Supplementary

Engineering Inorganic Hybrid Nanoparticles

—Tuning Combination Fashions of Au, Pt and Iron Oxide

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Synthesis of nanoparticles with different morphologies

1 Morphology-Controllable Synthesis of Pt Nanostructures

In this work, different Pt NPs were used as the templates for the synthesis of complex multi-component NPs (Pt-Au, Pt-IO and Pt-Au-IO). The details of the synthesis of Pt NPs were reported previously.6b

7 nm spherical Pt NP (i): In a typical synthesis process, 0.1 g Pt(acac)2 was dissolved into 3 mL OA at 70 ºC overnight. Then the resulting orange solution was injected into 10 mL OA at 250 ºC, and annealed at 220 ºC for one hour. The black solution was cooled down to room temperature by removing heating source. Ethanol (20 mL) was added into the reaction medium and samples were precipitated by centrifugation (8000 rpm, 10 minutes). The precipitate was dispersed into hexane and precipitated out by adding ethanol and centrifugation. The washing process was repeated twice. Finally, the products were kept in hexane for further characterizations. All other samples in this work were separated by the procedure described here.

Hierarchically Pt branched network NPs (ii): Typically, 0.1 g Pt(acac)2 was dissolved into 10 mL OA under flowing pure nitrogen gas and kept at 100 ºC for tow hours. Then the solution was carefully heated up to 135 ºC at a heating rate of 2 ºC per minute and annealed for 24 hours. The complexity of hierarchical structure could be tuned by modulating the annealing period.6b

Multirod Pt NPs (iii): Under identical conditions, 0.1 g Pt(acac)2 was dissolved totally into 3 mL OA at 70 ºC overnight. The resulting orange solution was injected into 10 mL OA at 250 ºC. Then the reaction medium was cooled quickly to 150 ºC and maintained for two hours.

2. Synthesis of Pt-IO Hybrid NPs

Heterodimers Pt-IO (iv): Firstly, the starting templates—spherical Pt NPs (i), were prepared by following the procedure described above. After the reaction medium of colloidal spherical Pt NPs was cooled to room temperature, 5 mL OA, 0.9 mL oleic acid and 20 mL octadecene were introduced into it. The solution was heated up to 90 ºC and maintained for half hour. Then 0.2 mL Fe(CO)5 was injected into it and kept for another one hour. Finally, the solution was annealed at 150 ºC for one hour followed by another annealing at 300 ºC for one hour.

Core-shell Pt@IO NPs (v): Similar to the reaction conditions of sample (iv), core-shell like NPs were formed when the amount of Fe(CO)5 was increased to 0.9 mL. A magnetic separation process was employed to purify core-shell NPs. Typically, the coarse black precipitate was redispersed into 20 mL hexane with 0.1 mL oleic acid and 0.1 mL OA. After sonication, magnetic core-shell NPs were collected by permanent magnet and the soluble particles were discarded. Such process was repeated 4-6 times till all NPs could be collected by the permanent magnet in the hexane solution.

Jelly-Like Pt-IO NPs (vi): Typically, the templates, multirod Pt NPs(iii), were formed in the procedure described above. 5 mL OA, 0.9 mL oleic acid and 20 mL octadecene were introduced into it. The solution was heated up to 90 ºC and maintained for half hour under flowing nitrogen gas. Then 0.3 mL Fe(CO)5 was injected into the solution and kept for another one hour. At the end, solution was annealed at 150 ºC and 280 ºC for one hour, separately.

Identically, flower like Pt-IO NPs could be formed by reduce the addition mount of Fe(CO)5 to 0.2 ml and final annealing temperature from 280 ºC to 240 ºC.

3 Synthesis of Pt-Au Hybrid NPs

Peanut-like Pt-Au NPs (vii): The starting templates, 7 nm spherical NPs, were synthesized by following the procedure used for sample (i). 10 mL toluene was added into the reaction solution after it cooled to room temperature. 0.3 g HAuCl4·3H2O and 1 mL OA was dissolved into 20 mL toluene. Then the solution was added into the reaction medium of spherical Pt NPs. Finally, the mixture was annealed at 60 ºC overnight.

Grape-like Pt-Au NPs (viii): Firstly, 0.1 g Pt(acac)2 and 10 mL OA were mixed, and heated up to 100 ºC and maintained overnight. Then the mixture were heated up to 130 ºC and maintained for one day. 20 mL toluene was added into the reaction solution after it cooled to room temperature. Secondary, 0.3 g HAuCl4·3H2O and 1 mL OA was dissolved into 20 mL toluene. Then the HAuCl4 solution was added into the reaction medium. Afterwards, the mixture was annealed at 40 ºC overnight.

Similarly, less complex grape-like Pt-Au NPs could be formed with less complex Pt branched network NPs as the starting templates.

Bud-like Pt-Au NPs (ix): Typically, precursor (multirod Pt NPs) was formed by procedure used for sample (iii). 0.2 g HAuCl4·3H2O and 1 mL OA was dissolved into 20

mL toluene. Then the HAuCl4 solution was added into the reaction medium of branched Pt networks and maintained for one day at room temperature.

Under identical reaction conditions, the Au size of the bud-like Pt NPs could be modulated systemically by tuning the quantity of gold precursor (HAuCl4·3H2O). 0.2, 0.3, and 0.4 g HAuCl4·3H2O would result in 6.7, 9.0 and 10.5 nm gold particles. On the other hand, the complexity of the Pt domain of the hybrid NPs could be tuned by modulating the annealing periods of Pt(acac)2 at the first step.

Seed-network-like Au-Pt NPs (x): The templates (bud-like Pt-Au NPs) were synthesized by following the procedure used for Sample (ix). After collection, the colloidal NPs were redispersed into 10 mL toluene. Then the solution was mixed with 0.4 g Pt(acac)2 and 10 mL OA. Then the solution was carefully heated to 135 ºC at a heating rate of 2 ºC per minute and kept for 1 day.

Peanut-network-like Au-Pt NPs (xi): Sample (x) was used as the starting template. Typically, half sample (x) was dissolved into 3 mL toluene. 0.2 g HAuCl4·3H2O and 5 mL OA were mixed with 30 mL toluene. Then the two solutions were mixed and kept for one day.

4 Synthesis of Au-Pt-IO Ternary Hybrid NPs

Jelly-Like (Au-Pt)@IO hybrid NPs (xii): Firstly, templates (bud-like branched Pt NPs) were formed by the synthesis procedure used for Sample (ix). After collected and redispersed into 5 mL hexane, the colloidal NPs were introduced into a mixed solution of 20 mL OA, 0.8 mL oleic acid and 20 mL octadecene. The solution was heated up to 90 ºC and maintained for half hour under flowing nitrogen gas. Then 0.4 mL Fe(CO)5 was injected into the solution and kept for another one hour. At the end, the solution was annealed at 150 ºC and 260 ºC for one hour, separately.

Au-(Pt@IO) hybrid NPs (xiii): Firstly, bud-like Pt-Au hybrid NPs with Au size of 10.5 nm were formed using the procedure used for Sample (ix). After cooling to room temperature, NPs were collected and redispersed into hexane. Secondary, 20 mL OA, 0.6 mL oleic acid and 20 mL octadecene were introduced into it. The solution was heated up to 90 ºC and maintained for half hour under flowing nitrogen gas. Then 0.1 mL Fe(CO)5 was injected into the solution and kept for one hour. The solution was annealed at 150 ºC and 250 ºC for one hour, separately.

Pt-(Au@IO) hybrid NPs (xiv): Firstly, bud-like Pt-Au hybrid NPs with an Au size of 6.5 nm were formed in procedure used for Ssample (ix). After cooling to room temperature, NPs were collected and redispersed into hexane. Secondary, 20 mL OA, 0.6 mL oleic acid and 20 mL octadecene were introduced into it. The solution was heated to 90 ºC and maintained for half hour under flowing nitrogen gas. Then 0.12 mL Fe(CO)5 was injected into the solution and kept for another one hour. The solution was annealed at 150 ºC and 250 ºC for one hour, separately.

Dumbbell-like Au-Pt-IO hybrid NPs (xv): The Pt-IO heterodimers were synthesized by following the procedure as used for Sample (iv). After collected, the NPs were dissolved into 20 mL toluene with 10 mL OA. Then the mixture was refluxed for two hours at 110 ºC under flowing nitrogen gas. 0.3 g HAuCl4·3H2O and 1 mL OA were dissolved into 20 mL toluene. After the solution with NPs was cooled to room temperature, the HAuCl4 solution was added under stirring condition. Finally, the mixture was heated up to 60 ºC and annealed overnight.

Flower-like (Au-Pt)@IO hybrid NPs (xvi) : The starting templates, bud-like Pt-Au binary metal NPs with Au size of 10.5 nm, were synthesized by following the procedure used for Sample (ix). Then the templates were attached selectively with Fe through the decomposition of Fe(CO)5 at 230 ºC.

Flower-like Pt-(Au@IO) hybrid NPs (xvii): Similarly, less complex flower-like Pt-Au binary hybrid NPs were synthesized in a similar procedure used for Sample (viii). Then the Au NPs were coated selectively by Fe as the procedure of Sample (xiv). The elemental Fe was oxidized automatically in the air.

Figures Captions

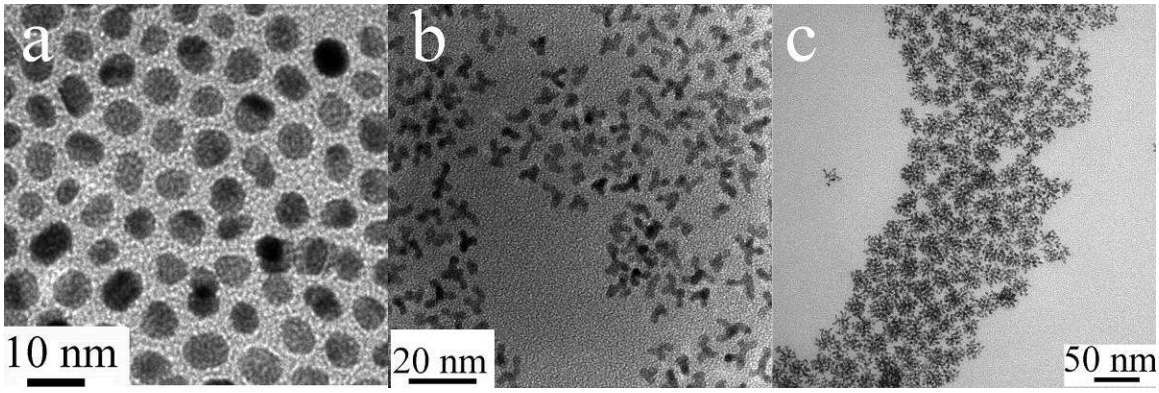


Figure S1. TEM images of Pt (a) spherical, (b) multirod and (c) branched network nonoparticles.

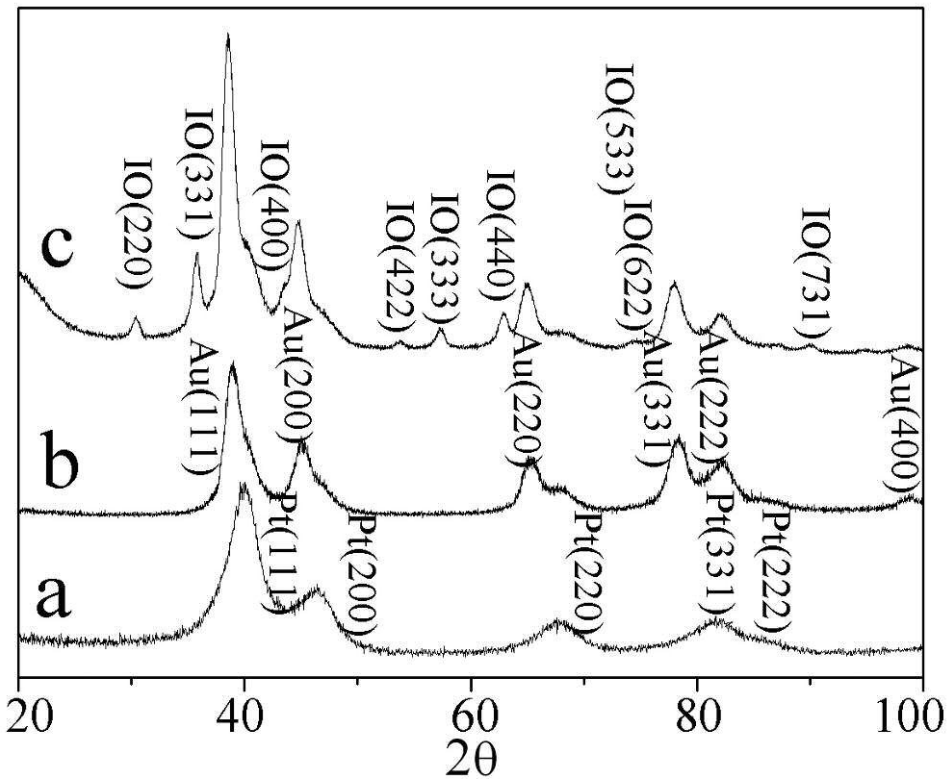
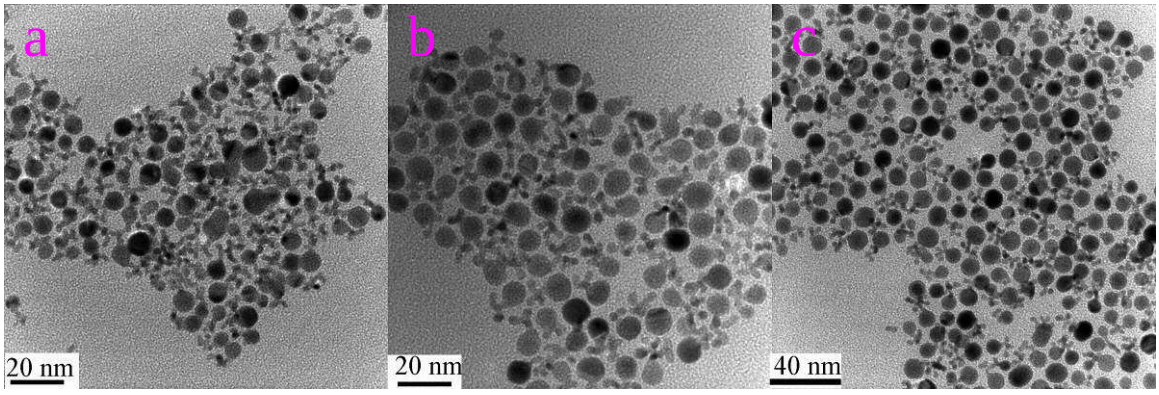


Figure S2. XRD patterns of (a) multirod Pt, (b) bud-like Pt-Au, and (c) jelly-like (Au-Pt)@IO hybrid NPs.



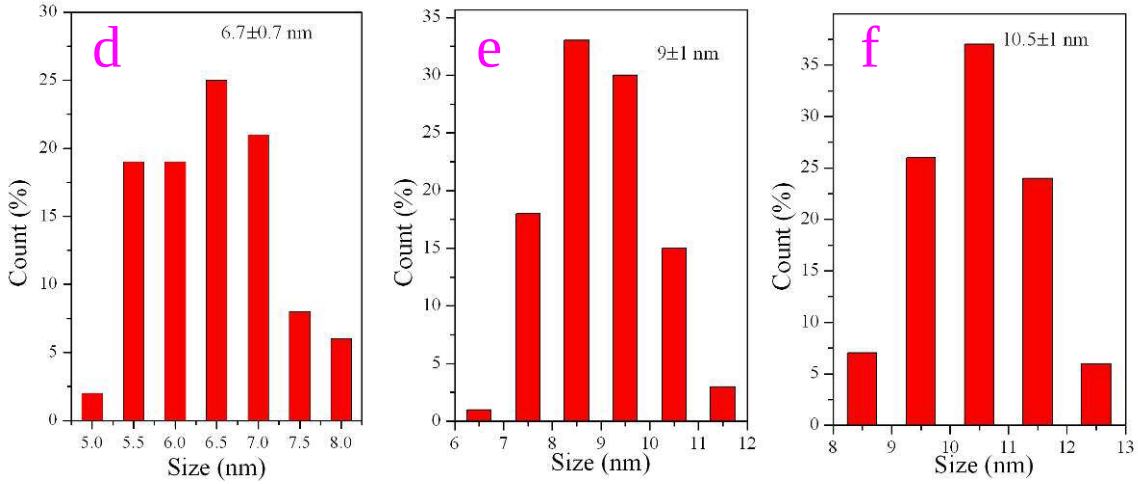


Figure S3. TEM images of bud-like Pt-Au binary metal nanoparticls with difference Au sizes: (a) 6.7 nm, (b) 9 nm, (c) 10.5 nm; and (d-f) the corresponding size distribution histograms of Au.

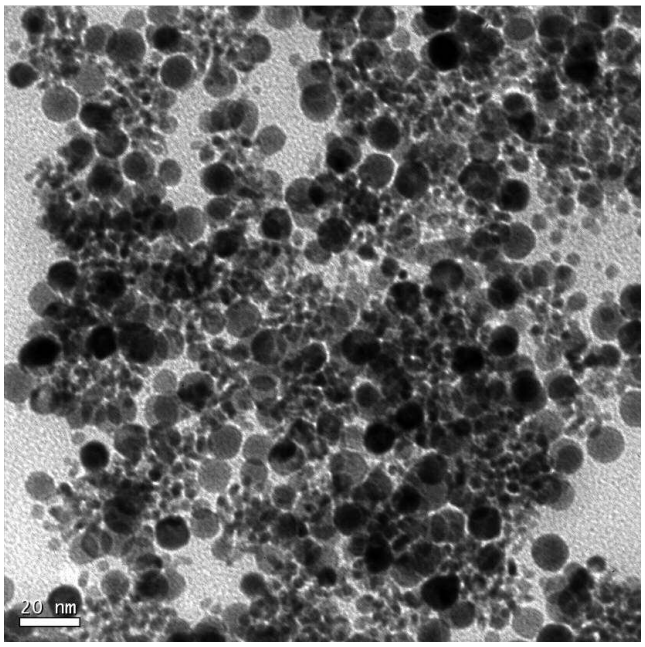


Figure S4. TEM image of grape-like Pt/Au nanoparticles with Pt branched network as vines.

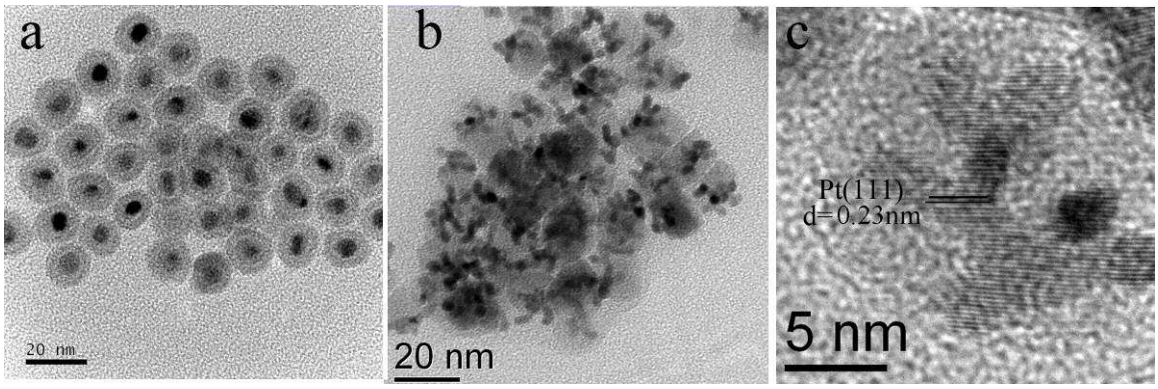


Figure S5. TEM images of (a) core-shell and (b) jelly-like IO-Pt NPs binary; (c) HRTEM images of jelly-like Pt-IO hybrid NPs

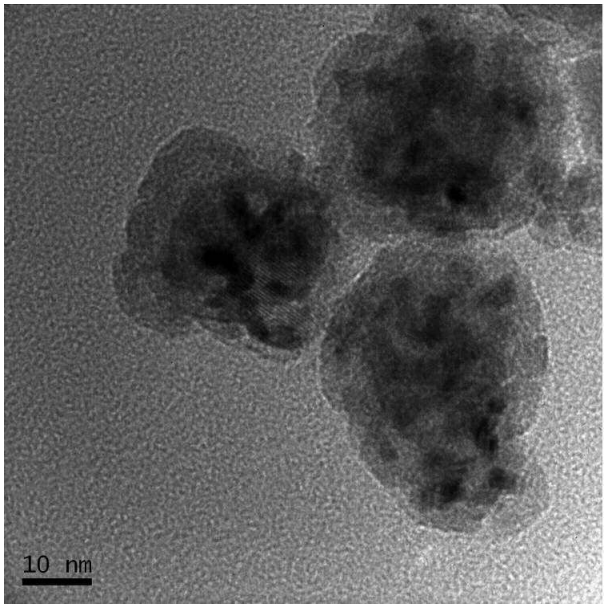


Figure S6. TEM image of jelly-like Pt@IO nanoparticles with and average size of 55 nm.

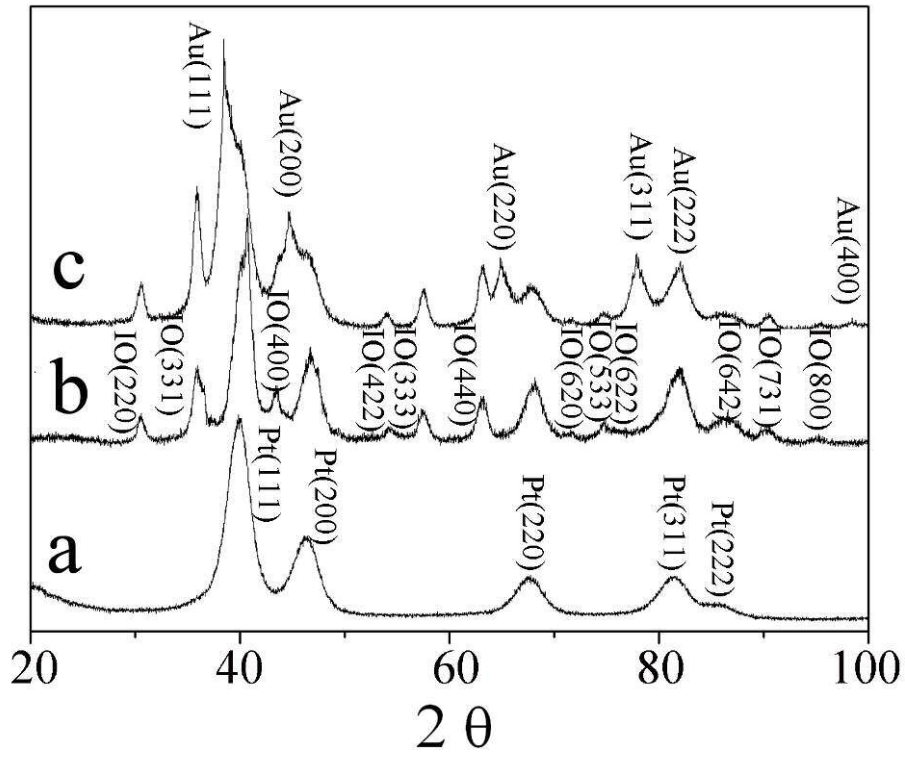


Figure S7: XRD patterns of (a) spherical Pt, (b) heterodimer-like Pt-IO, and (c) dumbbell -like Au-Pt-IO hybrid NPs.

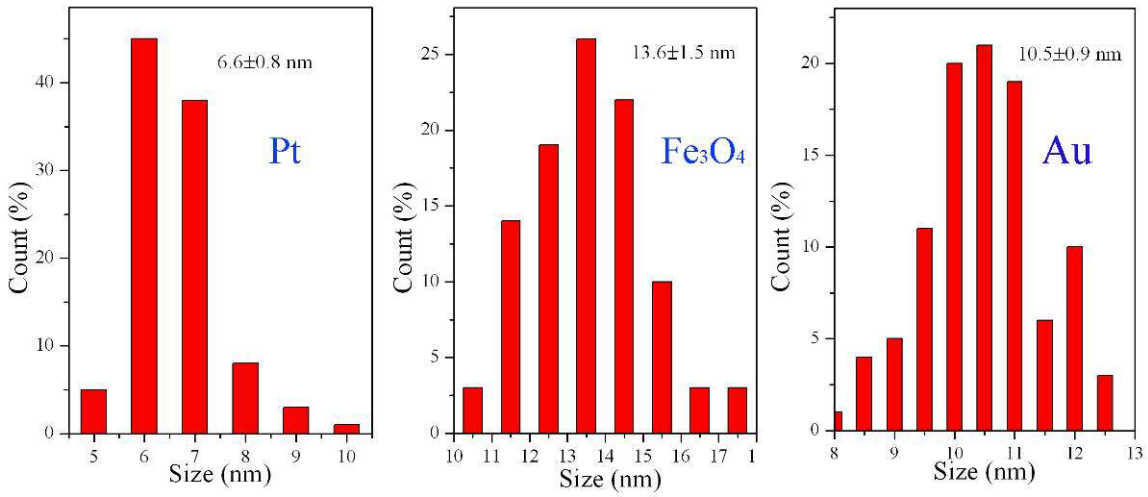


Figure S8. Size distribution histograms of different domains in Au-Pt-IO hybrid nanoparticles.

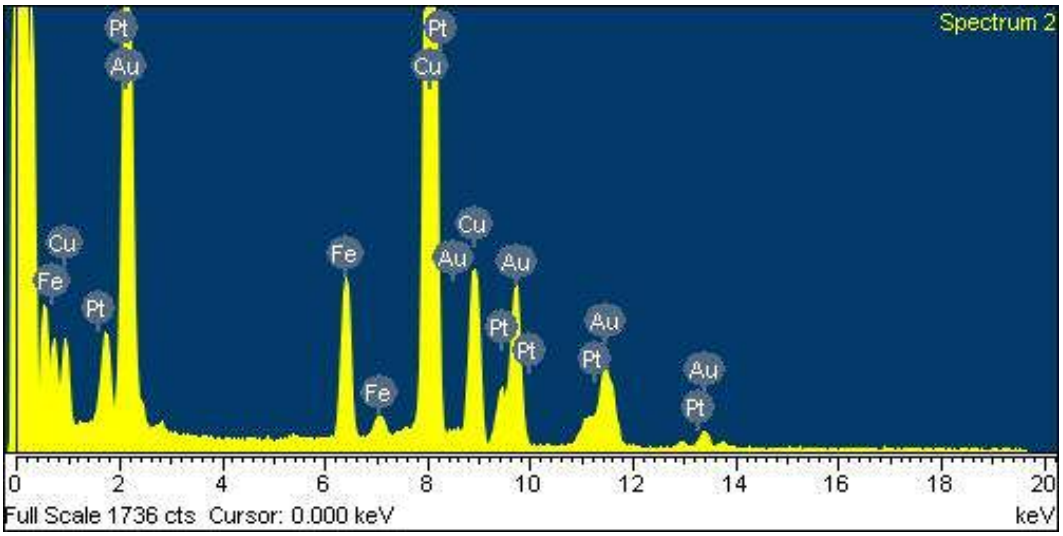


Figure S9. Energy dispersive x-ray (EDX) spectrum of dumbbell-like Au-Pt-IO hybrid nanoparticles.

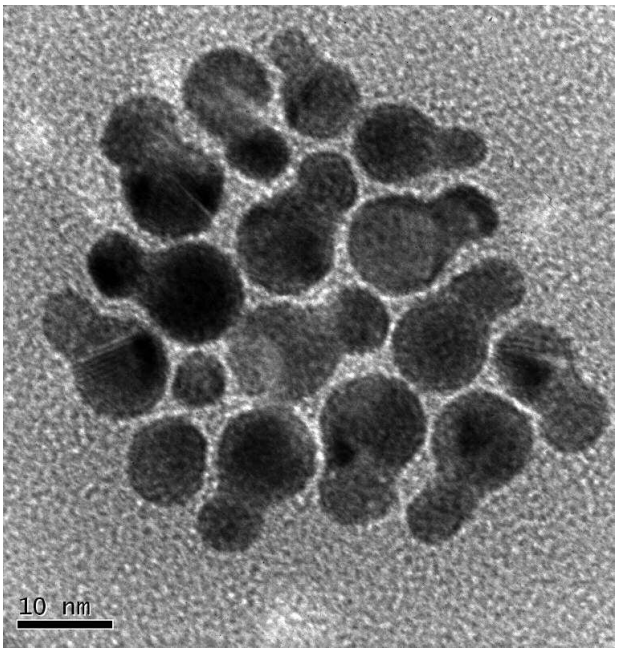


Figure S10. TEM image heterodimer like Au-Pt binary metal obtained through etching IO domains of dumbbell-like Pt-Au-IO with HCl.