts arrays on silicon substrate, which was 1cm x 1cm size. And then, photocatalytic hydrogen generation was performed in a 90 mL cylindrical quartz reactor. The heterogeneous catalyst sample (1cm x 1cm silicon wafer) was put in

5 the cylindrical quartz reactor. And then, the reactor was filled with 75 mL of water solution of 25 vol% methanol. The reactor was sealed with rubber septum and purged with argon (99.9%) for 30 min, and then irradiated with a 300 W xenon lamp equipped with cooling system and an IR cutting filter and the light intensity of 500 mW/cm^2. 200 μl of the photogenerated hydrogen was periodically captured from the reactor using a gas-tight syringe

10 with a volume reproducible adapter. The reaction product was analyzed using a gas chromatograph (7890A, Agilent Technologies) and a thermal conductivity detector (TCD) equipped with a packed column, 5Å molecular sieves, while using argon as the carrier gas. The concentration of the product gas was calculated from calibration curves created using a standard mixture gas and the retention time was determined. The cyclic reaction was

15 conducted in same condition, explained above. Each reaction was conducted for 3 h and repeated three times. After each photocatalytic reacation, the cylindrical quarts reactor was re-purged by argon (99.9%) for 30 min.

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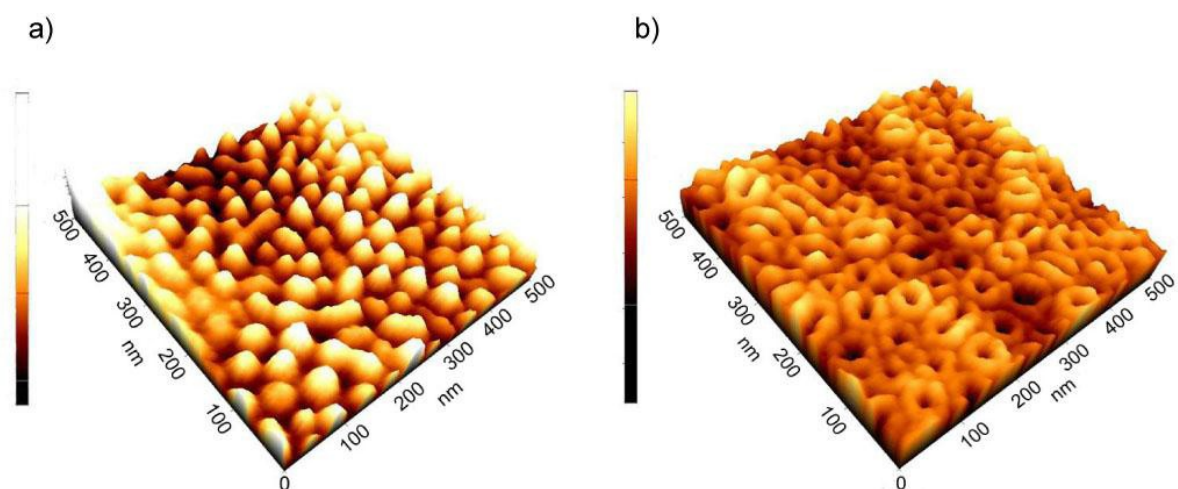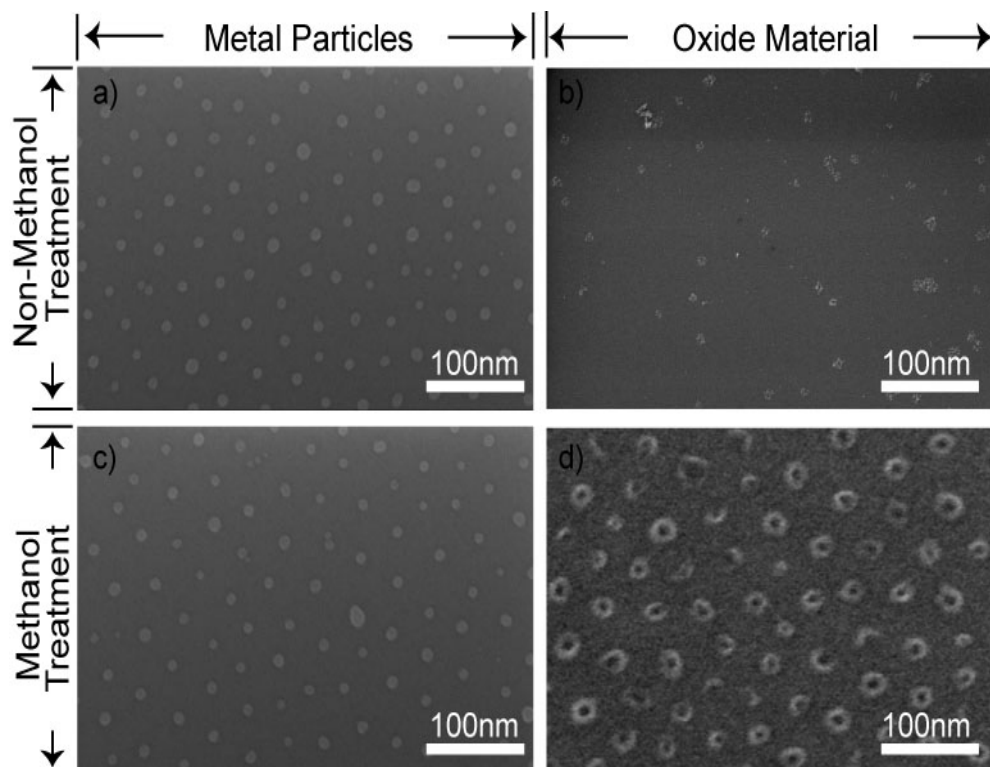*The Formation Mechanism of the Heterogeneous Exposed core/shell catalysts:*

a)

b)

Fig. S1 AFM images showing the mechanism of formation of the embodied micelles. a) A layer of untreated micelles. b) A layer of embodied micelles after the chemical treatment with methanol for 10 h.

Fig. S2 SEM images for proof of steric hindrance. a) Metal particles without the methanol treatment, b) Oxide material without the methanol treatment, c) Metal particles with methanol treatment, d) Oxide material with the methanol treatment.
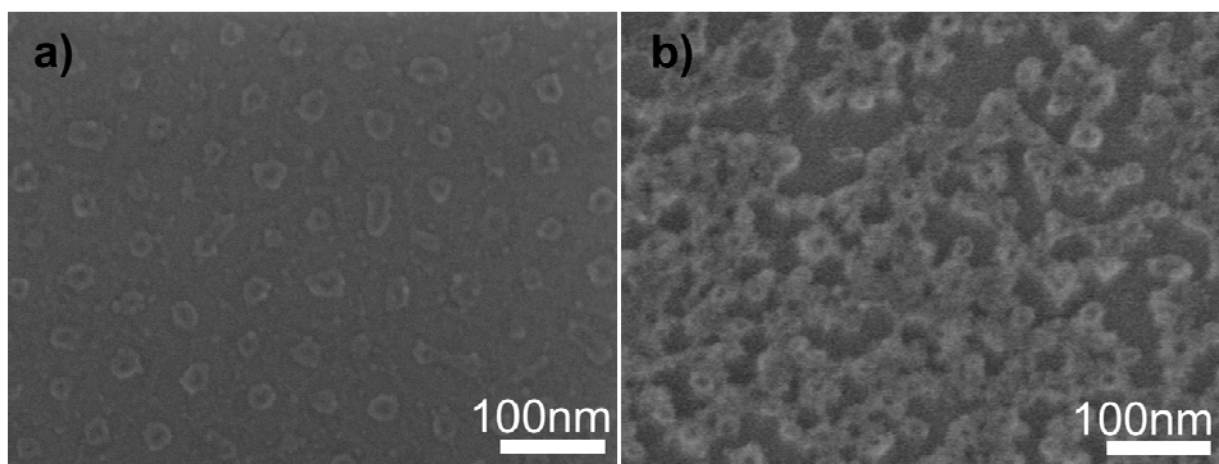
Fig. S3 SEM images for the effect of time variation of the oxide vaporization process (Fe-SiO$_2$). a) an oxide deposition for 2h, b) an oxide deposition for 10h. The metal concentration was fixed but the time of oxide deposition was changed.
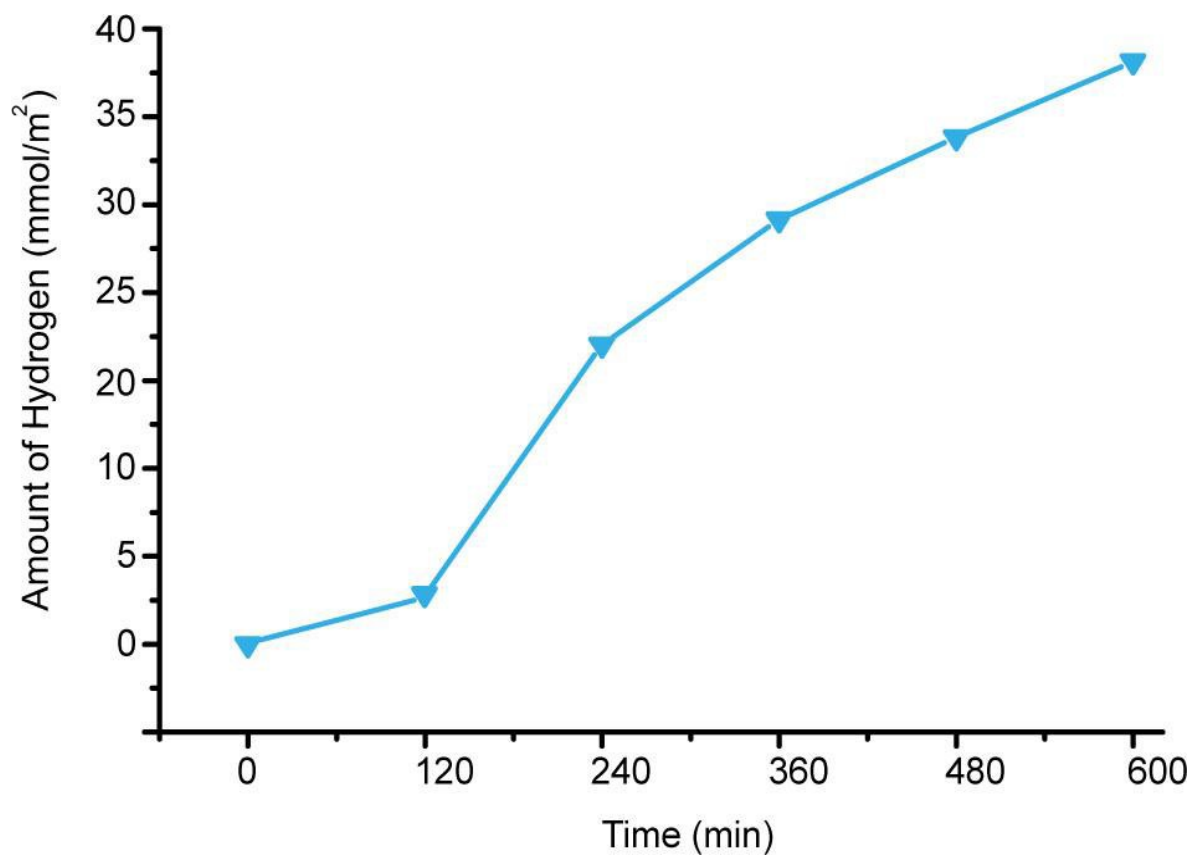
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Fig. S4 Amount of hydrogen generated over a period of 10 h.

Equation S1. Calculation of the apparant quantum yield

$$\text{Quantum Yield (\%)} = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$$

$$= \frac{2 \times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}} \times 100$$

1   The apparent quantum yield for hydrogen generation using the heterogeneous Pt-TiO$_2$

2   catalyst in our hydrogen generation system was determined to be 1.1%. The apparent quantum

3   yield was higher than other powder types Pt-TiO$_2$.

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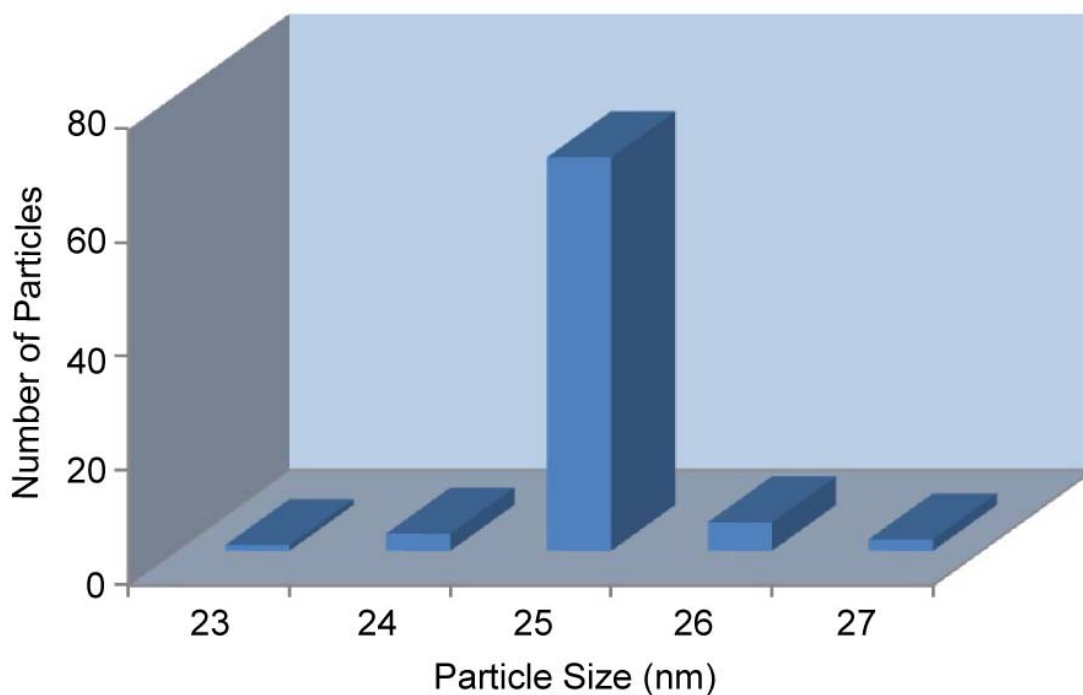
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6   **Fig. S5** Statistical size distribution of heterogeneous exposed core/shell catalysts which was

7   obtained for 80 heterogeneous exposed core/shell catalysts from an analysis of SEM images.