

# **Au(Core)-Pt(Shell) Nanocatalysts with the Shell Thickness Controlled at Monolayer Level: Extremely High Activity for Hydrogen Peroxide Decomposition**

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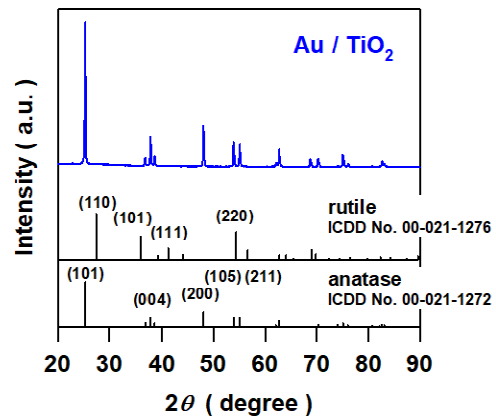


Figure S1. XRD pattern for Au/TiO<sub>2</sub>.

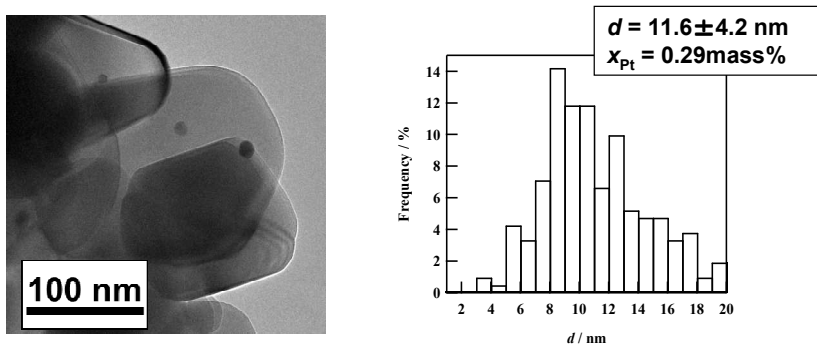
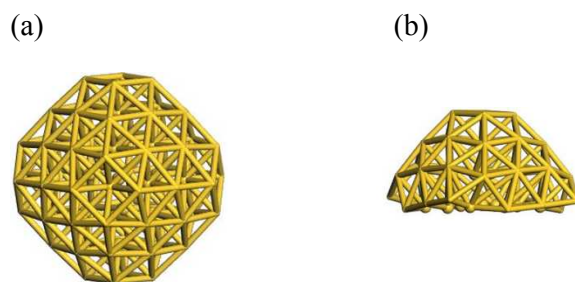
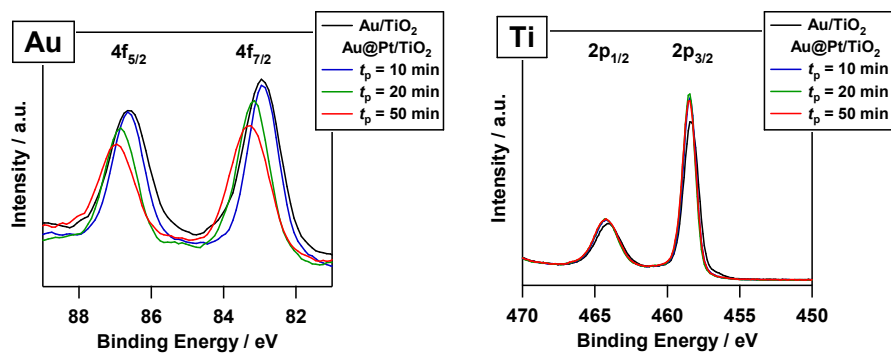


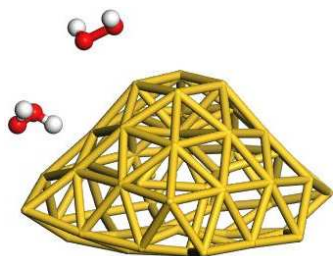
Figure S2. TEM image and particle size distribution for Pt/TiO<sub>2</sub>.



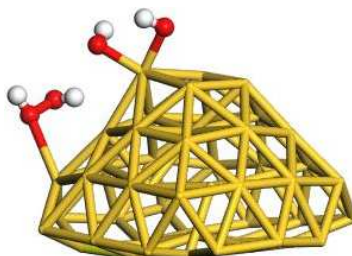
**Figure S3.** Cluster model of a sphere-shaped Au<sub>79</sub> (a) and the truncated Au<sub>50</sub> (b).



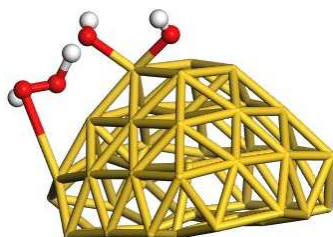
**Figure S4.** Au4f and Ti2p-XPS spectra of Au@Pt/TiO<sub>2</sub>.



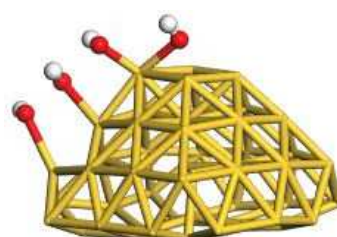
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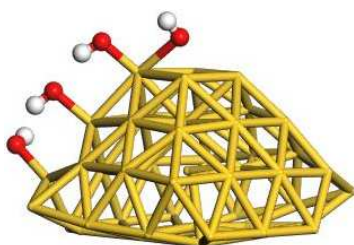
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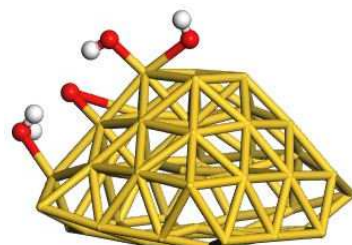
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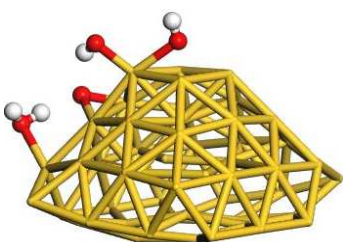
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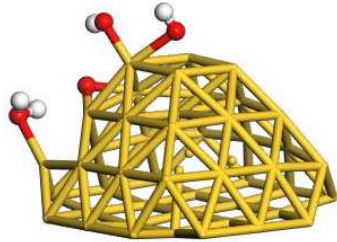
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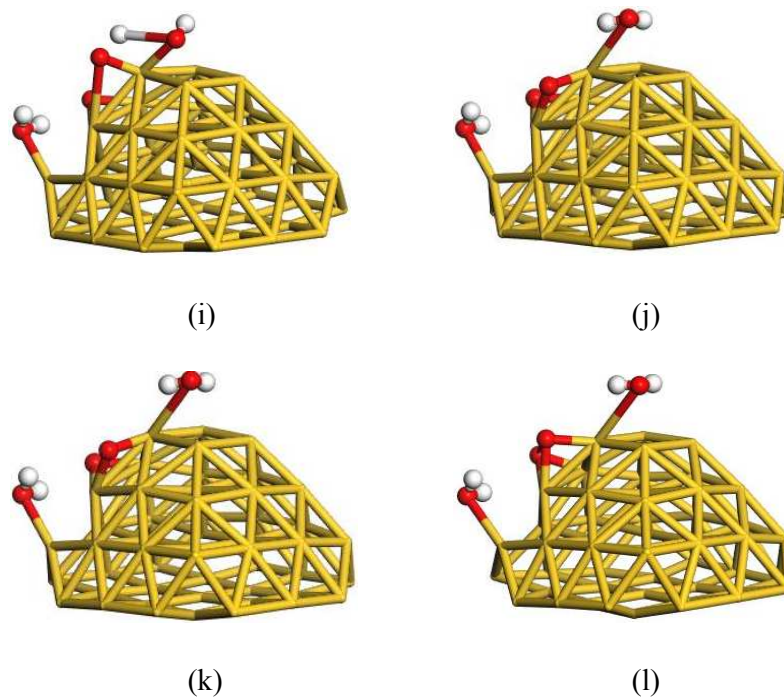
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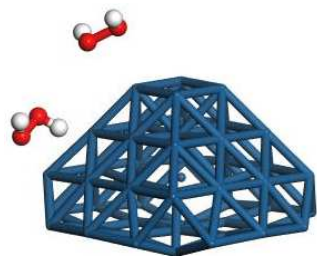
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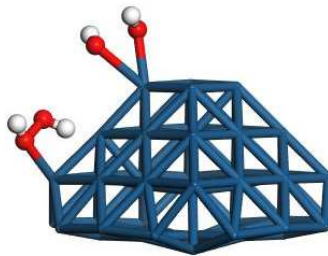
(h)



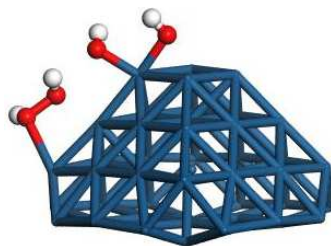
**Figure S5.** Optimized structures with Au<sub>50</sub> cluster in H<sub>2</sub>O<sub>2</sub> decomposition reaction. [a : Au<sub>50</sub>-2HOOH, b : TS1, c : Au<sub>50</sub>-2OH-HOOH, d : TS2, e : Au<sub>50</sub>-4OH, f : TS3, g : Au<sub>50</sub>-H<sub>2</sub>O-O-2OH, h : Au<sub>50</sub>-H<sub>2</sub>O-O-2OH(2), i : TS4, j : Au<sub>50</sub>-2H<sub>2</sub>O-2O, k : TS5, l : Au<sub>50</sub>-2H<sub>2</sub>O-O<sub>2</sub>] (red : O, white : H, yellow : Au)



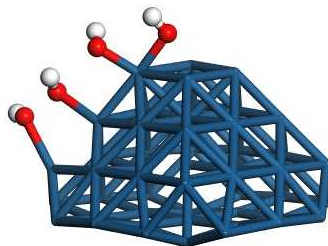
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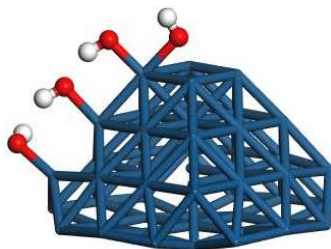
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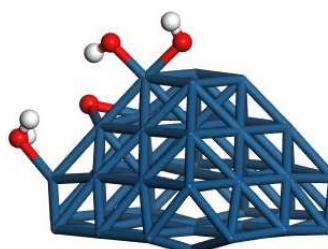
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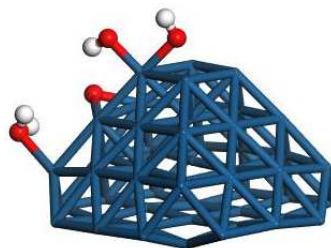
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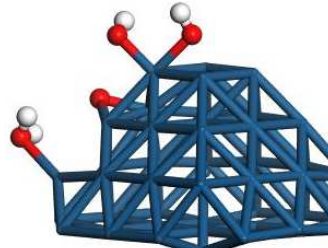
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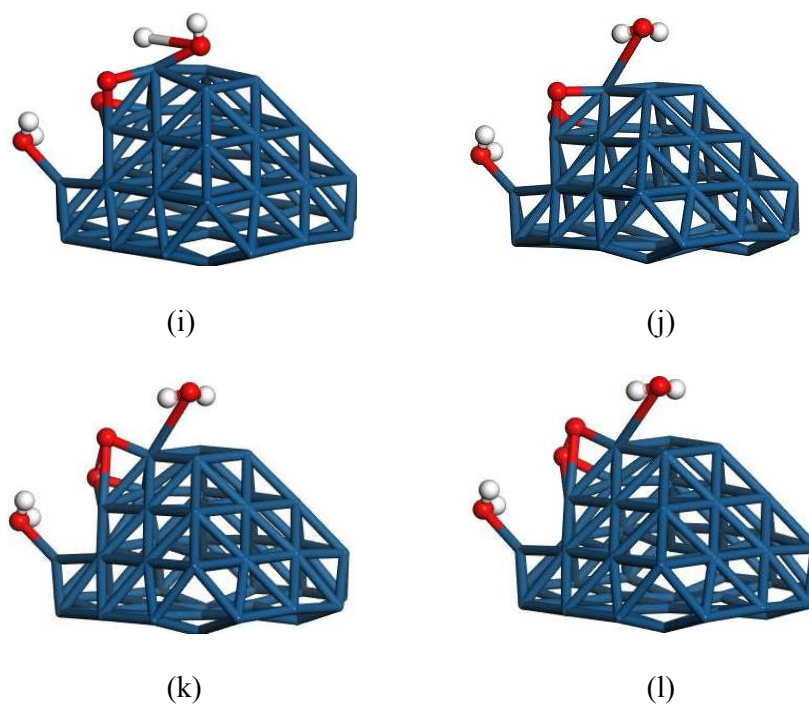
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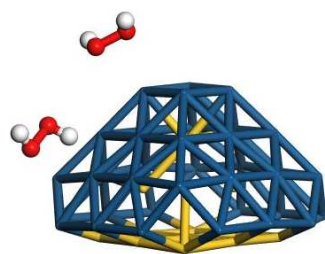
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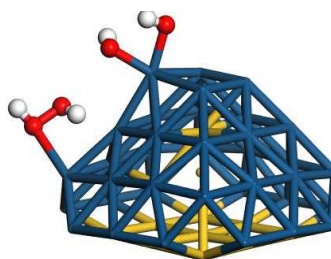
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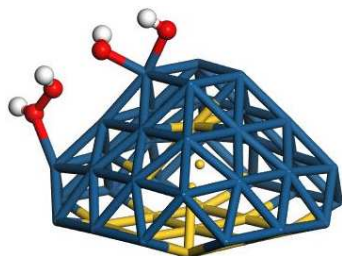
**Figure S6.** Optimized structures with  $\text{Pt}_{50}$  cluster in thermal decomposition reaction.  
 [a :  $\text{Pt}_{50}\text{-2HOOH}$ , b : TS1, c :  $\text{Pt}_{50}\text{-2OH-HOOH}$ , d : TS2, e :  $\text{Pt}_{50}\text{-4OH}$ , f :  
 TS3, g :  $\text{Pt}_{50}\text{-H}_2\text{O-O-2OH}$ , h :  $\text{Pt}_{50}\text{-H}_2\text{O-O-2OH(2)}$ , i : TS4, j :  $\text{Pt}_{50}\text{-2H}_2\text{O-2O}$   
 , k : TS5, l :  $\text{Pt}_{50}\text{-2H}_2\text{O-O}_2$ ] (red : O, white : H, blue : Pt)



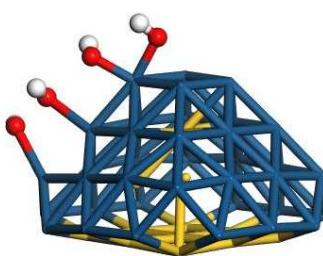
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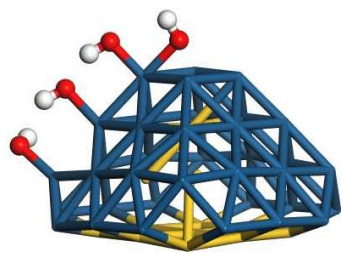
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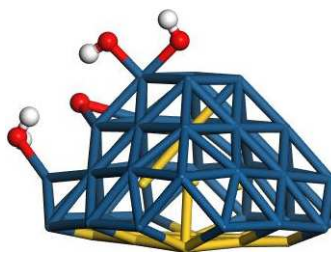
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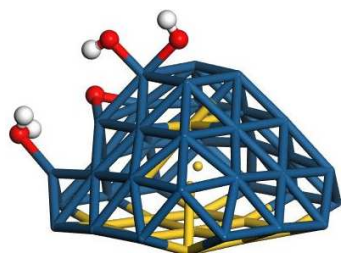
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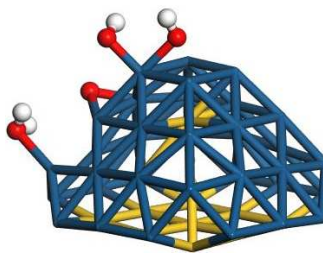
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(f)

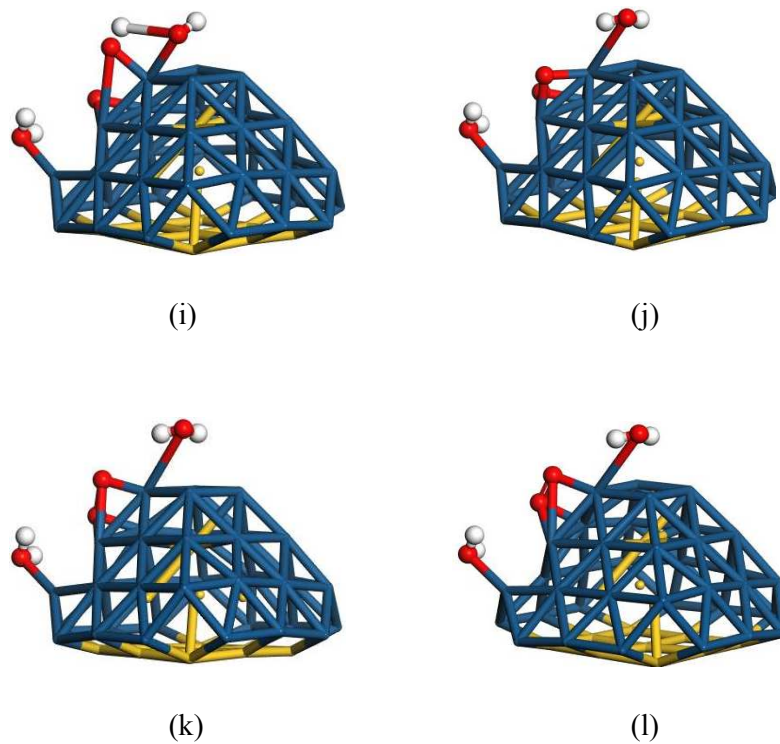


(g)

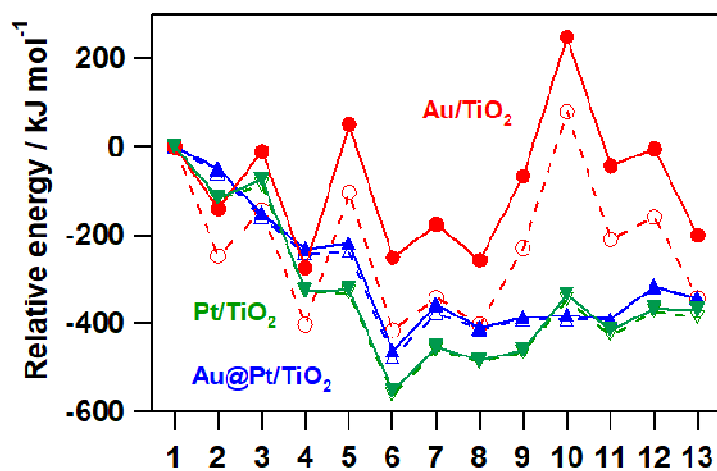


(h)





**Figure S7.** Optimized structures with  $\text{Au}_{14}@\text{Pt}_{36}$  cluster in thermal decomposition reaction. [a :  $\text{Au}_{14}@\text{Pt}_{36}-2\text{HOOH}$ , b : TS1, c :  $\text{Au}_{14}@\text{Pt}_{36}-2\text{OH}-\text{HOOH}$ , d : TS2, e :  $\text{Au}_{14}@\text{Pt}_{36}-4\text{OH}$ , f : TS3, g :  $\text{Au}_{14}@\text{Pt}_{36}-\text{H}_2\text{O}-\text{O}-2\text{OH}$ , h :  $\text{Au}_{14}@\text{Pt}_{36}-\text{H}_2\text{O}-\text{O}-2\text{OH}$ , i : TS4, j :  $\text{Au}_{14}@\text{Pt}_{36}-2\text{H}_2\text{O}-2\text{O}$ , k : TS5, l :  $\text{Au}_{14}@\text{Pt}_{36}-2\text{H}_2\text{O}-\text{O}_2$ ] (red : O, white : H, yellow : Au, blue : Pt)



**Figure S8.** Relative free energy change in the metal cluster-catalyzed thermal decomposition of H<sub>2</sub>O<sub>2</sub>. [1 : 2HOOH(gas), 2 : 2HOOH, 3 : TS1, 4 : 2OH-HOOH, 5 : TS2, 6 : 4OH, 7 : TS3, 8 : H<sub>2</sub>O-O-2OH, 9 : H<sub>2</sub>O-O-2OH(2), 10 : TS4, 11 : 2H<sub>2</sub>O-2O, 12 : TS5, 13 : 2H<sub>2</sub>O-O<sub>2</sub>]: the free energies are plotted by broken lines together with the SCF energies (solid lines).