Supporting Information

Hollow Au@TiO$_2$ Porous Electrospun Nanofibers for Catalytic Applications

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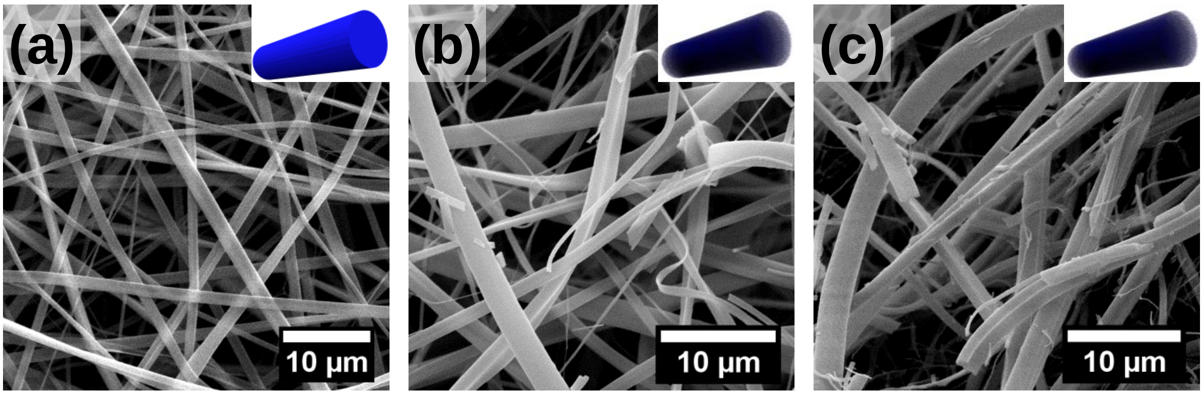

Fig. S1. (a) TIP+PVP nanofibers; (b) anatase titania nanofibers (calcined at 600°C), **(c)** Rutile titania nanofibers (calcined at 1000°C) [insets: corresponding schematic of the morphology of nanofibers], electrospinning and pyrolysis conditions are described in **table S2**.

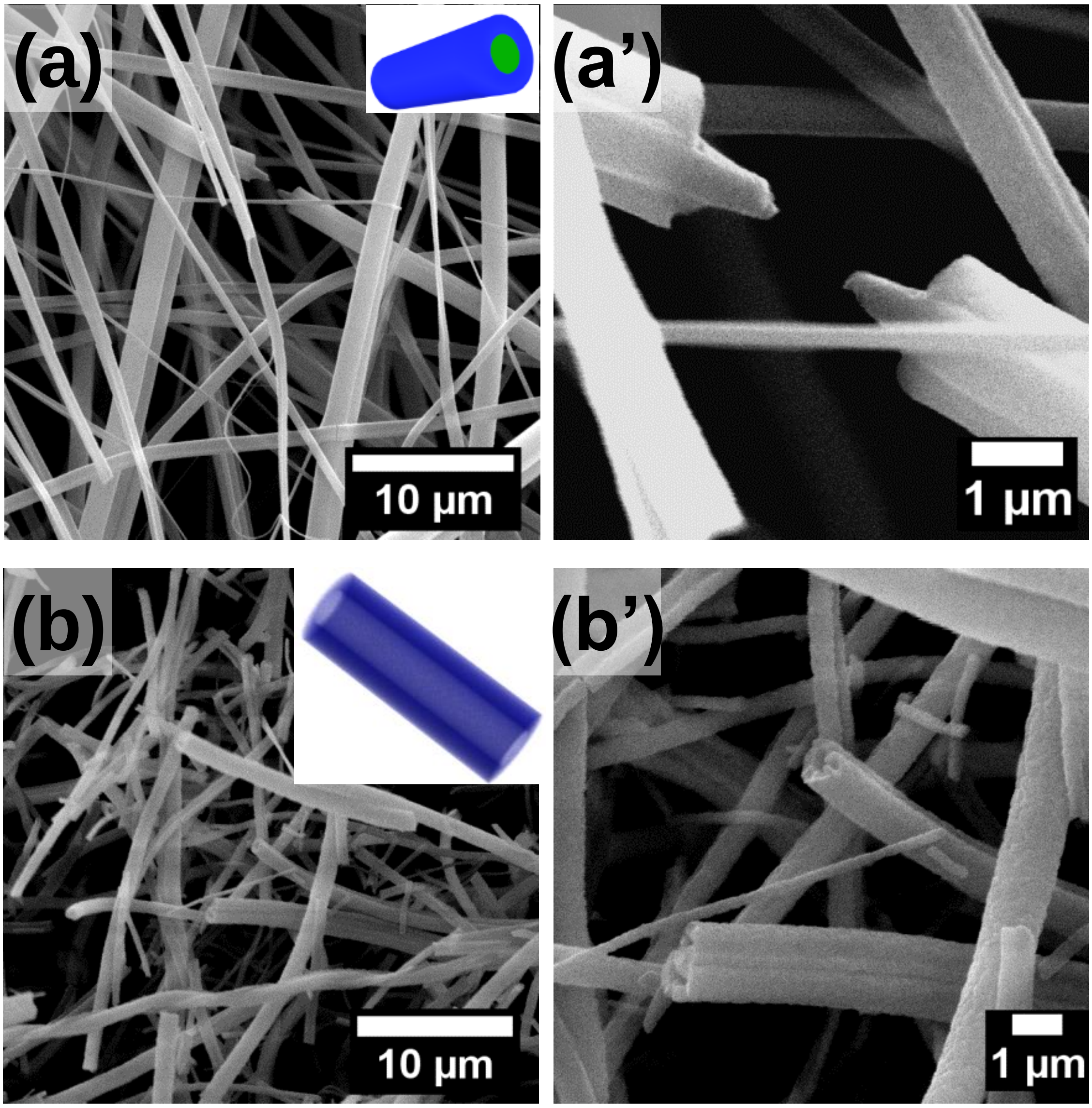

Fig. S2. SEM images of PVP/(TIP+PVP) core-shell Nanofibers **a), a')** before calcination **b), b')** after calcination (Hollow Titania Nanofibers) [insets: corresponding schematic of the morphology of nanofibers] electrospinning and pyrolysis conditions are described in **table S2**.

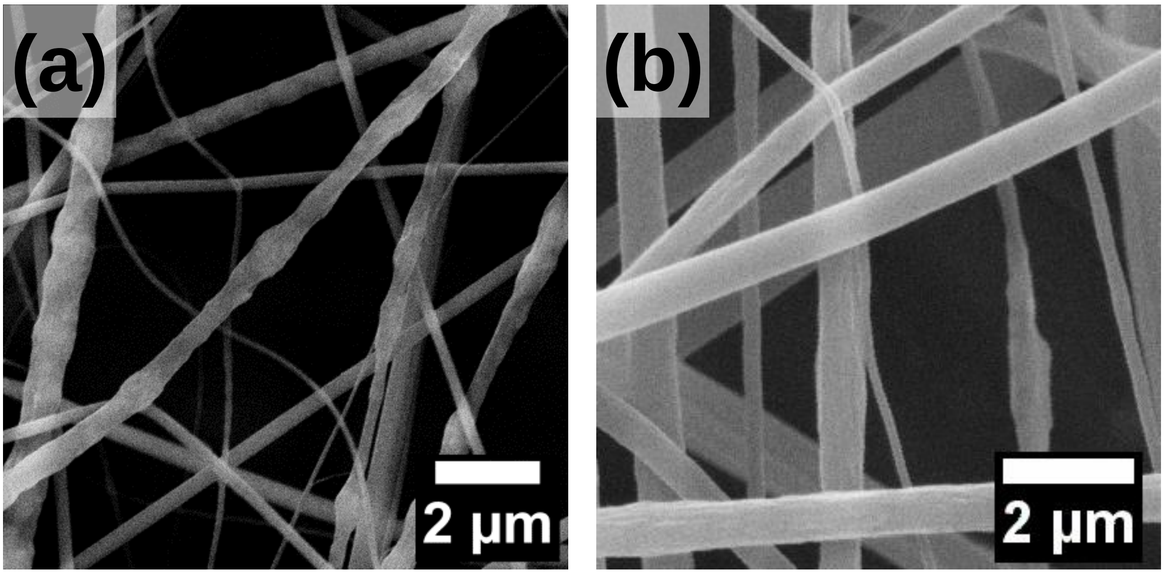

Fig. S3. SEM images of (AuNP+P4VP)/ (TIP/PVP) Nanofibers electrospun at **a)** 1.7 mL h^{-1}, 6 mL h^{-1}, 25 kV, 20 cm and **b)** 1.7 mL h^{-1}, 1 mL h^{-1}, 30 kV, 20 cm core flow rate, shell flow rates, voltage and distance between tip and collector.

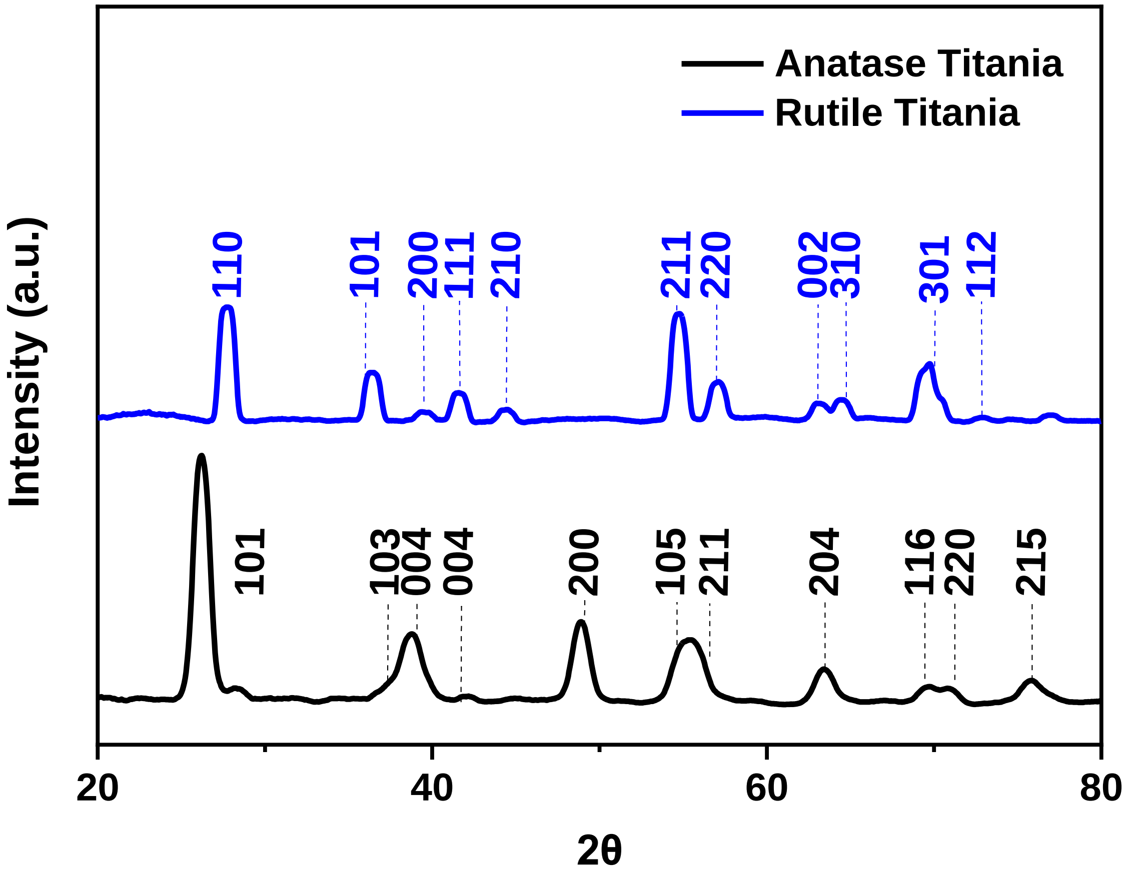

Fig. S4. X-ray diffraction patterns of TiO_2 nanofibers obtained after heat treatment at 600° C (in Black) and 1000° C (in Blue) showing the peaks corresponding to the anatase and rutile phases of titania in calcined titania nanofibers. SEM images of nanofibers are shown in **Figure S1b and S1c** respectively.

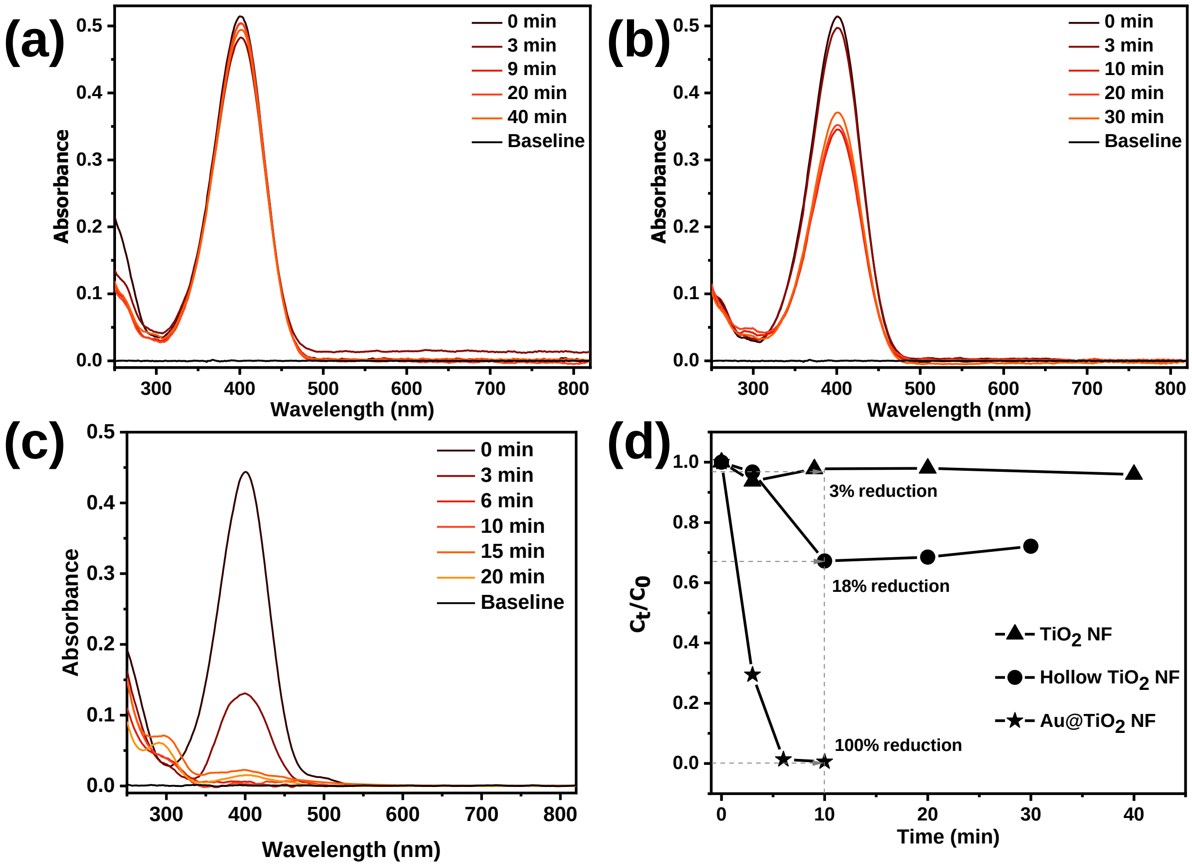

Fig. S5. Successive UV-Vis spectra taken during borohydride reduction of 4NP after addition of **(a)** TiO_2 **(b)** hollow TiO_2 and **(c)** Au@TiO_2 nanofiber catalysts and 4-NP. Experiment was carried out with initial concentrations $[4NP]_0 = 0.027$ mmol L^{-1} and $[NaBH4]_0 = 0.081$ mol L^{-1} **(b)** Conversion plot of ($A_t/A_0 \sim C_t/C_0$) versus time at 0.545 mg mL^{-1} concentrations of nanofiber catalyst.

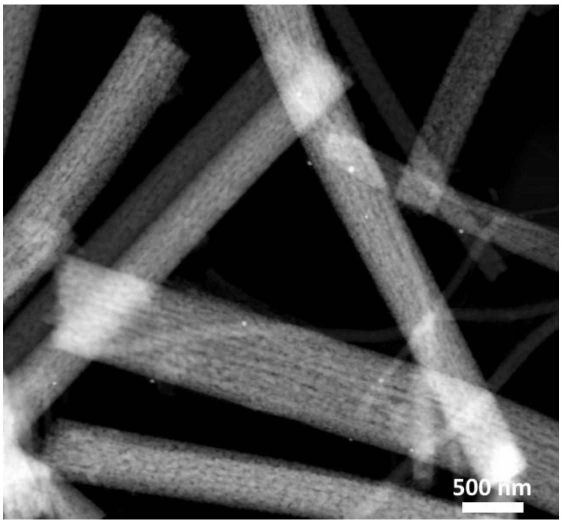

Figure S6. HAADF-STEM micrographs of Au@TiO_2 nanofibers after catalytic reaction. The image clearly shows that the structural integrity of nanofibers were maintained. The AuNPS could also be clearly seen in the nanofibers.

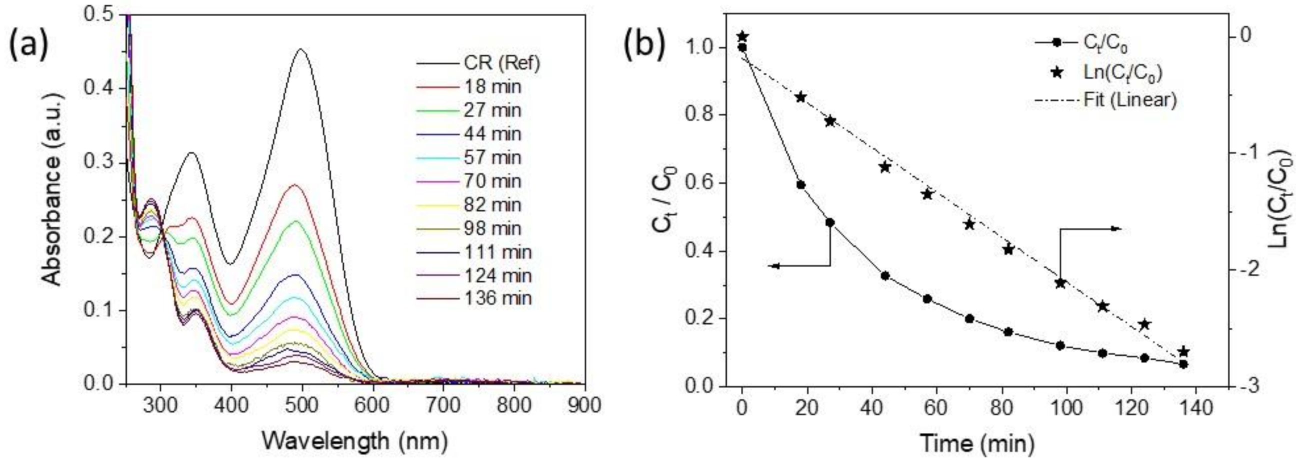

Fig. S7 (a) Successive UV-Vis spectra were taken during borohydride reduction of Congo red (CR) dye after the addition of Au@TiO_2 catalyst. Experiment was carried out with initial concentrations $[CR]_0 = 0.027$ mmol L^{-1} and $[NaBH4]_0 = 0.081$ mol L^{-1} **(b)** Conversion plot of ($A_t/A_0 \sim C_t/C_0$) versus time (circles), and Ln(C_t/C_0) ~ ln(A_t/A_0) versus time (stars) at 0.0205 mg mL^{-1} concentrations of Au@TiO_2 catalyst.

Au@TiO_2 nanofibers were also tested as a catalyst for catalytic reduction of Congo red dye, which is one of the water pollutants. Figure S7a shows the time-resolved changes in the UV-Vis spectra during catalytic reduction of Conge red in the presence of Au@TiO2 hollow nanofibers, whereas Figure S7b represents conversion plot, C_t/C_0, versus time, as well as ln(C_t/C_0) plot and its linear fit, determined form the changes of absorbance intensity of Conge red peak at 488 nm. As can be seen, in the presence of excess of sodium borohydride the catalytic reaction follows first order kinetics, with the apparent and normalized rate constants $K_{app} = 0.019$ min^{-1}, $K_m = 1.95 \cdot 10^5$ L min^{-1} mol^{-1}, respectively.

Table S1. Electrospinning parameters used for different nanofiber

	Samples		Flow rate	Vol.	Tip to collector Distance	Calcination condition
	Before Calcination	**After Calcination**	**mL/h**	**kV**	**cm**	**(Ramp rate: 5°C/min)**
1	TIP+PVP NF	TiO_2 NF	6	15	12	600°C, 4h

			Core	Shell			
2	PVP/(TIP+PVP) NF	Hollow TiO_2 NF	6	6	25	20	300°C, 30 min + 600°C, 4 h
3	(AuNP+P4VP)/(TIP+PVP) NF	Au@TiO2 NF	1.7	3	30	20	300°C, 30 min + 600°C, 4 h

Calculation of estimated weight fraction of Au in electrospun Au@TiO_2 nanofibers:

If FR_{core} is the flow rate of core-forming solution in mL h^{-1} and $[Au^0]_{core}$ is the concentration of gold in core-forming solution, then feeded amount of gold per hour in the core during electrospinning can be calculated as:

$$m(Au^0) = FR_{core} \times [Au^0]_{core}$$

$$m(Au^0) = \text{Flow Rate}_{core} \times \frac{\text{gold recieved from synthesis(mg)}}{\text{total volume of core forming solution (mL)}}$$

$$m(Au^0) = 1.7 \text{mL h}^{-1} \times \frac{0.985 \text{ mg}}{5 \text{ mL}} = 3.349 \times 10^{-4} \text{g h}^{-1}$$

Similiarly the amount of TiO_2 which will be present after pyrolysis of the composite nanofiber can be calculated as follows:

$$m(TiO_2) = FR_{Shell} \times [TIP]_{shell} \times \gamma$$

Where FR_{shell} is the flow rate applied for shell formation during electrospinning, $[TIP]_{shell}$ is the concentration of titanium (IV) isopropoxide in shell-forming solution and γ is the yield of TiO_2 from TIP. The $[TIP]_{shell}$ can be calculated as follows:

$$[TIP]_{shell} = \frac{V_{TIP} \times d_{TIP}}{V_{Total}} = \frac{3 \text{ mL} \times 0.96 \text{ g mL}^{-1}}{9 \text{ mL}} = 0.32 \text{ g mL}^{-1}$$

where V_{TIP}, V_{Total} and d_{TIP} are the volume TIP, total volume of shell forming solution and density of TIP respectively. The effect of PVP to the volume is neglected.

$$\gamma = \frac{M.W._{TiO_2}}{M.W._{TIP}} = \frac{79.866 \text{ g mol}^{-1}}{284.219 \text{ g mol}^{-1}} = 0.281$$

$$m(TiO_2) = 3 \text{ mL h}^{-1} \times 0.32 \text{ g mL}^{-1} \times 0.281 = 0.2697 \text{ g h}^{-1}$$

Total amount of remaining solid after pyrolysis:

$$m(Cat) = m(Au^0) + m(TiO_2)$$

$$m(Cat) = 0.0003349 + 0.2697 = 0.270035 \text{ g h}^{-1}$$

Estimated weight fraction of gold which should be present in the catalyst:

$$\omega_{Au^0/cat} = \frac{m(Au^0)}{m(Cat)} \times 100 = \frac{m(Au^0)}{m(Au^0) + m(TiO_2)} \times 100$$

$$\omega_{Au^0/cat} = \frac{3.349 \times 10^{-4}}{2.700 \times 10^{-1}} \times 100 = 0.124 \text{ wt. \%}$$

Determination of the number of moles normalized rate constant (K_m) and surface area normalized rate constant (K_s) for Au@TiO_2 catalyst:

The weight fraction of gold in Au@TiO_2 catalyst was determined using ICP-OES:

$$\omega_{Au^0/cat} = 0.094\%$$

The content of gold (Au^0) in moles per unit mass of Au@TiO_2 catalyst was calculated as follows:

$$C_{Au^0/cat} = \frac{\omega_{Au^0}}{MW_{Au^0} \times 100} = \frac{0.094}{196.67 \times 100} = 4.77 \times 10^{-6} \text{ mmol mg}^{-1}$$

Specific surface area of AuNP was calculated based on analysis of TEM images by measuring the size of particles (Au@TiO_2 sample):

$$S^*_{AuNP} = \frac{\sum S_{AuNP}}{\sum m_{AuNP}} = \frac{\sum S_{AuNP}}{\rho_{Au} \times \sum V_{AuNP}} = \frac{\sum 4\pi r^2_{AuNP}}{\rho_{Au} \times \sum 4/3\pi r^3_{AuNP}} = 38.82 \text{ m}^2 \text{ g}^{-1}$$

Concentration of Au in reaction solution:

$$M = 1.92 \times 10^{-5} \frac{g}{L} = \left\{1.92 \times 10^{-5} \frac{g}{L}\right\} \div \left\{196.67 \frac{g}{mol}\right\} = 9.76 \times 10^{-8} \frac{mol}{L}$$

Surface area concentration of Au in reaction solution:

$$M_s = S^*_{AuNP} \times M = \left(38.82 \frac{m^2}{g}\right) \times \left(1.92 \times 10^{-5} \frac{g}{L}\right) = 0.0007464 \text{ m}^2 \text{ L}^{-1}$$

Apparent rate constant of the reaction:

$$K_{app} = 0.642 \text{ min}^{-1}$$

$$K_m = \frac{K_{app}}{M} = \frac{0.642}{9.76} \times 10^8 = 6.58 \times 10^6 \frac{L}{mol. min} = 1.097 \times 10^5 \frac{L}{mol. s}$$

$$K_s = \frac{K_{app}}{M_s} = \frac{0.642}{0.0007464} = 860.13 \frac{L}{m^2 min} = 14.34 \frac{L}{m^2. s}$$