

Supporting Information

Fibrous, Ultra-small Nanorod Constructed- Platinum Nanocube Directly Grown on the ITO Substrate and their Heterogeneous Catalysis Application

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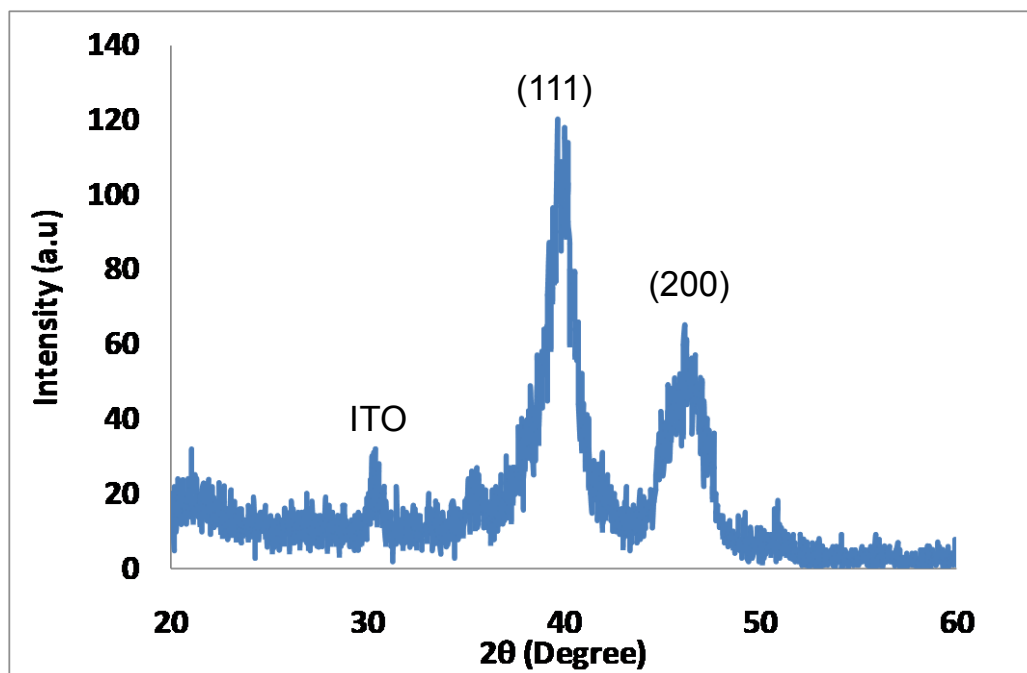


Figure S1. XRD spectrum of fibrous platinum nanocubes on the indium-tin oxide (ITO) substrate.

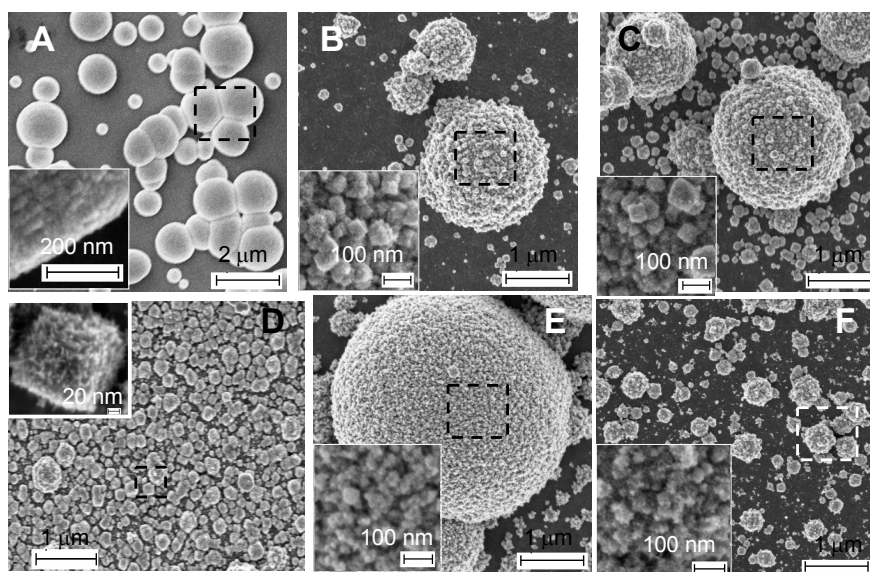


Figure S2. FESEM images of Pt nanostructures prepared using different concentrations of formic acid, namely 0.05 M (A), 1.0 M (B), 1.5 M (C), 1.75 M (D), 2.0 M (E) and 2.5 M (F). The SDS and K_2PtCl_6 are fixed at 0.01 M and 0.001 M, respectively. The growth temperature is 40 °C.

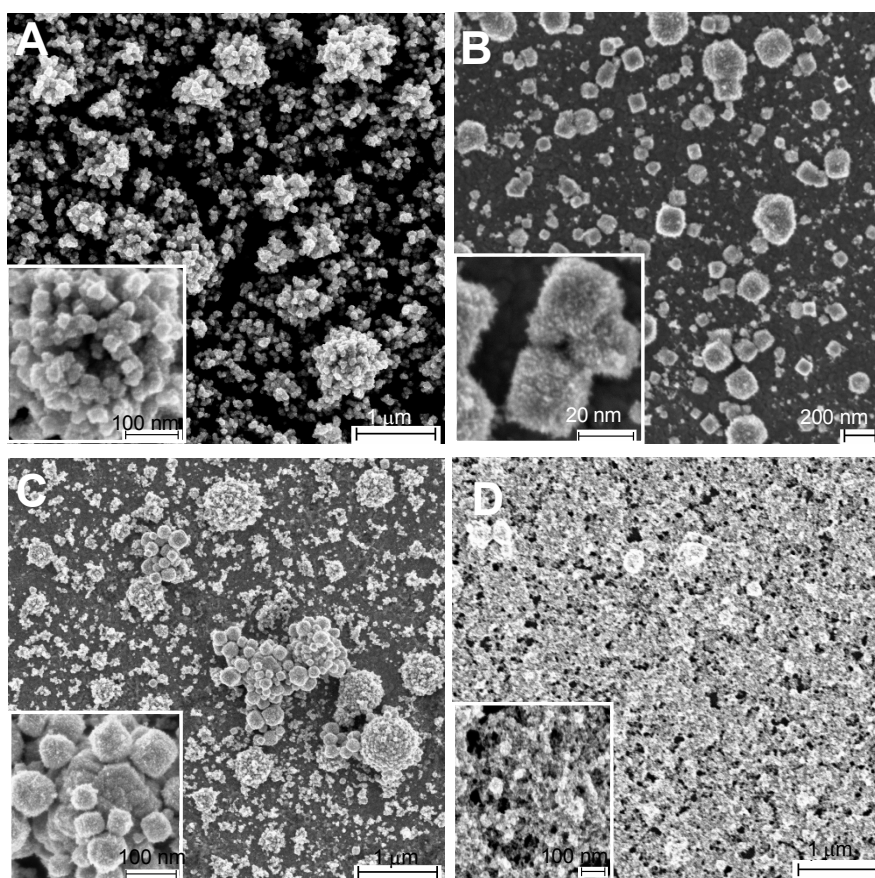


Figure S3. FESEM images of Pt nanostructures prepared at several growth temperatures, i.e. room-temperature (A), 30 °C (B), 60 °C (C) and 80 °C (D), using the optimum growth solution (0.01 M SDS, 0.001 M K_2PtCl_6 and 1.75 M formic acid).

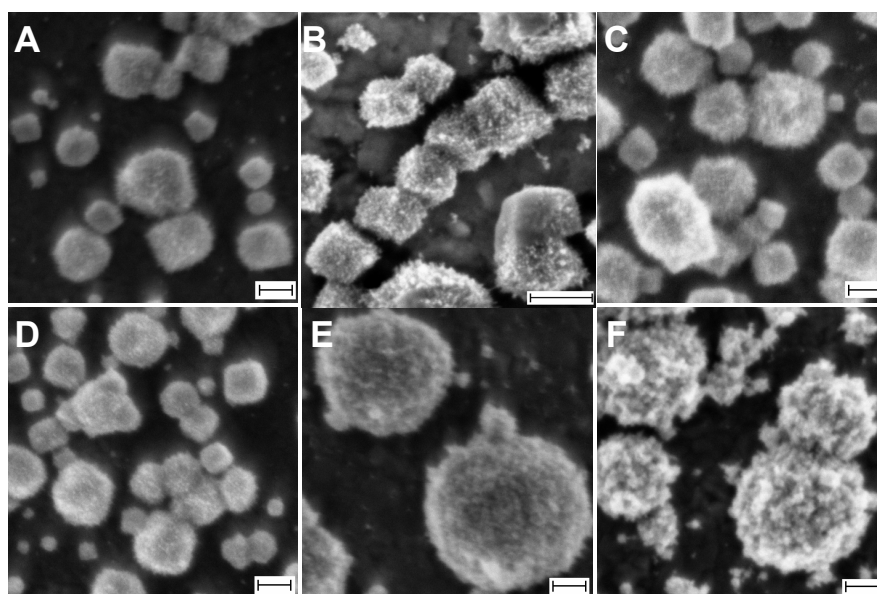


Figure S4. FESEM images of Pt nanostructures prepared using different SDS concentration, i.e. 5 (A), 10 (the optimum concentration) (B), 20 (C), 30 (D), 50 and 100 mM (F). The K_2PtCl_6 and formic acid concentration are 0.001 M and 1.75 M, respectively. Scale bars are 100 nm.

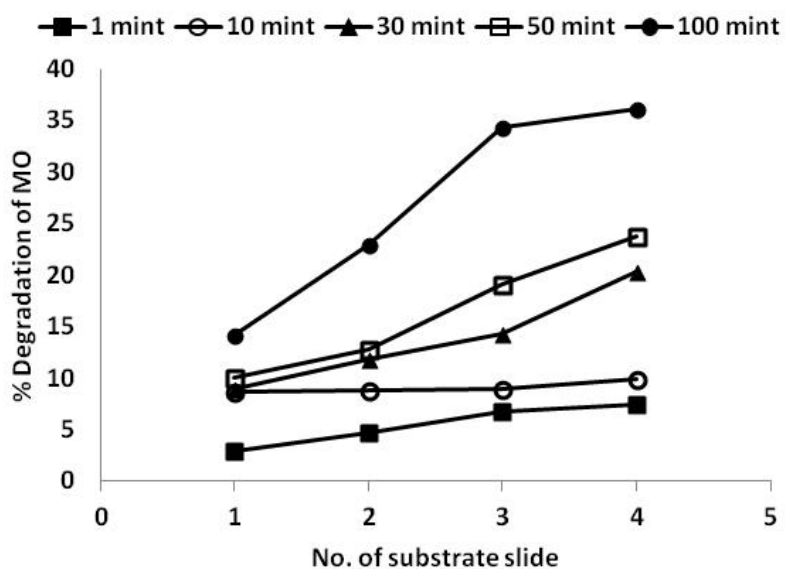


Figure S5. The typical performance of the catalytic degradation of methyl orange (MO) using multiple slides that contain PtNCs.

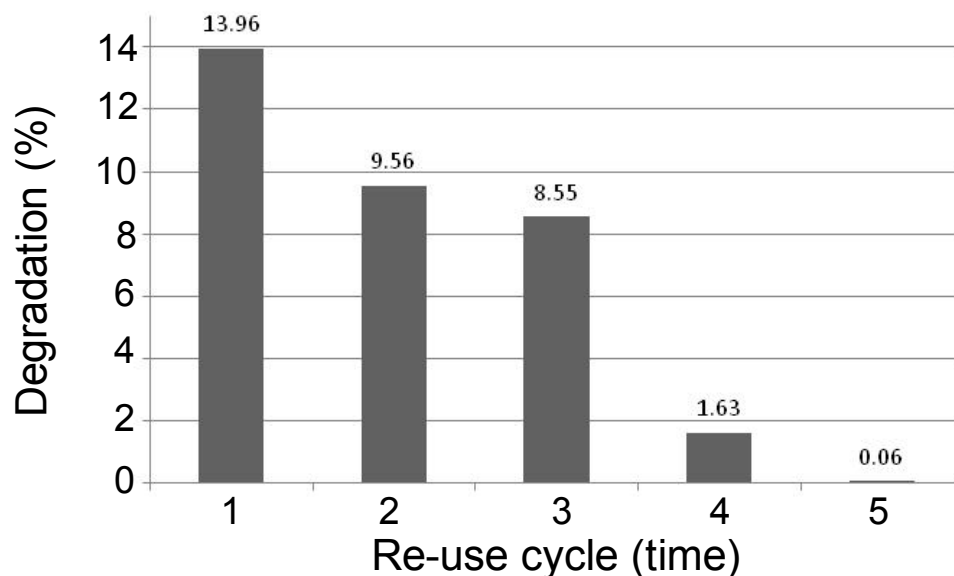


Figure S6. The re-usability performance of a single slide containing PtNCs in the catalytic degradation of methyl orange (MO). Bar 1 is the fresh sample.

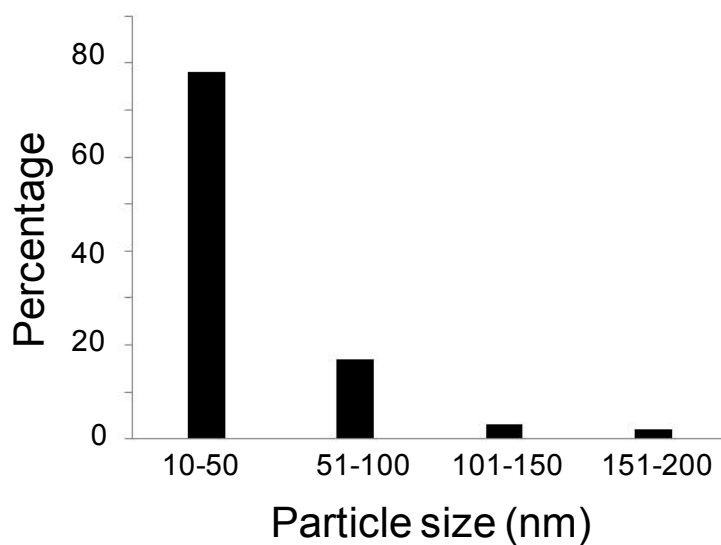


Figure S7. Distribution of nanocube size on the substrate.

Experimental Details

Synthesis of Platinum Nanocubes on ITO Substrate and Characterizations

In the typical procedure, the platinum nanocube on the indium-tin oxide (ITO) substrate surface (VinKarola instrument USA, sheet resistance of 9-22 Ω per square) was prepared by simply immersing the clean ITO substrate, which underwent a consecutive ultrasonication in

acetone and ethanol for 15 minutes each, into a 15 mL aqueous solution that contained 1mM K_2PtCl_6 (Fluka), 10 mM formic acid (Fluka) and 10 mM sodium dodecyl sulphate (SDS) (99.9 %, Fluka). This solution is called the optimum reaction condition. The ITO substrate was hung vertically inside the solution by using adhesive tape. During the reaction, the growth temperature was set to ca. 40 °C by placing the reaction container on a hot-plate. The solution was continuously stirred (500 rpm) during the reaction to obtain a homogenous condition inside the growth solution, and in the typical process the growth time used was 3 hours. After completing the growth process, the samples were taken from the solution, rinsed with copious amounts of pure water, and dried with a flow of nitrogen gas.

The effect of SDS and the formic acid concentrations on the structural growth of the platinum nanocrystals was studied by varying the concentrations from 0.05 to 100 mM and from 0.05 to 2.5 M for SDS and formic acid, respectively. The effect of the growth temperature on the structural growth of the platinum nanocube was also examined using five different growth temperatures, namely 25, 30, 40, 60 and 80 °C. The optimum reaction condition was used for this purpose.

Characterizations

The morphology and the atomic structure of the as prepared sample was characterized using a field emission-scanning electron microscopy (FESEM) Zeiss Supra 55VP FE SEM model and a high-resolution transmission electron microscopy (HRTEM) model Zeiss Libra 200FE. The phase of the nanocubes was obtained from the X-ray diffraction (XRD) experiment using the XRD Bruker D8 system with a $CuK\alpha$ irradiation and a scanning rate of 0.025-°/s.

High-Resolution Transmission Electron Microscopy (HRTEM) analysis

For the HRTEM analysis, the following procedure was used: Firstly, the PtNCs on the ITO substrate were peeled off by scratching the surface with a wet, clean cotton bud. By this approach, nanocubes on the surface can be transferred onto the cotton bud. After that, the cotton bud was ultrasonicated in ethanol to disperse the particles into the solution. Finally, a small drop of the solution was drop on a carbon film-coated copper grid and left to dry at room temperature.

Heterogeneous Catalytic Reduction of Methyl Orange

The heterogeneous catalytic property of a platinum nanocube on the ITO substrate was examined in this study by observing the nature of the methyl orange dye degradation from sodium borohydride in the presence of platinum nanocubes. By simply placing the platinum nanocube on an ITO substrate sample in an aqueous solution (5 mL) that contained 20.0 mg L⁻¹ of methyl orange and 4.0 x 10⁻⁵ M of sodium borohydride, the methyl orange degradation was examined by recording the optical absorption spectra of the solution. The spectrum was recorded every 10 minutes within 100 minutes of the reaction time, and its degradation was determined from a decrease in the optical absorption band that centered at 464 nm. Throughout the experiment, the catalytic degradation was evaluated ex-situ and the absorption spectra were recorded in an optical cell after a defined time.

The heterogeneous catalytic experiment using several ITO substrates containing platinum nanocubes was also carried out to understand the relationship between catalyst volume and the degradation rate. The degradation characteristic of methyl orange without the presence of a platinum nanocube catalyst was also studied to validate the heterogeneous catalytic properties of the platinum nanocube. All of the experiments were carried out at room-temperature (ca. 25 °C).

Recovery and reuse of pt-nanocube as a catalyst

After observing the heterogeneous catalytic degradation property of the PtNCs for 100 mins of the reaction, the ITO substrate containing Pt-nanocubes were taken out of the solution, washed three times with deionized water and then dried under N₂ flow as before. The substrate having PtNCs were reused in a fresh MO solution to check its second performance as a catalyst in a solution prepared by the procedure given in the previous section. A similar process was repeated for five times to see any changes in the performance of catalytic activity of the reused PtNCs.

Calculation of the mass of particles grown on the ITO substrate

To compare the catalytic property of the fibrous PtNCs to already reported work, we calculated the total mass of particles that grow on 1.5 cm x 1.2 cm (approximately 1.8 x 10⁸ μm²) of ITO substrate using the following method.

By considering the nanocube as solid and using the average edge-length of the nanocubes of 30 nm, according to the particle analysis using the FESEM result (see Figure

S7), we get the volume of one particle as $V = 2.7 \times 10^{-5} \mu\text{m}^3$. By using the mass density of platinum (d) as high as $21.45 \times 10^{-12} \text{g}/\mu\text{m}^3$, the mass of one particle (M_t) is:

$$\begin{aligned} M_t &= d \times V = 2.145 \times 10^{-11} \text{g}/\mu\text{m}^3 \times 2.7 \times 10^{-5} \mu\text{m}^3 \\ &= 5.8 \times 10^{-16} \text{g}. \end{aligned}$$

From the FESEM analysis, the surface particles density (ρ_s) was obtained as high as approximately 50 particles/ μm^2 . Therefore, the total number of particles (P_t) on the substrate surface of area (A) of $1.8 \times 10^8 \mu\text{m}^2$ ($1.8 \text{ cm} \times 1.0 \text{ cm}$) is:

$$\begin{aligned} P_t &= \rho_s \times A = 50 \text{ particles}/\mu\text{m}^2 \times 1.8 \times 10^8 \mu\text{m}^2 \\ &= 9.0 \times 10^7 \text{ particles}. \end{aligned}$$

Now, the total mass (T_m) on the substrate will be:

$$\begin{aligned} T_m &= P_t \times M_t = 9.0 \times 10^7 \times 5.8 \times 10^{-16} \text{g} \\ &= 5.22 \times 10^{-8} \text{g}. \end{aligned}$$

By considering that the fibrous nanocubes are about 30% of the solid cube, the total mass of the PtNCs on the surface become $0.015 \mu\text{g}$. Since the atomic weight of the Pt is 195 g/mol , the Pt load on the surface is $7.7 \times 10^{-11} \text{ mol}$.

Table 1 shows the comparison of efficiency of the present result compared to the recently reported method. The efficiency was calculated based on the following formula:

$$\eta = \frac{(\%)_{\text{Degradation}}}{M_{\text{Catalyst}} \times M_{\text{NaBH}_4}}$$

Where, $(\%)_{\text{Degradation}}$ is percent degradation of MO at maximum time, M_{catalyst} is concentration of catalyst in MO solution, M_{NaBH_4} is concentration of NaBH₄ used.

Table 1. Comparison of percentage of efficiency of our grown PtNCs with the reported method.

No	Conc. of Pt-particles ($\mu\text{g}/\text{mL}$)	Conc. of NaBH ₄ (M)	η	Temp $^{\circ}\text{C}$	Time (min)	Ref.
1	0.004	5.0×10^{-5}	85	20	90	Our data
2	1.562	377.0×10^{-5}	0.009	20	40	[1]

It is revealed from the data that our PtNCs is highly efficient, which is 10^3 higher efficiency than the reported results.

References

- (1) Gupta, N.; Singh, H. P.; Sharma, R. K. *Journal of Molecular Catalysis A: Chemical* **2011**, 335, 248.