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Supporting Information

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Metal-Compound-Induced Vesicles As Efficient Directors for Rapid Synthesis of Hollow Alloy Spheres

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***Synthesis: Hollow PdAu spheres*:** To a mixture of $KAuCl_4$ (4.8 mL, 5×10^{-3} M in H_2O), $PdCl_2$ (1.6 mL, 0.01 M in acetonitrile) solutions, 40 mL of tetrabutylammonium bromide (**Bu_4NBr**) solution (0.01 M, in H_2O) was added and stirred for 3 min., a freshly prepared $NaBH_4$ solution (2 mL, 0.1 M) was added quickly in one pot. After vigorous stirring for 1 min, the product was collected by centrifugation and re-dispersed in water. This purification procedure was repeated for several times to remove the excess Bu_4NBr and byproducts.

***Hollow PdAg spheres*:** The synthesis procedures are similar to that of PdAu except $AgNO_3$ (3.2 mL, 5×10^{-3} M in H_2O) was used instead of $KAuCl_4$.

***Hollow AuAg spheres*:** To a mixture of $KAuCl_4$ (3 mL, 5×10^{-3} M in H_2O), and $AgNO_3$ (3 mL, 5×10^{-3} M in H_2O) solutions, 30 mL of Bu_4NBr solution (0.01 M, in H_2O) was added and stirred for 3 min., a freshly prepared $NaBH_4$ solution (2 mL, 0.1 M) was added quickly in one pot. After vigorous stirring for 1 min, the product was collected by centrifugation and re-dispersed in water. This purification procedure was repeated for several times to remove the excess Bu_4NBr and byproducts.

***Hollow AuPt spheres*:** The synthesis procedure is similar to that of AuAg except K_2PtCl_6 (1.6 mL, 5×10^{-3} M in H_2O) solutions was used instead of $AgNO_3$.

***Hollow PdAuPt spheres*:** To a mixture of $KAuCl_4$ (3.2 mL, 5×10^{-3} M in H_2O), $PdCl_2$ (1.6 mL, 0.01 M in acetonitrile), and K_2PtCl_6 (1.6 mL, 5×10^{-3} M in H_2O) solutions, 30 mL of Bu_4NBr solution (0.01 M, in H_2O) and H_2O (10 mL) was added and stirred for 3 min, a freshly prepared $NaBH_4$ solution (2 mL, 0.1 M) was added quickly in one pot. After vigorous stirring for 1 min, the product was collected by centrifugation and re-dispersed in water. This purification procedure was repeated for several times to remove the excess Bu_4NBr and byproducts.

***Hollow PdAuAg spheres*:** To a mixture of $KAuCl_4$ (3.2 mL, 5×10^{-3} M in H_2O), $PdCl_2$ (1.6 mL, 0.01 M in acetonitrile), and $AgNO_3$ (1.6 mL, 5×10^{-3} M in H_2O) solutions, 40 mL of Bu_4NBr solution (0.01 M, in H_2O) and H_2O (10 mL) was added and stirred for 3 min, a freshly prepared $NaBH_4$ solution (2 mL, 0.1 M) was added quickly in one pot. After vigorous stirring for 1 min, the product was collected by centrifugation and re-dispersed in water. This purification procedure was repeated for several times to remove the excess Bu_4NBr and byproducts.

***Hollow PdCoPt and PdPtRu spheres*:** The synthesis procedures are similar to that of PdAuPt except $CoCl_2$ (or $CoSO_4$) (3.2 mL, 5×10^{-3} M in H_2O) or $RuCl_3$ (3.2 mL, 5×10^{-3} M in H_2O) were used instead of $KAuCl_4$.

XRD measurements:

X-ray power diffraction (XRD) measurement of the as-prepared samples was performed on a Rigaku D/max rA X-ray diffractometer with

graphite-monochromatized Cu Kα radiation (λ = 1.54187 Å) using a scanning rate of 0.06° s^{-1}. Figure S1 (top) shows the XRD patterns of as-prepared AuPdPtAg sample, which is consist with a single-phase fcc structure. Figure S1 (bottom) shows the XRD patterns of as-prepared AuPdAg sample.

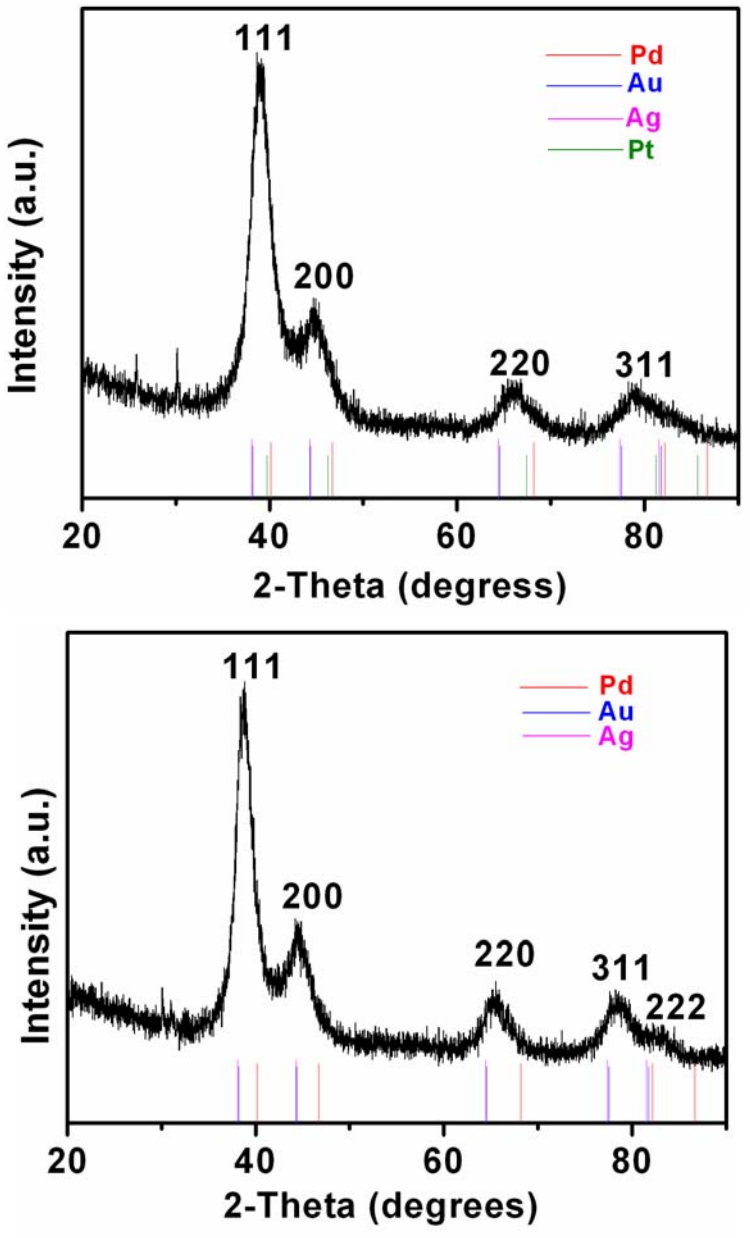

Figure S1. XRD patterns of hollow $Au_{27}Pd_{43}Pt_{19}Ag_{11}$ (top) and $Au_{38}Pd_{41}Ag_{21}$ (bottom) spheres. Color lines indicate the standard peak positions of different metals.

EDS Spectra

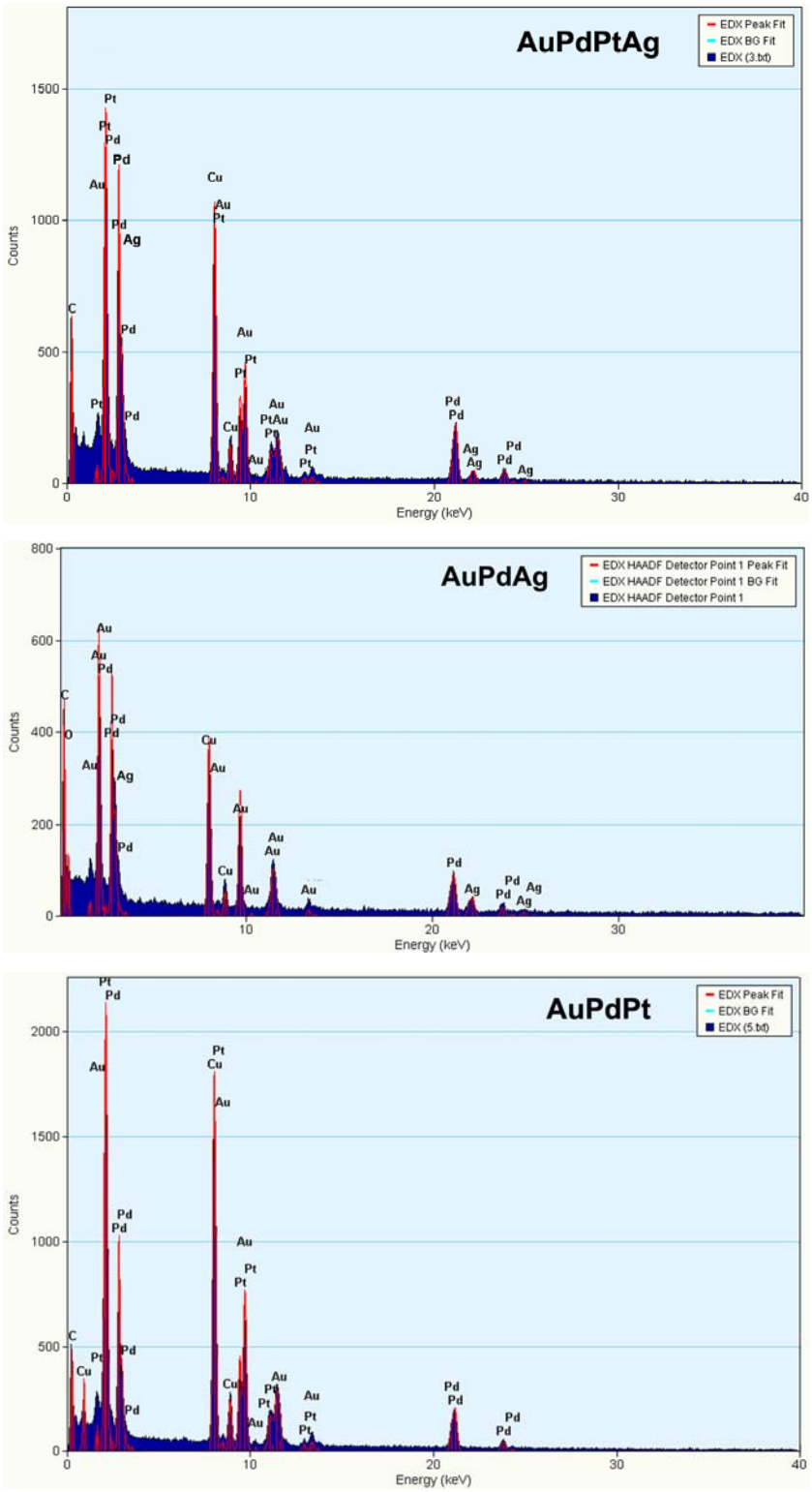

Figure S2. EDS data for AuPdPtAg, AuPdAg, and, AuPdPt, respectively.

XPS Analysis

The XPS spectra of hollow AuPdPtAg spheres were shown in **Figure S3**. In the survey spectra, the peaks for O can be attributed to the O_2, CO_2, or H_2O adsorbed on the surface of the sample, whereas weak C, N, and Br peaks can be attributed to the small amount of surfactant Bu_4NBr.

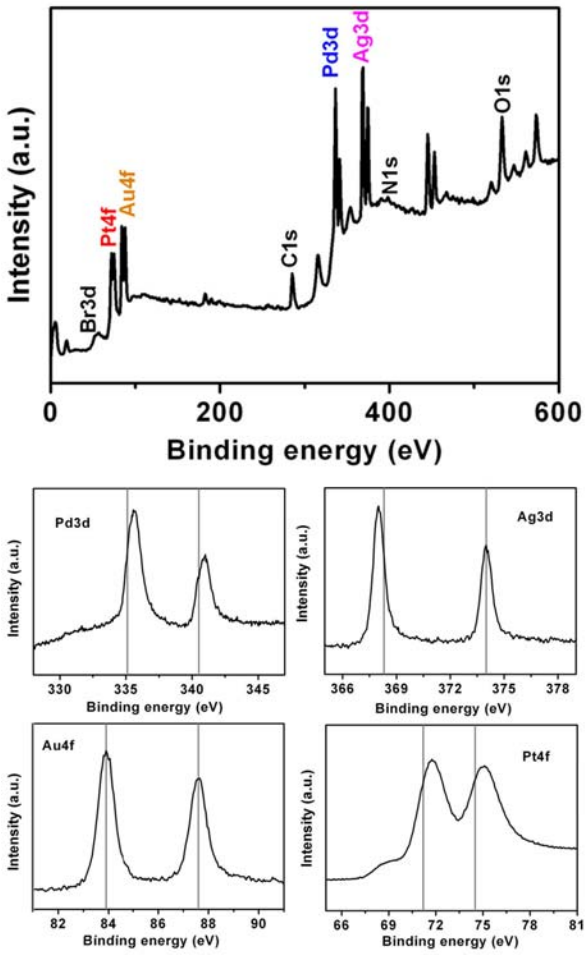

Figure S3.

The binding energies of different metals in alloys AuPdPtAg, AuPdAg, AuPdPt, and pure metals were illustrated in Table S1.

Table S1. XPS data

	Standard	**AuPdPtAg**	**AuPdAg**	**AuPdPt**
$Pd3d_{5/2, 3/2}$	**335.2/340.5**	**335.7/ 341.95**	**335.6/341**	**335.4/ 340.7**
$Au4f_{7/2, 5/2}$	**83.9/87.6**	**83.9/ 87.65**	**83.85/ 87.55**	**83.85/ 87.55**
$Pt4f_{7/2, 5/2}$	**71.2/74.5**	**71.75/ 75.1**	----------	**72.2/ 75.45**
$Ag3d_{5/2, 3/2}$	**368.3/374.0**	**368.0/ 373.95**	**367.95/373.95**	----------

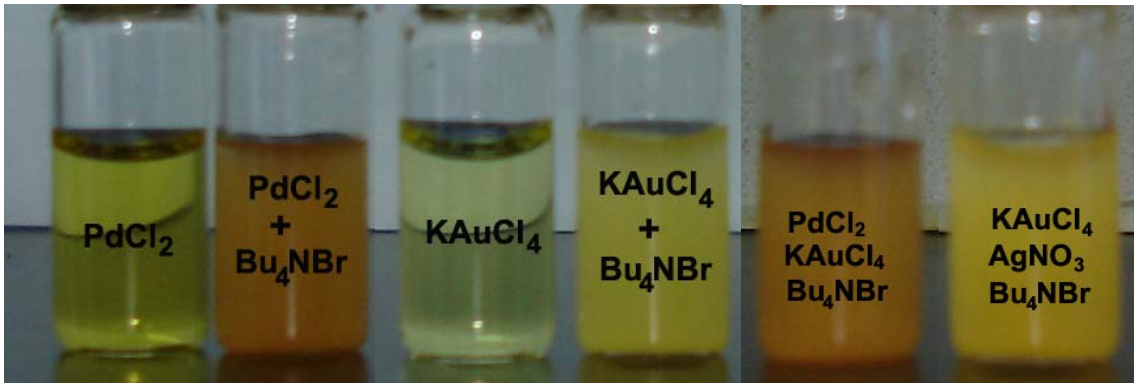

Figure S4. The spontaneous formation of vesicles were evidenced by distinct turbidity of the mixture.

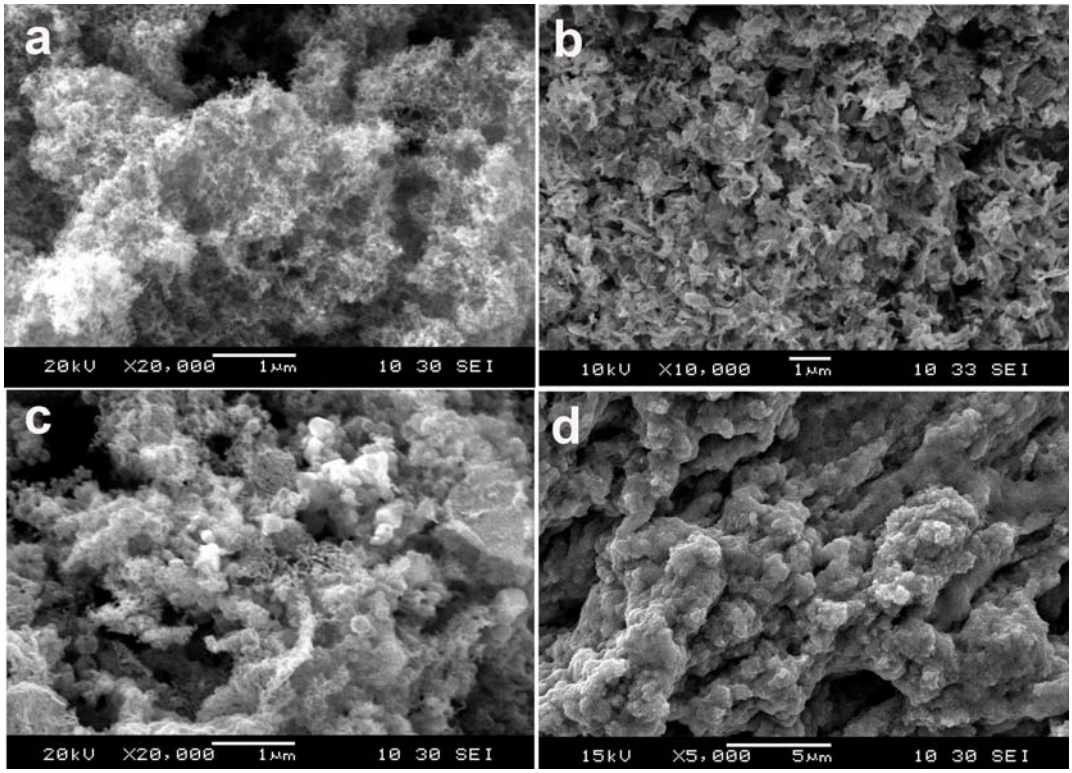

Figure S5. SEM images of PdAuPtAg samples prepared in control experiments. a) synthesized in ethanol system at the presence of Bu_4NBr; b) in water system at the presence of Bu_4NBr, sonicating for 3 min. before reduction by $NaBH_4$; c) in water system at the presence of Et_4NBr; d) in water system at the presence of Me_4NBr.

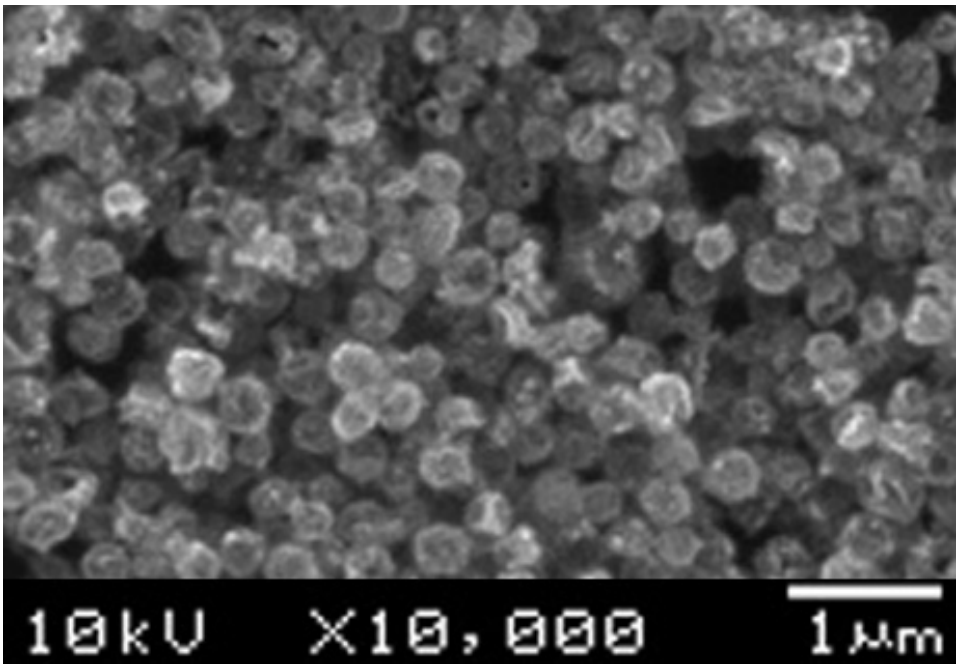

Figure S6. SEM image of RuPdPt hollow spheres.

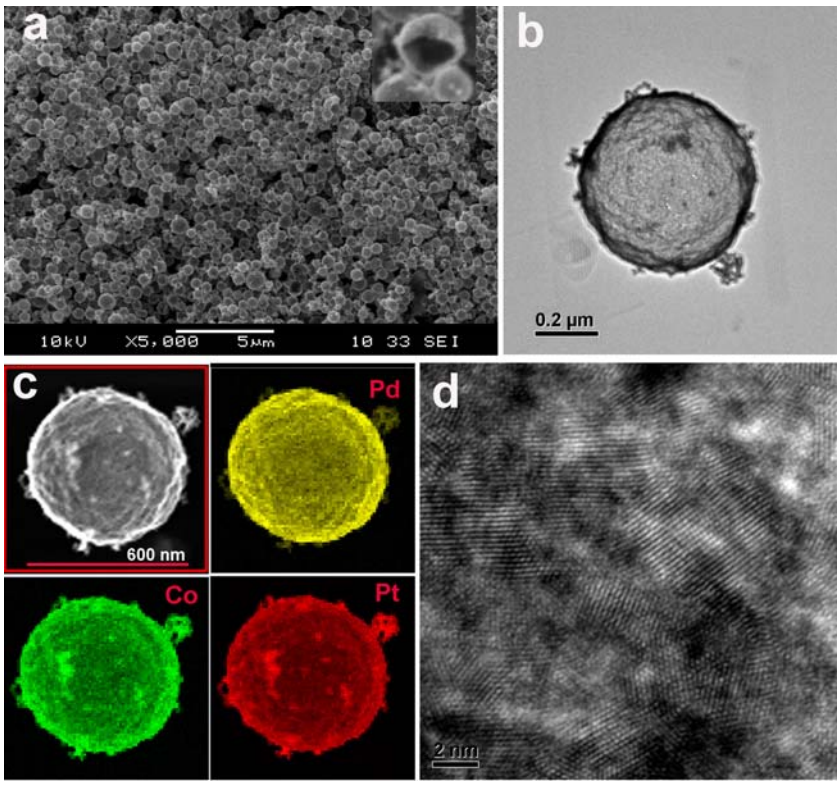

Figure S7. a) SEM image of hollow CoPdPt spheres. Inset: enlarged view of a cracked hollow sphere; b) TEM image of a representative hollow spheres; c) elemental mapping of Co-Pd-Pt; d) HRTEM image of the hollow shell.