Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

In-situ observation of the crystal structure transition of Pt-Sn intermetallic nanoparticles during deactivation and regeneration

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Synthesis of intermetallic nanoparticles PtSn@mSiO$_2$. The detailed synthesis of the iNPs has been reported in our previous work[1]. For a typical synthesis, Pt@mSiO$_2$ solution was centrifuged and redispersed in 40 mL tetraethylene glycol. The SnCl$_2$·2H$_2$O with a molar ratio of Pt:Sn=1:1 was then added before the mixture was sonicated to obtain a homogeneous mixture. The mixture was then heated to 280 °C in argon for 2 hours using a temperature-controlled heating mantle.

In-situ TEM. In-situ TEM experiments were carried out on a FEI Talos F200S TEM microscope with a resolution of 0.16 nm was operated at 200 kV. The as-prepared PtSn@mSiO$_2$ nanoparticles were first ultrasonically dispersed in deionized water and then dropped onto the SiNx membrane with microholes, which was mounted onto

Protochips Atmosphere TEM holder. The local heating on the MEMS device is based on the Joule heating of a micropatterned metal heater. The resistance of the heater has a linear response to temperature in the range from room temperature to 1000 °C. The as-prepared specimen was first heated to 500 °C in O_2 (760 torr) for about 30 min to totally oxidize the intermetallic nanoparticles and then was cooled to room temperature and evacuate oxygen. Then a mixture of H_2/N_2 (v/v=1/10, 760 torr) was introduced into the microscope chamber. Once the target pressure was reached and stabilized, the specimen was heated again to the target temperature of 350 °C. During the above process, TEM images and videos were recorded using FEI CCD camera software. The FFT was obtained from Velox software.

All the time scales marked in in-situ TEM images are the relative time. Before acquiring TEM images or videos, the samples were annealed in a reactive environment at the target temperature for ~5 min with e-beam shut down. The real starting time to record was more than 5 min after introducing the carbon precursor.

Ex-situ HAADF-STEM. STEM experiments were carried out on a FEI Talos F200S electron microscope with a HAADF detector. The STEM images were recorded at 200 kV using an inner and outer collection angle of 38 and 200 mrad, respectively. EDX elemental maps were acquired from a Bruker super-X detection system.

Imitate the decarbonization and regeneration processes: For the decarbonization process, 2 g nanoparticles were put in the porcelain boat and then heated them at 500 °C in the muffle for 4 h. After that, the oxidized PtSn@mSiO_2 nanoparticles were obtained. For the regeneration process, the oxidized nanoparticles were put into another porcelain boat and inserted into a tube furnace. The nanoparticles were then heated at 350°C under 10%H_2 (H_2/N_2=1/10) in the tube furnace for 4-6h. After this, the regenerated PtSn@mSiO_2 iNPs were obtained.

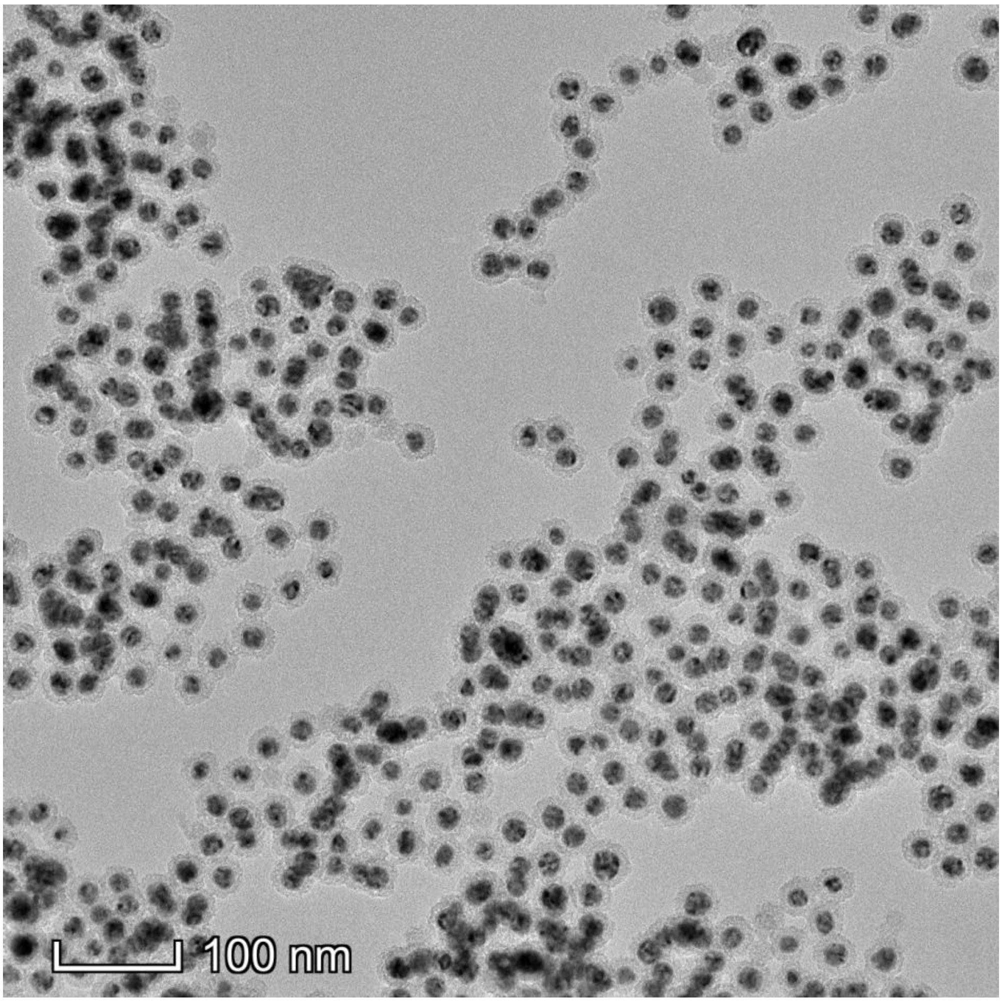

Figure S1: PtSn@mSiO_2 nanoparticles after being heated at 500°C in air for 4h.

Figure S1 shows PtSn@mSiO_2 nanoparticles that have been heated for 4h in the muffle furnace at 500°C in air. Most nanoparticles were in irregular shape in contrast to the spherical shown in Figure 1a. The Pt-SnO_2 cores are confined within the SiO_2 shells. Most nanoparticles exhibited phase segregation.

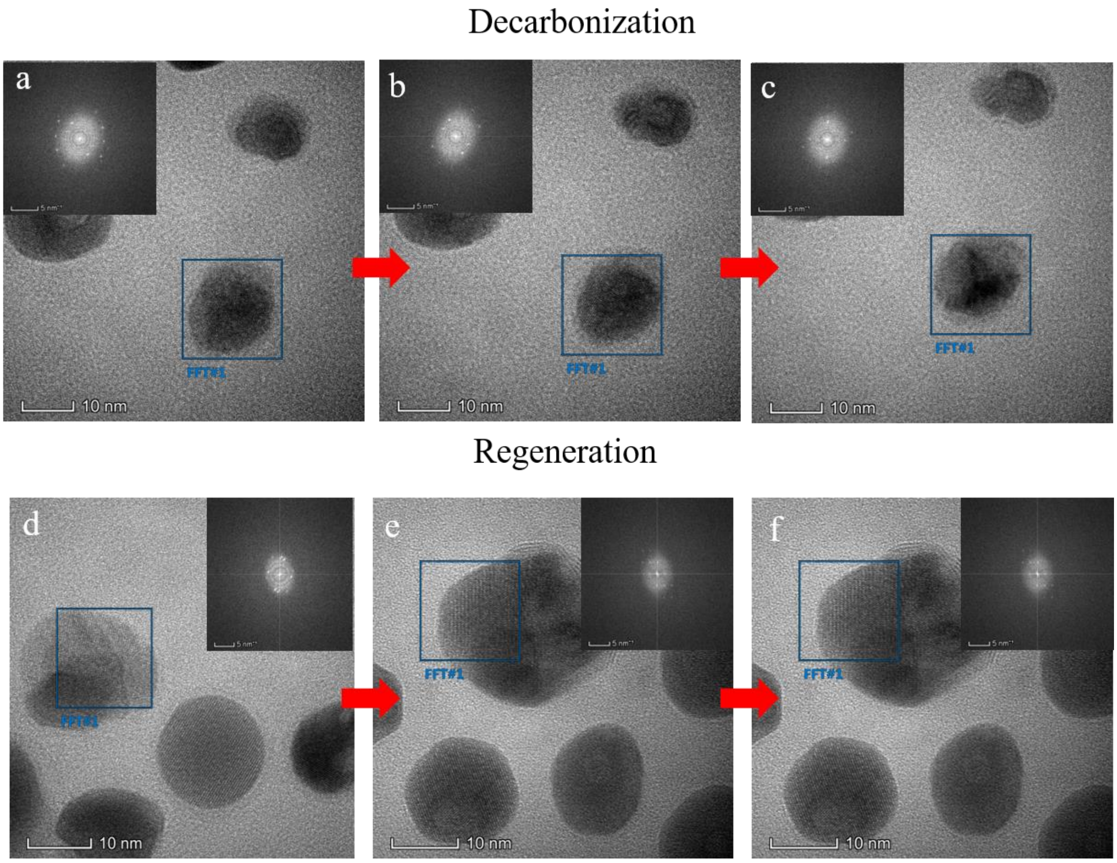

Figure S2. TEM images of PtSn@mSiO$_2$ nanoparticles after decarbonization (a-c) and regeneration (d to f) treatments. The corresponding FFT patterns of the selected areas are shown as insets.

As shown in Figure S2, we have investigated the structural transition of the PtSn@mSiO$_2$ nanoparticles during the decarbonization and regeneration process. Figure S2a-c are the TEM images and corresponding FFT patterns of the PtSn@mSiO$_2$ nanoparticles during the decarbonization process. At the beginning of the process in Figure S2a, the particles maintain the regular shape, and FFT patterns also show some details and ordered arrangement. As the process proceeds in Figure 2b, the PtSn@mSiO$_2$ nanoparticles gradually lost regular shape and the FFT patterns become distorted, and some diffraction points disappeared. In the end, the PtSn@mSiO$_2$ nanoparticles became totally irregular shape, and the FFT patterns become out-of-order and show fewer diffraction points than the pristine FFT patterns.

Figure 2d-f are TEM images and corresponding FFT patterns describing the PtSn@mSiO$_2$ nanoparticles and their crystal structure evolution during the regeneration process. At the beginning of the process in Figure S2d, the oxidized particles possess the irregular shape, and FFT pattern shows disordered arrangements. As the process proceeds in Figure 2e, the PtSn@mSiO_2 nanoparticles gradually formed regular shape, and the FFT patterns become ordered. In the end, the PtSn@mSiO_2 nanoparticles formed regular shape again, and the FFT patterns return to ordered arrangement. This in-situ observation confirms that after the decarbonization process, the PtSn@mSiO_2 nanoparticles lost regular shape, and the crystal structure was totally changed. After the regeneration process, the nanoparticles return their pristine shape and crystal structure.

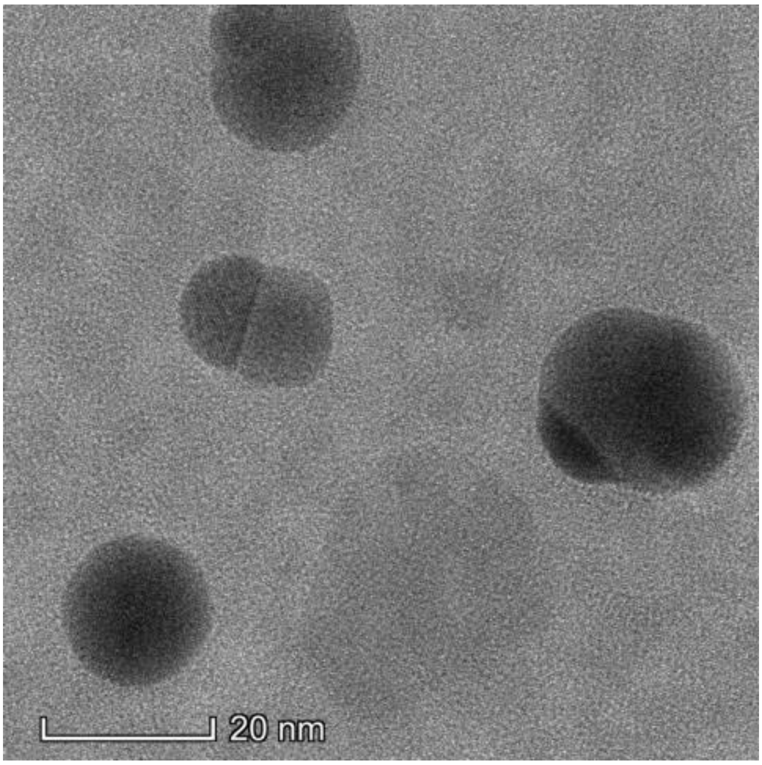

Figure S3 TEM images of PtSn@mSiO_2 when heated under 760 torr pure oxygen at 500℃.

Figure S3 shows that when PtSn@mSiO_2 nanoparticles were oxidized by oxygen, it clearly separated into two different parts. The nanoparticles still maintain the stable shape, and they were not disintegrated due to the SiO_2 shell protection. A clear phase boundary appears in the the nanoparticles, which means that PtSn was separated into two parts with different phases under oxygen atmosphere under 500°C. No clear phase segregation was observed for the particle at the bottom-left of the image, which could occur when the Pt and SnO_2 phases are sitting on top of each other.

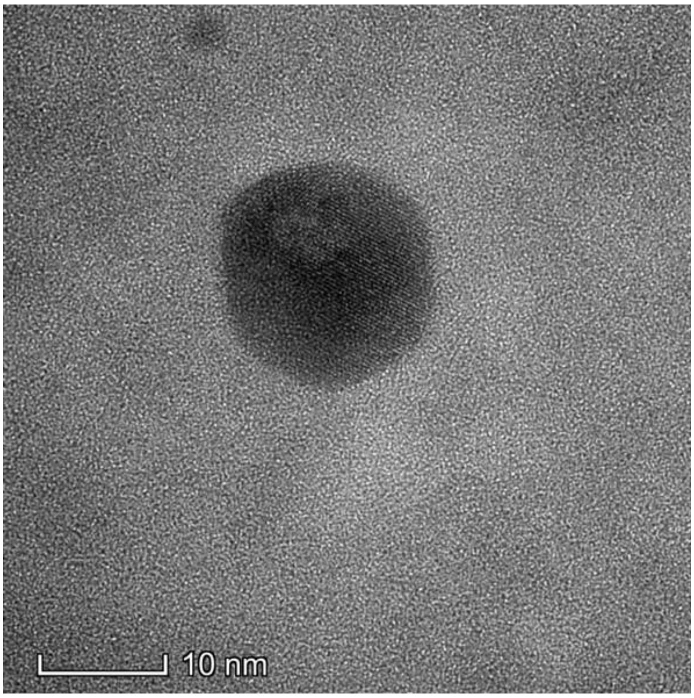

Figure S4 High-magnification TEM image of one PtSn@mSiO_2 nanoparticle after regeneration process. The nanoparticle regains its regular shape and ordered crystal structure.

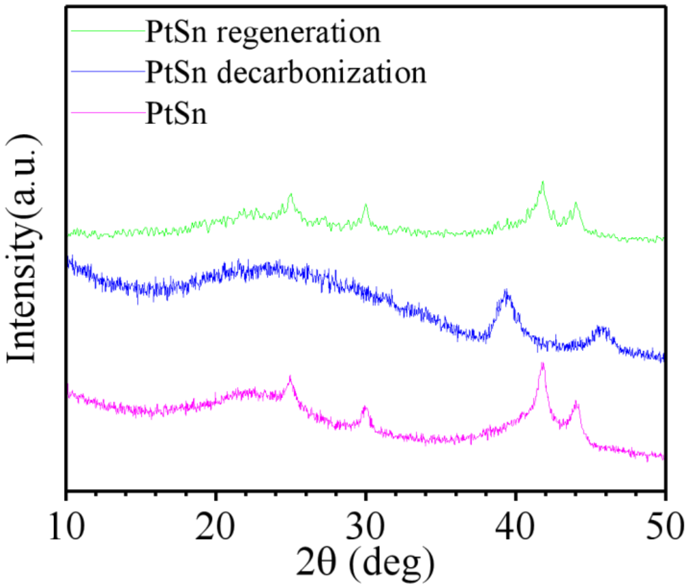

Figure S5. PXRD of pristine PtSn@mSiO_2 and that after decarbonization and regeneration processes.

We measured the powder X-ray diffraction (PXRD) patterns to study the phase transition of intermetallic nanoparticles. The purple curve in Figure S5 is the PXRD pattern of the pristine PtSn@mSiO_2 nanoparticles, which shows differection peaks at 25°, 30°, 42° and 44°, corresponding well with previous report on PtSn intermetallic compound.[1] The blue curve is PXRD measured after catalyst decarbonization, which shows two diffraction peaks at 39° and 45°, clear different from the pristine PtSn@mSiO_2 nanoparticles, indicating dramatic structural change after the decarbonization process. The green curve corresponding to the catalyst after regeneration, which shows fully recoved diffraction peaks corresponding to PtSn intermetallic compound, confirming that the PtSn@mSiO_2 returns to its pristine structure after the regeneration process.

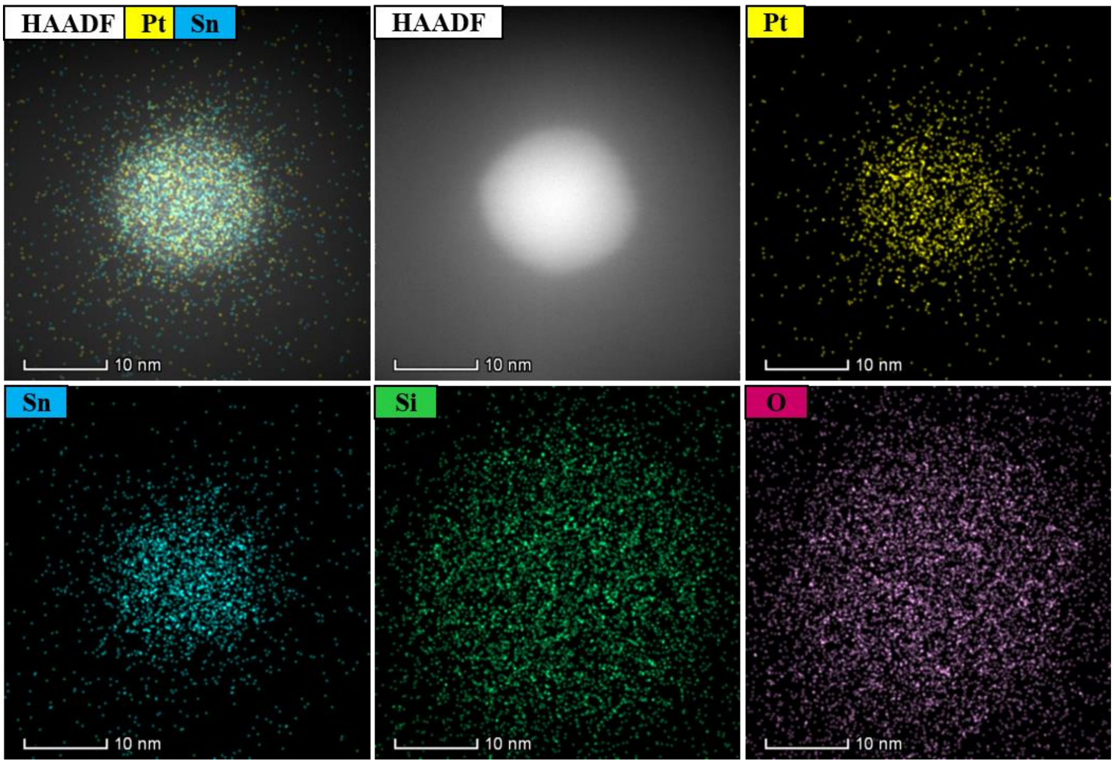

Figure S6. HAADF-STEM elemental distribution of initial state PtSn@mSiO_2 iNPs. Pt: yellow; Sn: blue; Si: green; O: purple.

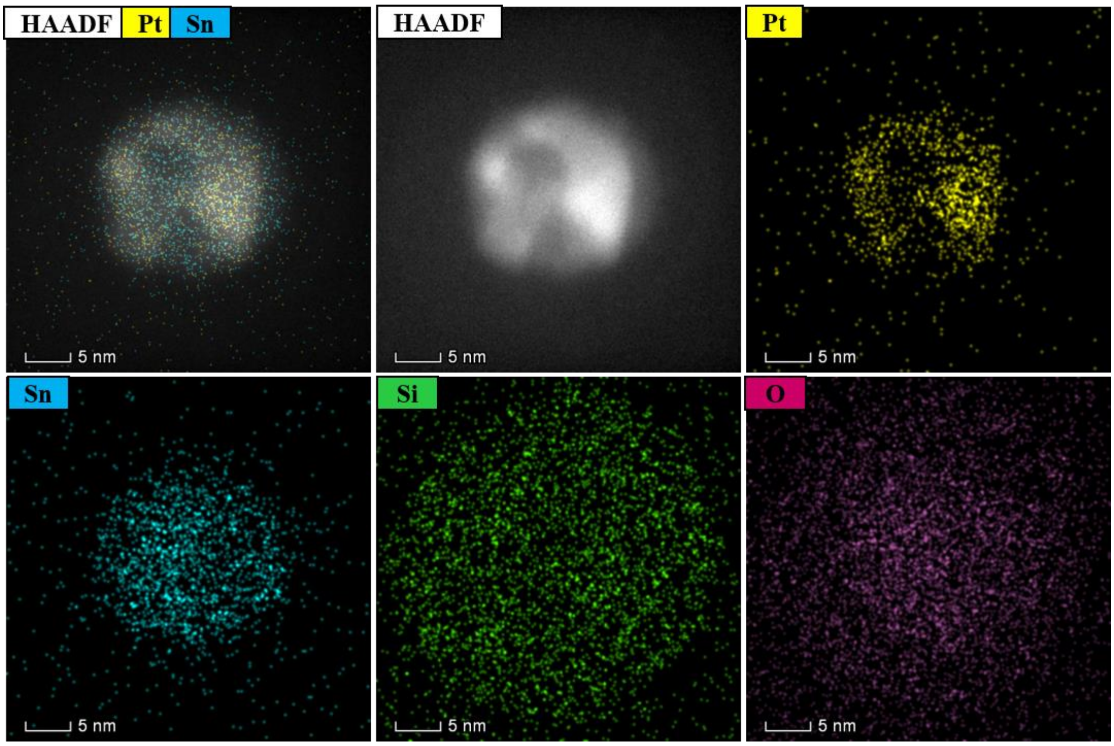

Figure S7. HAADF-STEM elemental distribution of after deactivation state PtSn@mSiO_2 iNPs. Pt: yellow; Sn: blue; Si: green; O: purple.

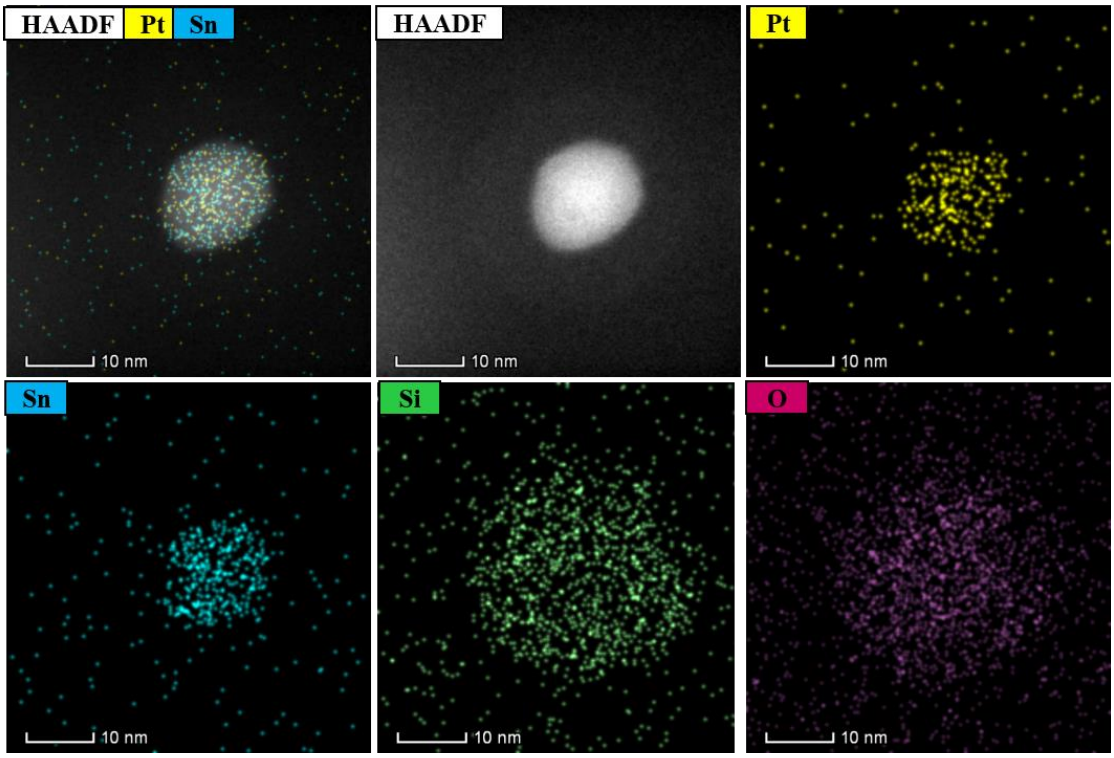

Figure S8. HAADF-STEM elemental distribution of after regeneration state PtSn@mSiO_2 iNPs. Pt: yellow; Sn: blue; Si: green; O: purple.

1. Maligal-Ganesh, R. V.; Xiao, C.; Goh, T. W.; Wang, L.-L.; Gustafson, J.; Pei, Y.; Qi, Z.; Johnson, D. D.; Zhang, S.; Tao, F.; Huang, W., A Ship-in-a-Bottle Strategy To Synthesize Encapsulated Intermetallic Nanoparticle Catalysts: Exemplified for Furfural Hydrogenation. *ACS Catalysis* **2016,** *6* (3), 1754-1763.