

Supporting Information

Synthesis of Platinum Nanoparticles Supported on Poly(acrylic acid) Grafted MWNTs and their Hydrogenation of Citral

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1. Characterization of Pt/PAA-g-MWNTs by X-ray energy dispersive spectroscopy (EDS)

The presence of Pt in MWNTs was confirmed by X-ray energy dispersive spectroscopy (EDS, Figure S1).

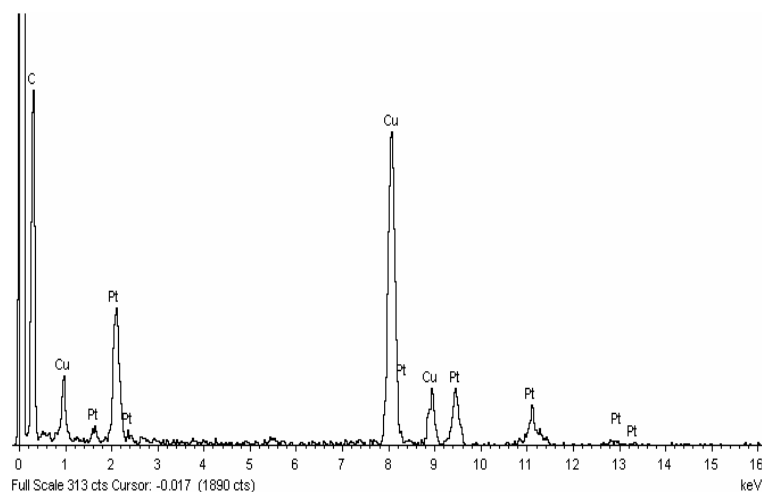


Figure S1. EDS spectroscopy of Pt/PAA-g-MWNTs.

2. Additional evidence for PAA as the nucleation sites for deposition of Pt nanoparticles

It has been suggested that the functional groups (-OH, -COOH) on the surface of MWNTs were served as preferred nucleation sites for reducing metal ions from solution due to the coordination reaction or an ion-exchange reaction with the Pt precursors.¹⁻³ To confirm the carboxylic acid groups in PAA in our experiments possess similar function, a small amount of H_2PtCl_6 was added into EG solution in the presence of PAA-g-MWNTs. After stirring for 30 min, the PAA-g-MWNTs were centrifugated out and washed with deionized water for five times. As seen from the HRTEM images, the colour of the PAA shell appeared light before interaction with Pt precursors (Figure S2A). However, it became dark after interaction with Pt precursors (Figure S2B), confirming the preferential interaction between Pt precursors and PAA.

Because the coordination ability of carboxylic acid is much stronger than that of chloride ion⁴, and the bulky ligands can destabilize the six-coordinated Pt (IV) state⁵, the Pt precursors, H_2PtCl_6 would interact favorably with PAA grafted on MWNTs surface via a coordination substitution reaction or an ion-exchange reaction, which in turn accelerates the nucleate rate of Pt nanoparticles.

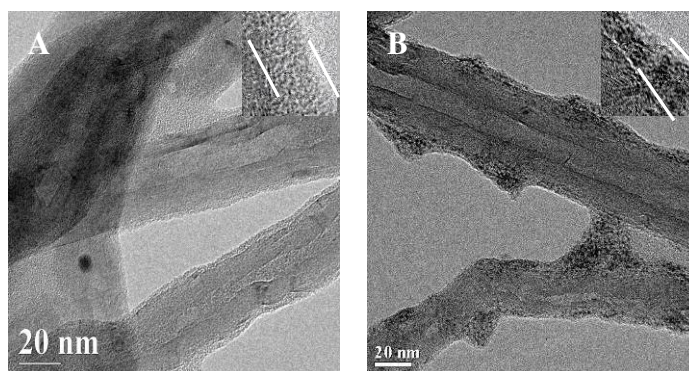


Figure S2. HRTEM images of PAA-g-MWNTs before (A) and after (B) interaction with Pt precursors.

3. Separation of MWNTs with different graft densities of PAA by varying centrifugation strength

Three samples of PAA-g-MWNTs with different PAA grafting densities were obtained by centrifugation of PAA-g-MWNTs dispersion with different strengths, 3000, 8000 and 12000 rpm, respectively. The SEM images (Figure S3) showed no obvious difference in morphology, but the grafted amount of PAA is different, the PAA grafting amount was measured by TGA (Figure 4).

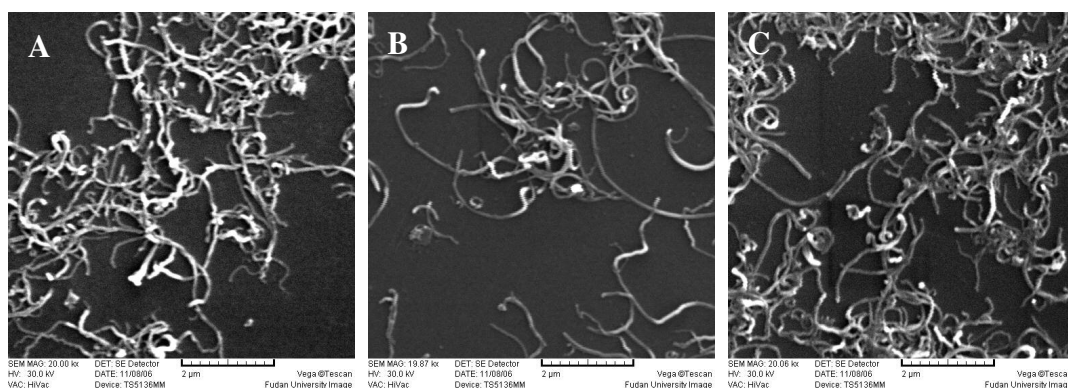


Figure S3. SEM images of MWNTs centrifugated from solution at different strength (A) 3000 rpm, (B) 8000 rpm, and (C) 12000 rpm.

4. GC characterization of citral hydrogenation products

The raw material, citral ($\text{C}_{10}\text{H}_{16}\text{O}$, Purity $\geq$ 95.0%) was purchased from Sinopharm Chemical Reagent Co. Ltd. In order to measure the proportion of citral hydrogenation products, Nerol ($\text{C}_{10}\text{H}_{18}\text{O}$, purity $\geq$ 90%, GC), geraniol ($\text{C}_{10}\text{H}_{18}\text{O}$, purity $\geq$ 96%, GC), citronellol ($\text{C}_{10}\text{H}_{20}\text{O}$, 90%-95% pure, GC) and citronellal ($\text{C}_{10}\text{H}_{18}\text{O}$, purity $\geq$ 80%, GC) were all purchased from Sigma-Aldrich and served as external standard for gas chromatography (GC). The ratio of trans-citral (geraniol) to cis-citral (nerol) in feed was ~ 1 (Figure S4A). The GC characterizations of citral hydrogenation products catalyzed by different Pt nanoparticles were shown in Figure S4B-D. Conversion, monohydrogenation selectivity and stereoselectivity (ratio of geraniol to nerol) were calculated based on GC results, and summarized in Table 1.

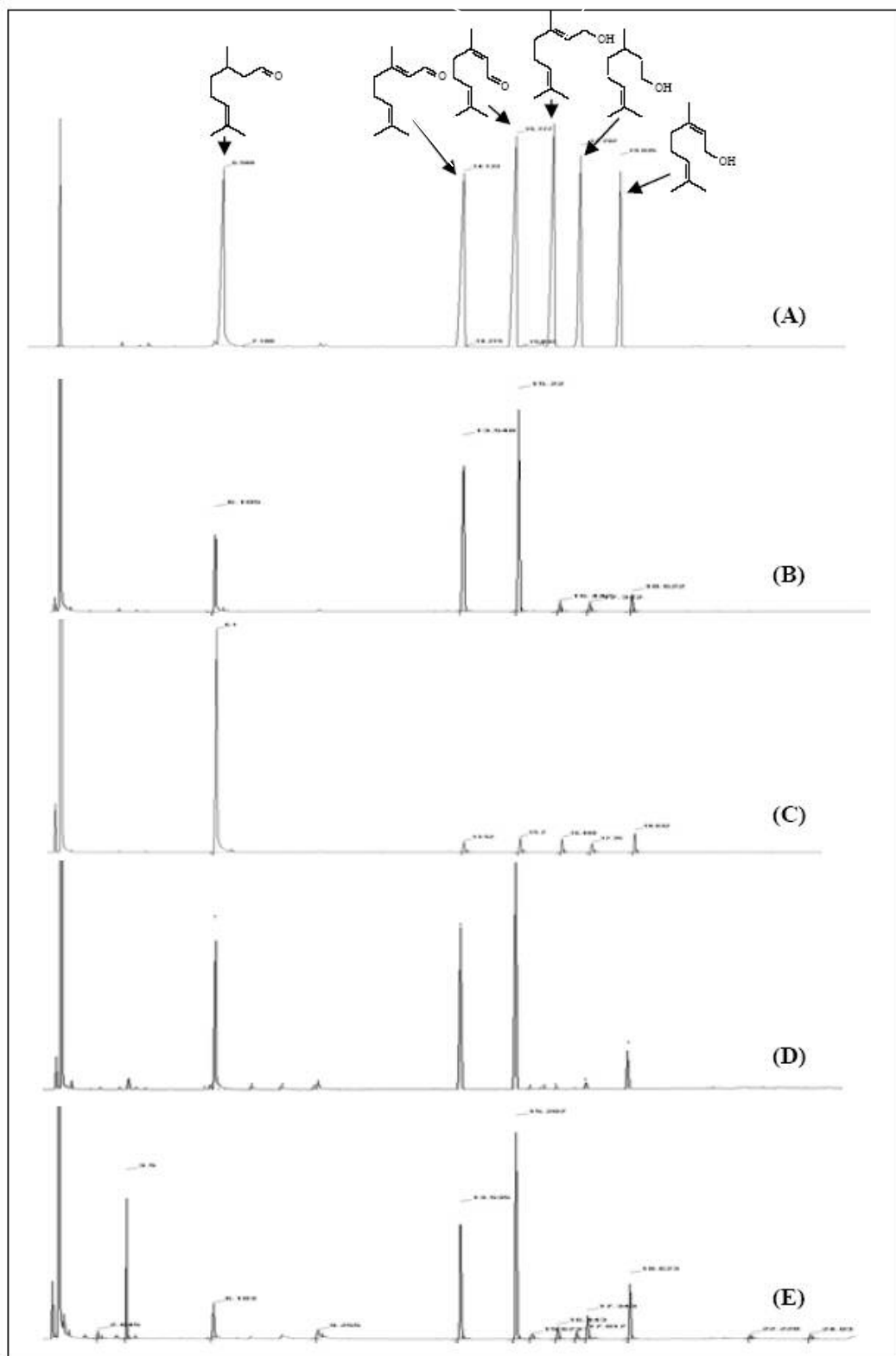


Figure S4. GC curves of (A) external standards and the citral hydrogenation products catalyzed by (B) Pt/AC, (C) irregular Pt/MWNTs, (D) tetra- and octahedral Pt/MWNTs, and (E) tetra- and octapods Pt/MWNTs. Reaction condition: T=60°C;

$P(H_2) = 1.0 \text{ MPa}$; $W_{Pt}/W_{CNT} = 0.05 \text{ g}$; $W_{citra} = 0.5 \text{ g}$; $V_{hexane} = 25 \text{ mL}$; Rotate speed = 500 rpm and reaction time, 2 h.

References:

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