Supplementary Information

Highly Efficient Three-Solvent Methodology for Separating Colloidal Nanoparticles

Zhe Tan,[†,a] Yuhan Liu,[†,a] Bo Huang*[,a,b]

† These authors contributed equally.

*Correspondence and requests for materials should be addressed to

B. Huang (email: bohuang@xjtu.edu.cn).

[a]*Institute of Chemical Engineering and Technology, Xi'an Jiaotong University, Innovation Harbour, Xi-xian New District, Xi'an 712000, China.*

[b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

Experimental Section

Synthesis of $Pd_{0.5}Rh_{0.5}$ NPs. To synthesize $Pd_{0.5}Rh_{0.5}$ alloy NPs, an EG solution (20 ml) containing K_2PdCl_4 (88 mg, 0.27 mmol) and $Na_3RhCl_6 \cdot 12H_2O$ (157 mg, 0.26 mmol) was added into a mixture solution of PVP (275 mg) and DEG (80 ml) at 220 ˚C under magnetic stirring condition. The reaction was kept for 15 min and cooled to room temperature. The dark brown solution was mixed with different solvent systems, and the mixture solution was centrifuged under the condition of 9000 rpm, 3 min.

Synthesis of Pt NPs. To synthesize Pt NPs, a mixture solution of EG solution (20 ml), water (5 ml) and K_2PtCl_6 (243 mg, 0.5 mmol) was added into DEG (80 ml) containing PVP (275 mg) at 220 ˚C under magnetic stirring condition. The reaction was kept for 13 min and cooled to room temperature. The process of centrifugation is the same as above.

Synthesis of Cu-Pd NPs. To synthesize $Cu_{0.5}Pd_{0.5}$ alloy NPs, an EG solution (20 ml) containing K_2PdCl_6 (99 mg, 0.25 mmol) and $Cu(CH_3COO)_2 \cdot H_2O$ (50 mg, 0.25 mmol) was added into a mixture solution of PVP (275 mg) and DEG (80 ml) at 220 ˚C under magnetic stirring condition. The reaction was kept for 12 min and cooled to room temperature. The process of centrifugation is the same as above.

Characterizations. The crystal structures were investigated by X-ray powder diffraction (XRPD) analysis using a Bruker D8 Advance diffractometer (Cu $K\alpha$ radiation). Transmission electron microscopy (TEM) images were captured using a Talos F200X operated at 200 kV accelerating voltage.

Formula 1

Sedimentation coefficient in centrifugation is expressed as follows:

$$S = \frac{d^2(\sigma - \rho)}{18\mu}$$

S: sedimentation coefficient; d: mean diameters of particles; σ: density of particles; ρ: density of solvents; μ: viscosity of solvents.

According to Formula 1, the large mean diameters and density of particles, as well as small density and viscosity of solvents, can lead to high sedimentation coefficient, which indicates easier separation.

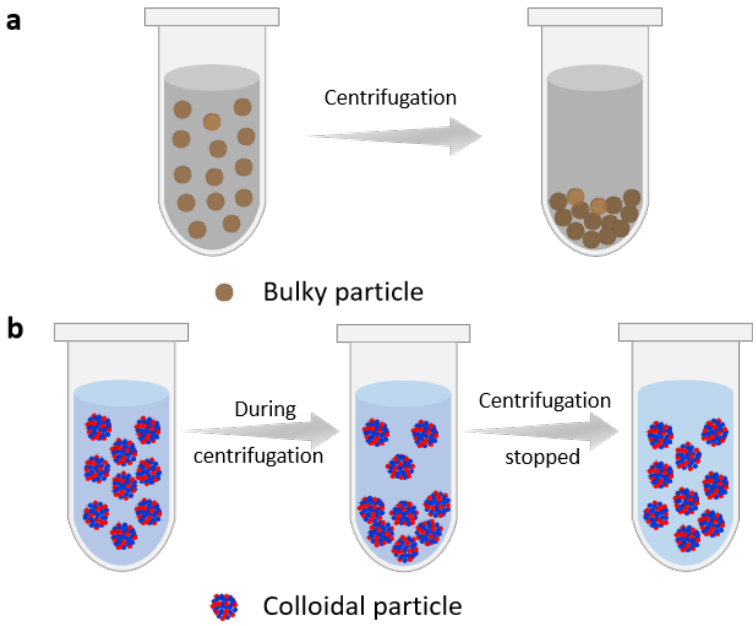

Fig. S1 Traditional theory applied on centrifugation processes in systems of (a) bulky particles and (b) colloidal particles.

From the traditional theory of centrifugation (Fig. S1), for case of bulky particles, they are mainly affected by buoyancy, friction and centrifugal forces during the centrifugal process, and the repulsion was negligible between bulky particles, therefore they can be centrifugated as precipitates (Fig. S1a). For the case of colloidal particles, since there is large repulsion between them, even the colloidal particles can be concentrated at the bottom of tube by centrifugation, they will redisperse homogeneously and cannot be separated if the centrifugation stopped (Fig. S1b). Therefore, the traditional theory could not explain the separation mechanism of immiscible nanoalloys.

Table S1. Toxicological Information

Chemical Name	Oral rat LD50
Acetone	5800 mg/kg
Diethyl ether	1215 mg/kg
Ethyl acetate	5620 mg/kg
Petroleum ether	3400 ppm

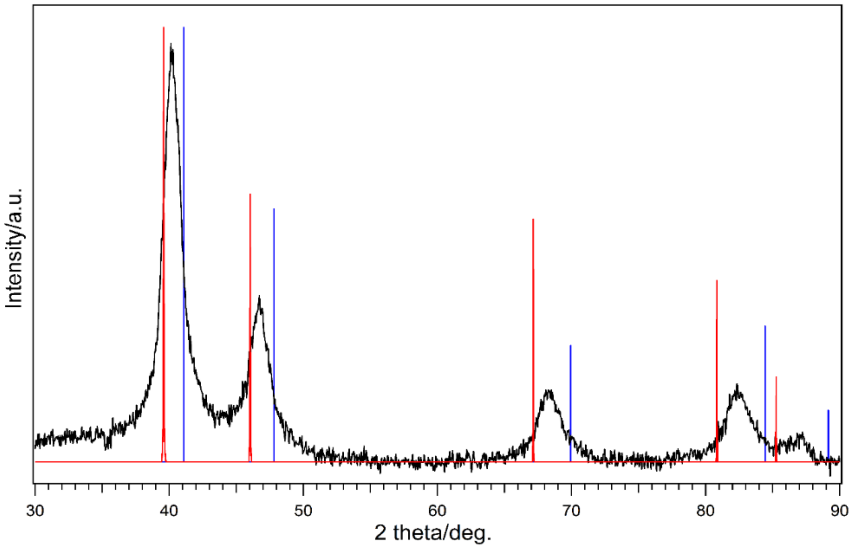

Fig. S2. XRPD patterns of $Pd_{0.5}Rh_{0.5}$ alloy NPs (black), compared with fcc-Pd NPs (red) and fcc-Rh NPs (blue) at 303 K. The radiation wavelength was 1.54056 Å.

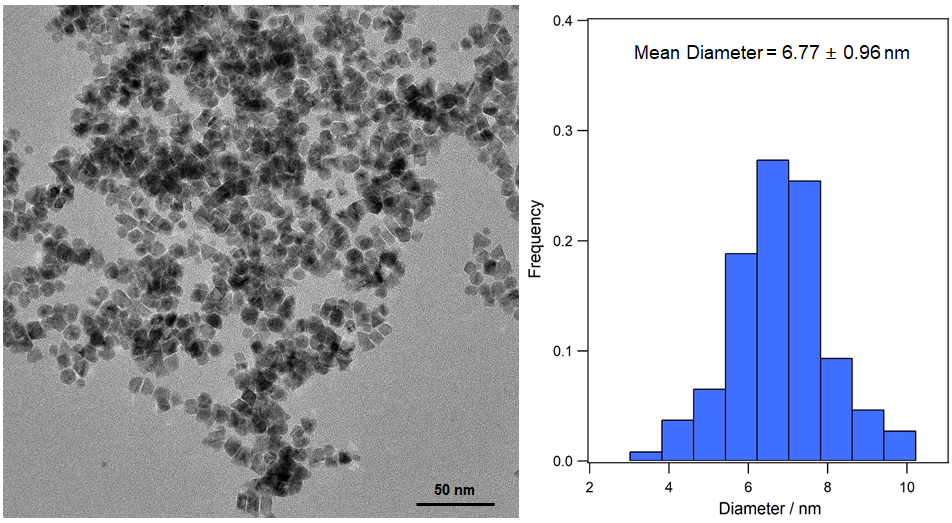

Fig. S3. TEM image and histogram of $Pd_{0.5}Rh_{0.5}$ alloy NPs. Single distribution is shown.

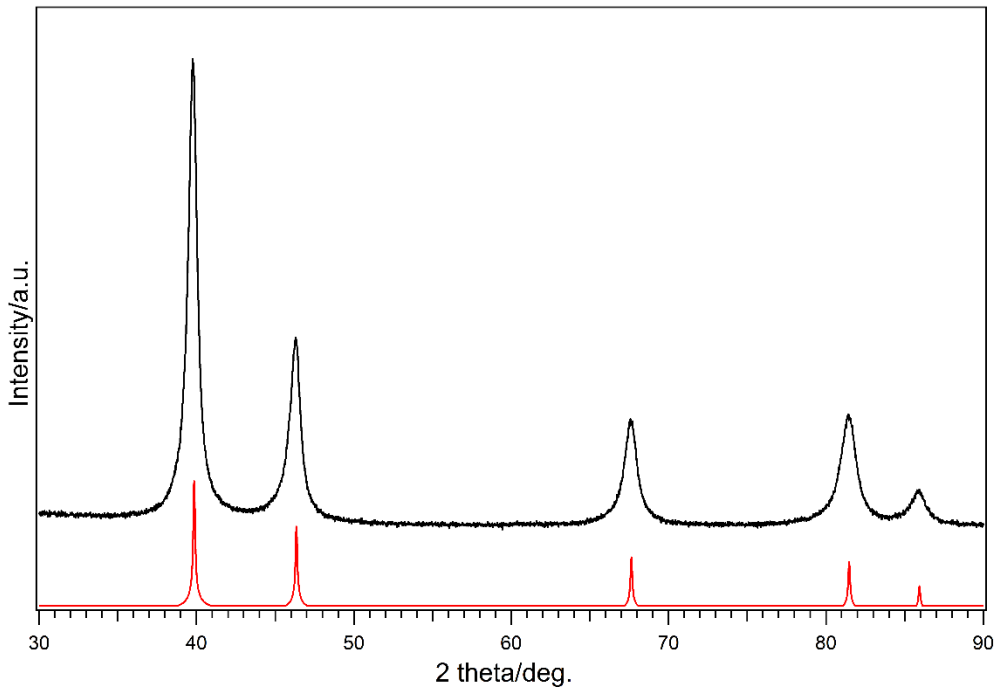

Fig. S4. XRPD patterns of Pt NPs (black), compared with fcc-Pt NPs (red) at 303 K. The radiation wavelength was 1.54056 Å.

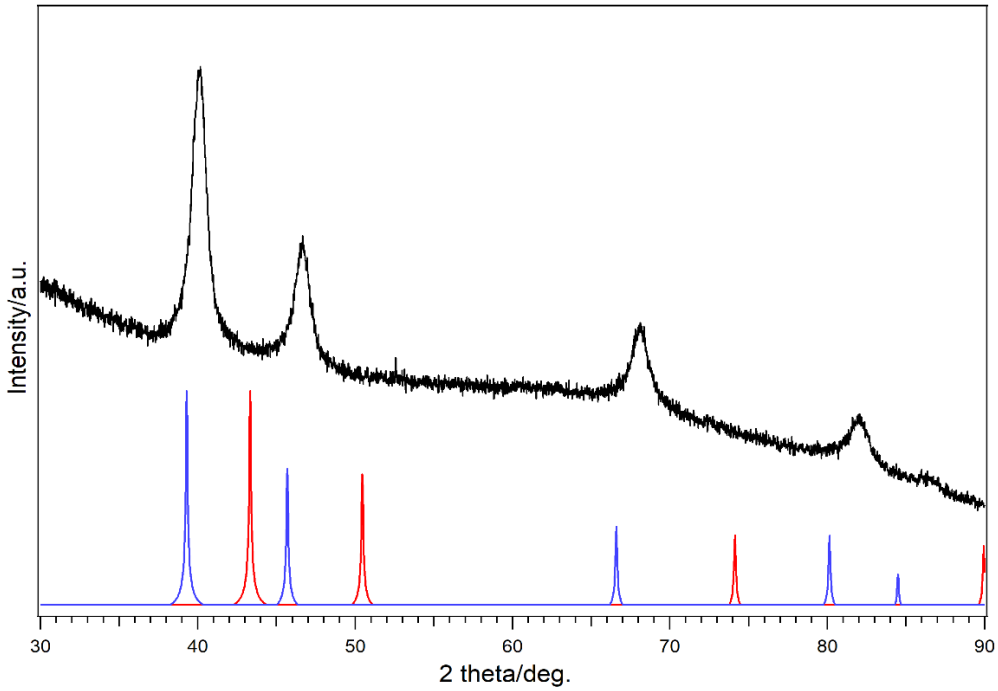

Fig. S5. XRPD patterns of Cu-Pd alloy NPs (black), compared with fcc-Cu NPs (blue) and fcc-Pd NPs (red) at 303 K. The radiation wavelength was 1.54056 Å.

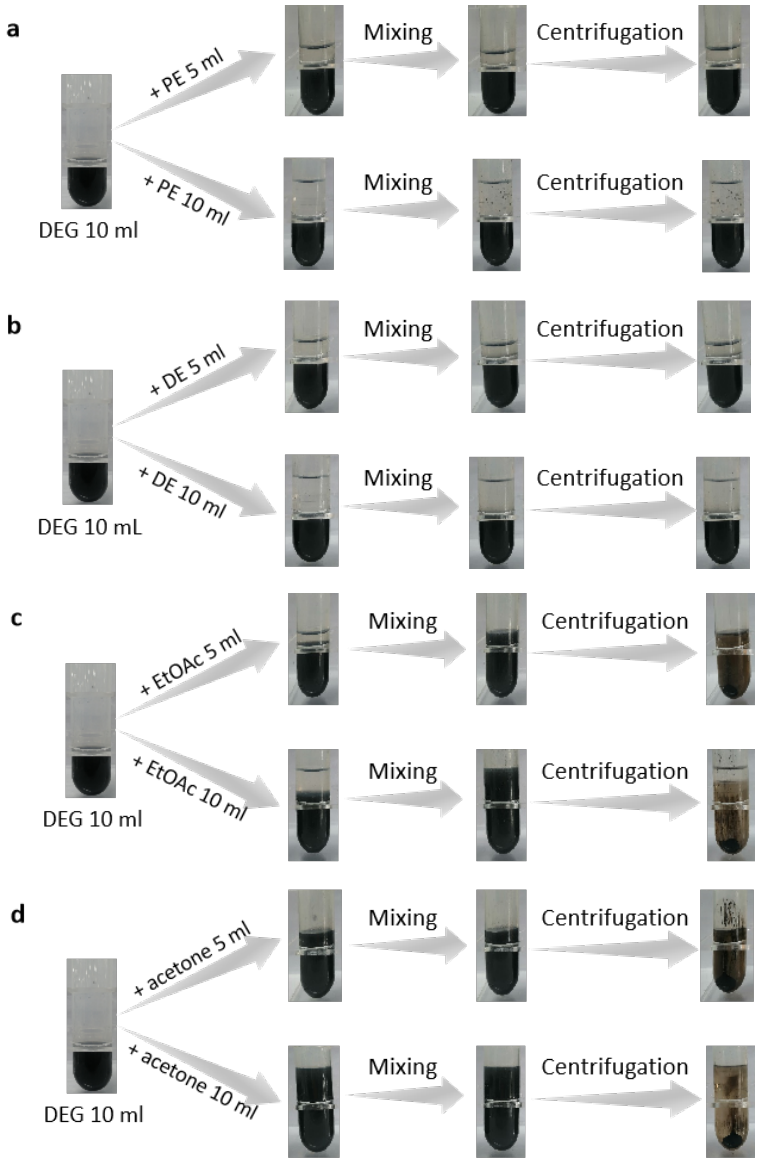

Fig. S6 The experimental procedures for the two-solvent systems: 10 ml of DEG with 5, 10 ml of (a) petroleum ether, (b) diethyl ether, (c) EtOAc and (d) acetone.

*DEG= diethyl glycol, PE= petroleum ether, DE= diethyl ether, EtOAc= ethyl acetate. The same below.

In DEG-petroleum ether system, we added 5, 10 ml of petroleum ether in different tubes, respectively (Fig. S6a). The petroleum ether was not miscible with DEG solution after mixing. After centrifugation, the NPs have not been separated from the solution. In DEG-diethyl ether system, similar phenomena were observed (Fig. S6b).

In DEG-EtOAc system, we added 5, 10 ml of EtOAc in the two tubes, respectively (Fig. S6c). After mixing, the EtOAc solvent was miscible with DEG solution. However, the mixed solution layered after several seconds (Fig. S7). After centrifugation, the colours of the upper solution were dark brown and brown (some NPs remaining) for the corresponding tubes.

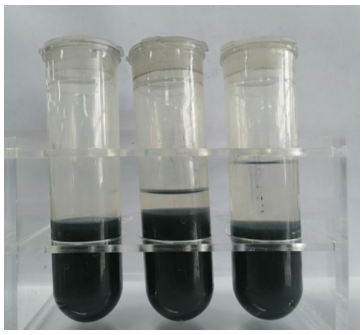

Fig. S7 DEG-EtOAc system held for several seconds after mixing

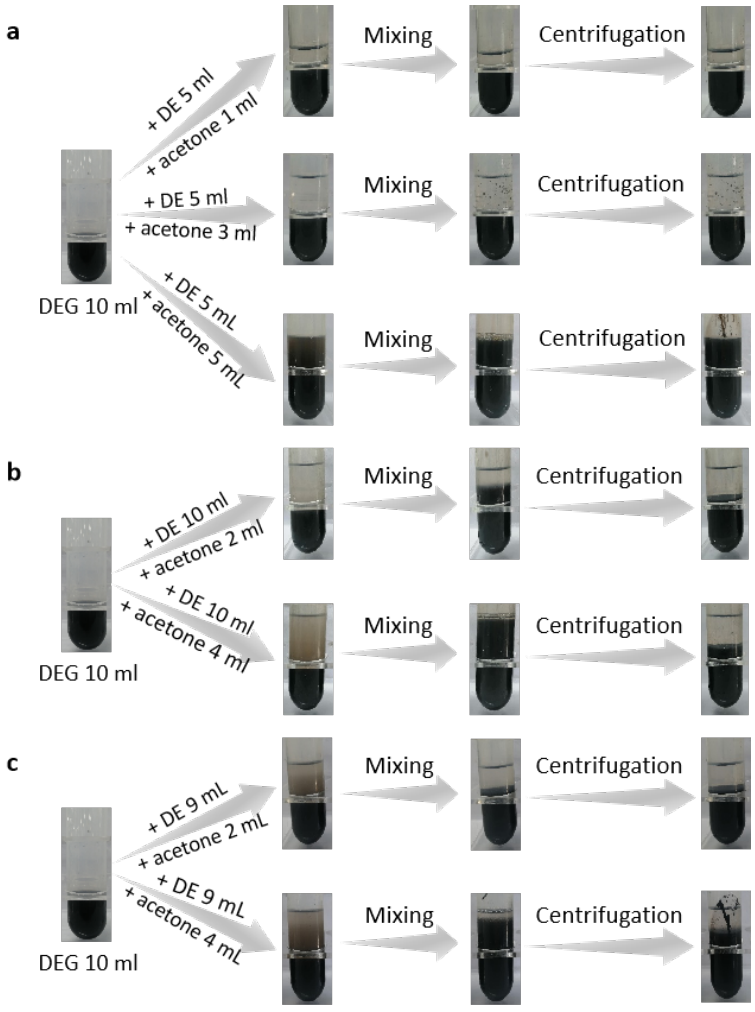

Fig. S8 The experimental procedures for the three-solvent DEG-diethyl ether-acetone system at the different combinations.

In Fig. S8a, 5 ml of diethyl ether and 1, 3, 5 ml of acetone were added to the three tubes containing 10 ml of DEG solution, respectively (Fig. S8a). After mixing, the solution with 1 ml of acetone layered, while the solutions in the other two tubes were mixed homogeneously. After mixing, the solutions were mixed homogeneously. After

centrifugation, the $Pd_{0.5}Rh_{0.5}$ NPs could not be separated at these solvent ratios, due to the insufficient solvent volumes.

In Fig. S8b, 10 ml of diethyl ether and 2, 4 ml of acetone were added in the two tubes, respectively (Fig. S8b). After mixing, 10, 10, 4 ml and 10, 10, 6 ml of DEG-diethyl ether-acetone can be mixed as one single phase. After centrifugation, the $Pd_{0.5}Rh_{0.5}$ NPs could not be separated successfully.

In Fig. S8c, the amount of diethyl ether was reduced to 9 ml, together with 2, 4 ml of acetone (Fig. S8c). The experimental phenomena were similar to the case of Fig. S8b.

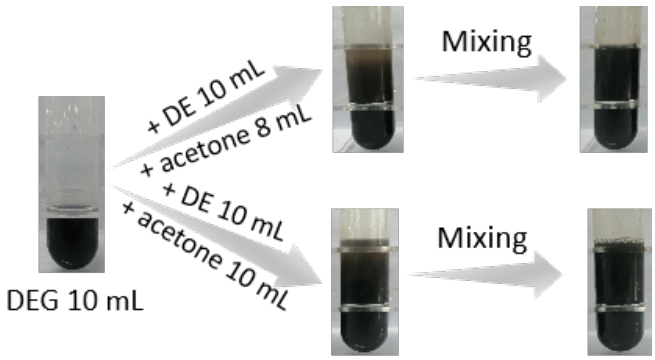

Fig. S9 The experimental procedures for the three-solvent DEG-diethyl ether-acetone system at the different combinations: 10 ml of DEG with 10 ml of diethyl ether and 8, 10 ml of acetone.

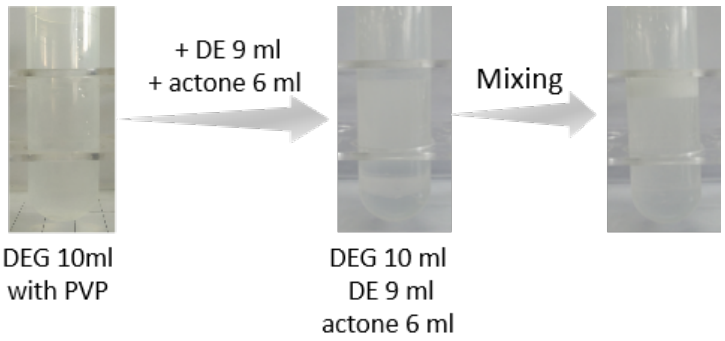

Fig. S10 The experimental procedures for the three-solvent DEG-diethyl ether-acetone combinations: 50 mg of PVP, 10 ml of DEG with 9 ml of diethyl ether and 6 ml of acetone.

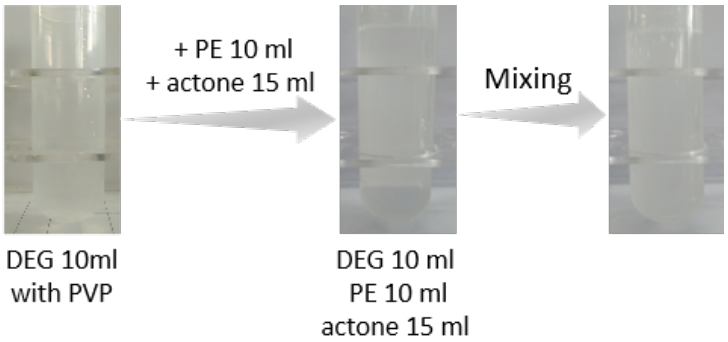

Fig. S11 The experimental procedures for the three-solvent DEG-petroleum ether-acetone combinations: 50 mg of PVP, 10 ml of DEG with 10 ml of petroleum ether and 2 ml of acetone.

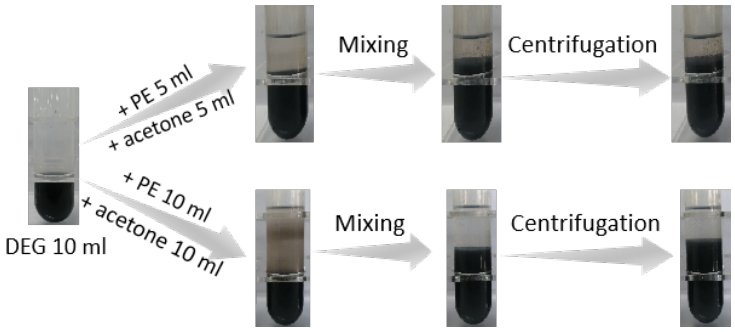

Fig. S12 The experimental procedures of the three-solvent DEG-petroleum ether-acetone system at different combinations.

In Fig. S12, 5, 10 ml of petroleum ether and 5, 10 ml of acetone were added to the two tubes containing 10 ml of DEG solution, respectively. After mixing and centrifugation, the added solvents could not mix with DEG solution, therefore failed to separate the $Pd_{0.5}Rh_{0.5}$ NPs. The main reason for the insolubility of the DEG-petroleum ether-acetone system was considered as too low polarity of petroleum ether.

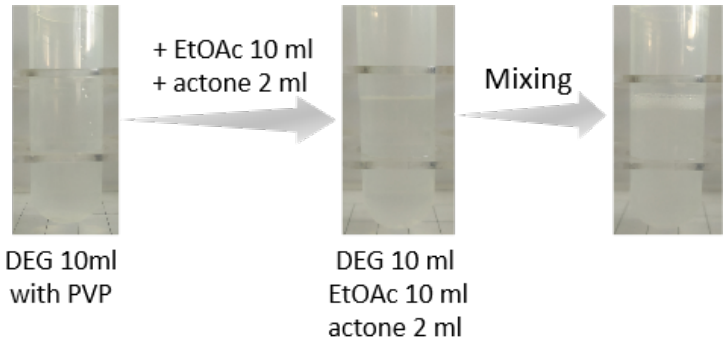

Fig. S13 The experimental procedures for the three-solvent DEG-EtOAc-acetone combinations: 50 mg of PVP, 10 ml of DEG with 10 ml of EtOAc and 2 ml of acetone.

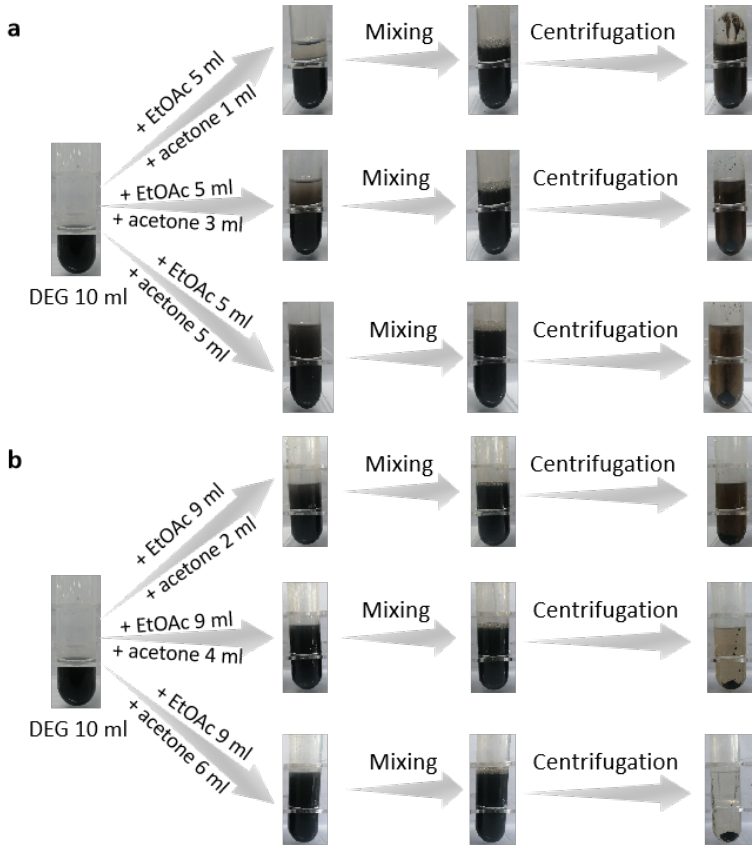

Fig. S14 The experimental procedures of the three-solvent DEG-EtOAc -acetone system at different combinations.

In DEG-EtOAc-acetone system, 5 ml of EtOAc and 1, 3, 5 ml of acetone were added in the different tubes, respectively (Fig. S14a). The added solvents can be mixed with DEG solution, but only small amounts of froth were observed at top of solutions in the three tubes. After centrifugation, even there were black precipitates at the bottom, the upper solutions were not transparent with some residual NPs.

Searching for the solvents ratio to completely separate the $Pd_{0.5}Rh_{0.5}$ NPs, the amount of EtOAc and acetone was increased (Fig. S14b). We added 9 ml of EtOAc and 2, 4, 6 ml of acetone in the three tubes. All the solutions in the different tubes can be mixed homogeneously and formed small amounts of froth. After centrifugation, the mixed solutions containing 2 and 4 ml of acetone were partially separated, there were still much NPs remaining in the solutions. The mixed solution containing 6 ml of acetone was almost separated, still with a little amount of NPs in the solution.

Table S2. Summary of the Separation Experiments

Solvent System		Volume of Solvents (mL)*					After mixing		After Centrifugation
		DEG	PE	DE	EtOAc	Acetone	Solubility	Amount of Froth	Separation Efficiency
1st generation	DEG-PE	10	5	-	-	-	Layered	-	Low
		10	10	-	-	-	Layered	-	Low
		10	15	-	-	-	Layered	-	Low
	DEG-DE	10	-	5	-	-	Layered	-	Low
		10	-	10	-	-	Layered	-	Low
		10	-	15	-	-	Layered	-	Low
	DEG-EtOAc	10	-	-	5	-	Soluble	-	Low
		10	-	-	10	-	Soluble	-	Medium
		10	-	-	15	-	Soluble	-	High
	DEG-Acetone	10	-	-	-	5	Soluble	-	Low
		10	-	-	-	10	Soluble	-	Medium
		10	-	-	-	15	Soluble	-	High
2nd generation	DEG-DE-Acetone	10	-	5	-	1	Layered	-	Low
		10	-	5	-	3	Soluble	-	Low
		10	-	5	-	5	Soluble	Small	Low
		10	-	10	-	2	Layered	-	Low
		10	-	10	-	4	Layered	-	Low
		10	-	10	-	6	Soluble	**Large**	**Completely**
		10	-	9	-	2	Layered	-	Low
		10	-	9	-	4	Layered	-	Low
		10	-	9	-	6	Soluble	**Large**	**Completely**
3rd generation	DEG-PE-Acetone	10	5	-	-	5	Layered	-	Low
		10	10	-	-	10	Layered	-	Low
		10	10	-	-	15	Layered	-	Low
	DEG-EtOAc - Acetone	10	-	-	5	1	Soluble	Small	Low
		10	-	-	5	3	Soluble	Small	Low
		10	-	-	5	5	Soluble	Small	Medium
		10	-	-	10	2	Soluble	**Large**	**Completely**
		10	-	-	10	4	Soluble	**Large**	**Completely**
		10	-	-	10	6	Soluble	**Large**	**Completely**
		10	-	-	9	2	Soluble	Small	Low
		10	-	-	9	4	Soluble	Small	High
		10	-	-	9	6	Soluble	Small	High

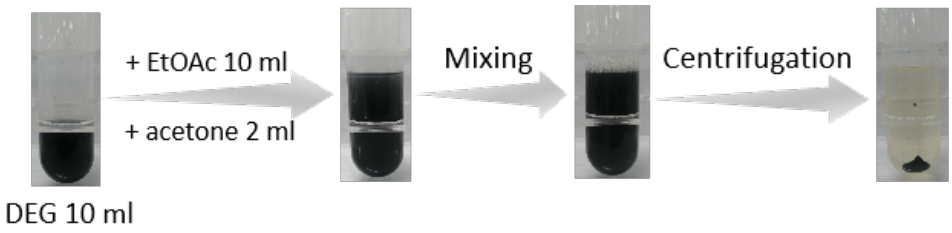

Fig. S15 The experimental procedures of the three-solvent DEG-EtOAc-acetone system at different combinations to separate Pt NPs.

According to Fig. S15, the 3rd generation solvent system of DEG-EtOAc-acetone can separate Pt NPs.

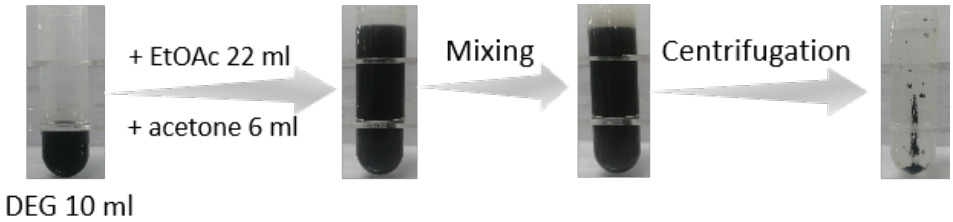

Fig. S16 The experimental procedures of the three-solvent DEG-EtOAc-acetone system at different combinations to separate Cu-Pd NPs.

According to Fig. S16, the 3rd generation solvent system of DEG-EtOAc-acetone can separate Cu-Pd NPs.