

Supporting Information

A General and Facile Approach to Disperse Hydrophobic Nanocrystals in Water with Enhanced Long-Term Stability

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Experimental section

Synthesis of Hydrophobic Colloidal Nanocrystals.

OA-capped Fe_3O_4 NCs¹ In a typical experiment, 10.80 g of iron (III) chloride and 36.50 g of sodium oleate was dissolved in a mixture solvent composed of 80 mL ethanol, 60 mL distilled water and 140 mL hexane. The resulting solution was heated to 70 °C and kept for four hours. When the reaction was completed, the upper organic layer containing the iron–oleate complex was washed three times with 30 mL distilled water in a separatory funnel. After washing, hexane was evaporated off, resulting in iron-oleate complex in a waxy solid form. Then, 36.00 g of the iron-oleate complex synthesized as described above and 5.70 g of oleic acid were dissolved in 200.00 g of 1-octadecene at room temperature. The reaction mixture was heated to 300 °C and kept for 1 hour. The resulting solution was then cooled to room temperature when the initial transparent solution became turbid and brownish black. 500 mL of ethanol was added into the solution to precipitate the nanocrystals, which were separated by centrifugation. After that, the precipitation was washed by cyclohexane/ethanol for twice. Finally, the product was redispersed in OA.

OA-capped TiO_2 nanorods² 30 mL of OA was added into a three-necked flask and

vented at 110 °C for 30 min to remove the low boiling point impurities. Then 3 mL of TBOT was injected into the three-necked flask under nitrogen atmosphere. The mixture was heated to 270 °C and kept for 3 h. The reaction process can yield the low boiling point impurities, so we need to evacuate the impurities with a glass syringe. After centrifugation, the precipitation was washed by cyclohexane/ethanol for twice. The final result was dispersed in OA.

OA-capped PbS QDs³ The synthesis of oleic-acid-capped PbS QD was performed based on a modified recipe previously documented. ODE was dried by heating to 100 °C under vacuum for 24 h and then placed in a glovebox. All experiments were performed under nitrogen atmosphere using standard air-free Schlenk line techniques. A solution of 0.4 mmol of PbO (89 mg), 1 mmol of oleic acid (282 mg), and 8 g of dried ODE was degassed at 100 °C in a 50 mL three-neck flask for 1 h under vacuum. The solution was then heated for an additional 1 h to 150 °C under nitrogen. After adjusting the solution to 130 °C, a solution of 0.2 mmol of (TMS)₂S (42.2 ul) dissolved in 1 mL ODE was rapidly injected into the hot solution. The NCs were grown at 130 °C for 2 min and the reaction was rapidly quenched by placing the flask in a room-temperature water bath and injecting 5 mL of anhydrous hexane, then purified by precipitation twice in hexane/isopropyl alcohol and once in hexane/acetone. Finally, the product was redispersed in OA.

OAm-capped Au NCs⁴ Typically, 18 mL of OAm was added into a three-necked flask and vented at 100 °C for 30 min to remove the low boiling point impurities. Then the solution was heated to 150 °C under nitrogen atmosphere. Subsequently, a solution of 0.03 g of chloroauric acid (HAuCl₄·3H₂O) dissolved in 2 mL of OAm was injected into the three-necked flask. The heating mantle was removed to cool down to room temperature when the mixture became red. After centrifugation, the precipitation was washed by cyclohexane/ethanol for twice. The final product was dispersed in OAm.

TOPO-capped TiO₂ nanodots⁵ Typically, TOPO (5 g) was heated at 150 °C for 5 min in vacuum to remove any low boiling point materials. After heating to 200 °C under N₂ atmosphere, TBOT (1.4 mL) was injected into the hot liquid. The resulting mixture was then heated to 320 °C, followed by a rapid addition of 0.55 mL of TiCl₄. The

solution was kept at 320 °C for 20 min to ensure complete reaction. After cooling to 80 °C, 10 mL of acetone was added to yield a white precipitate, which was isolated by centrifugation and subsequently washed with a toluene/acetone mixture to remove excess TOPO. The final product was dispersed in OA.

Phase transfer of hydrophobic nanoparticles

OA-capped Fe₃O₄ NCs 0.1 mL of as-synthesized Fe₃O₄ NC dispersed in OA (~30 mg/mL) was injected into 4 mL of mixture of sodium oleate and water/ethanol (the volume ratio can be in the range of 1:1 to 3:1). The resulting mixture was subjected to gentle shaking. After the nanocrystals dissolved into the solution completely, the result was isolated by centrifugation. The precipitate could then be redispersed in water.

OA-capped TiO₂ nanorods 0.1 mL of as-synthesized TiO₂ nanorods dispersed in OA (~20 mg/mL) was injected into 4 mL of mixture of sodium oleate and water/ethanol (the volume ratio can be in the range of 1:1 to 3:1). The resulting mixture was subjected to gentle shaking. After the nanocrystals dissolve into the solution completely, the result was isolated by centrifugation. The precipitate was dispersed in water to form a stable colloidal dispersion.

OA-capped PbS NCs 0.1 mL of as-synthesized PbS NCs dispersed in OA (~30 mg/mL) was injected into 4 mL of mixture of sodium oleate and water/ethanol (the volume ratio can be in the range of). The resulting mixture was subjected to gentle shaking. After the nanocrystals dissolve into the solution completely, the result was isolated by centrifugation. The precipitate was dispersed in water to form a stable colloidal dispersion.

OA-capped CdSe NCs 0.1 mL of as-synthesized CdSe NCs dispersed in OA (~20 mg/mL) was injected into 4 mL of mixture of sodium oleate (0.025 M) and water/ethanol (the volume ratio can be in the range of 1:1 to 3:1). The resulting mixture was subjected to gentle shaking. After the nanocrystals dissolve into the solution completely, the result was isolated by centrifugation. The precipitate was dispersed in water to form a stable colloidal dispersion.

OA-capped TiO₂ nanodots The purified TiO₂ nanodots were first dispersed in 2 mL of OA. 0.1 mL of above colloidal solution was injected into the mixture of sodium oleate (0.025 M) and water/ethanol (the volume ratio can be in the range of 1:1 to 3:1). The resulting mixture was subjected to gentle shaking. After the nanocrystals dissolve into the solution completely, the result was isolated by centrifugation. The precipitate was dispersed in water to form a stable colloidal dispersion.

OAm-capped Au NCs 0.1 mL of as-synthesized Au NC dispersion in OAm (~55 mg/mL) was injected into 4 mL of mixture of sodium oleate (0.025 M) and water/ethanol (the volume ratio can be in the range of 1:1 to 3:1). The resulting mixture was subjected to gentle shaking. After the nanocrystals dissolve into the solution completely, the result was isolated by centrifugation. The precipitate was dispersed in water to form a stable colloidal dispersion.

Using other amphiphilic ligand We used OAm-capped Au NCs as a sample. Sodium oleate was replaced by sodium decanoate, sodium myristate, dopamine hydrochloride and hexadecyltrimethylammonium bromide, respectively. The other conditions are the same as described above.

Table S1. Summary of phase transferred hydrophobic nanocrystals and the detailed information.

NC	Surfactant	Second ligand	Original solvent	Solvents used	Surface charge
Au	OAm	Oleate	OAm	H ₂ O/EtOH	-
Fe ₃ O ₄	OA	Oleate	OA	H ₂ O/EtOH	-
TiO ₂	OA	Oleate	OA	H ₂ O/EtOH	-
PbS	OA	Oleate	OA	H ₂ O/EtOH	-
CdSe	OA	Oleate	OA	H ₂ O/EtOH	-
TiO ₂	TOPO	Oleate	OA	H ₂ O/EtOH	-
Au	OAm	Oleate	OAm	H ₂ O/IPA	-
Au	OAm	Oleate	OAm	H ₂ O/DMF	-
Fe ₃ O ₄	OA	Oleate	OA	H ₂ O/IPA	-
Fe ₃ O ₄	OA	Oleate	OA	H ₂ O/DMF	-
Au	OAm	Decanoate	OAm	H ₂ O/EtOH	-
Au	OAm	Myristate	OAm	H ₂ O/EtOH	-
Au	OAm	Dopamine	OAm	H ₂ O/EtOH	+
Au	OAm	CTAB	OAm	H ₂ O/EtOH	+

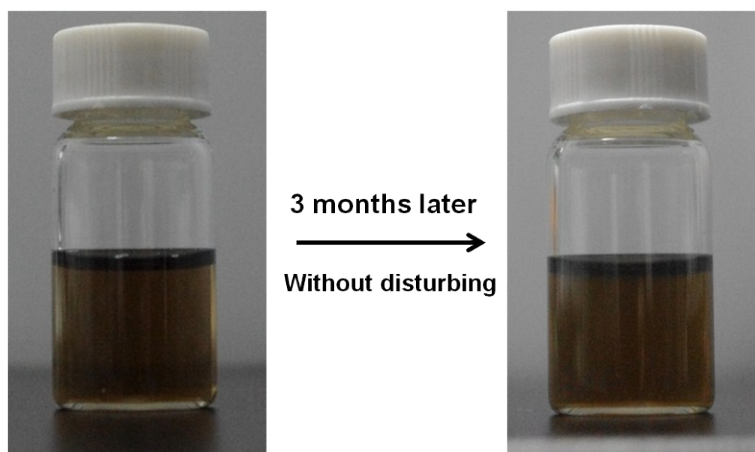


Figure S1. Photographs of Fe_3O_4 nanocrystals stored in water. No aggregation or precipitation has been observed after three months.

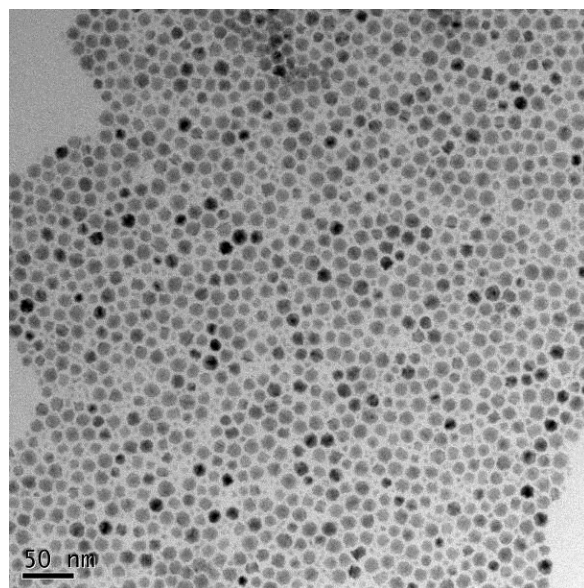


Figure S2. Low magnification TEM image of CdSe quantum dots after phase transfer.

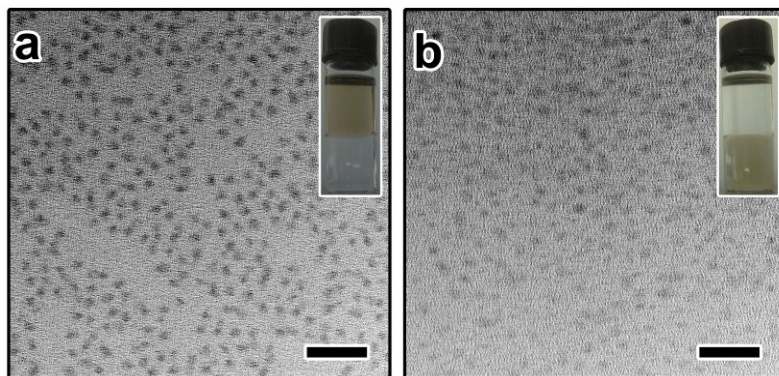


Figure S3. TEM images of PbS nanocrystals (a) before (in hexane) and (b) after (in water) phase transfer. The scale bars are 20 nm.

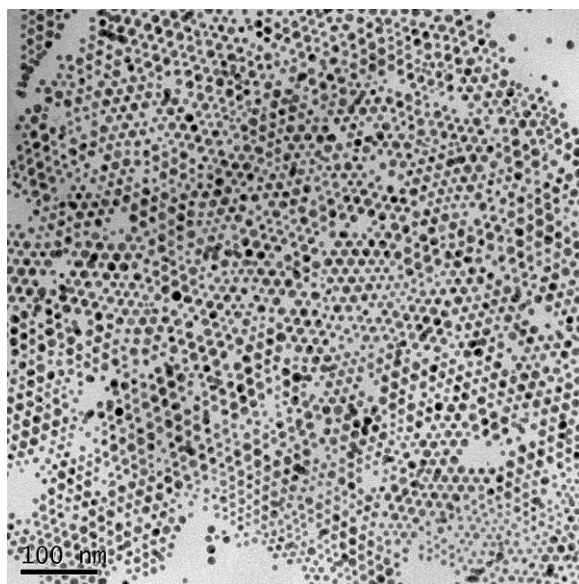


Figure S4. Low magnification TEM image of Au nanocrystals after phase transfer.

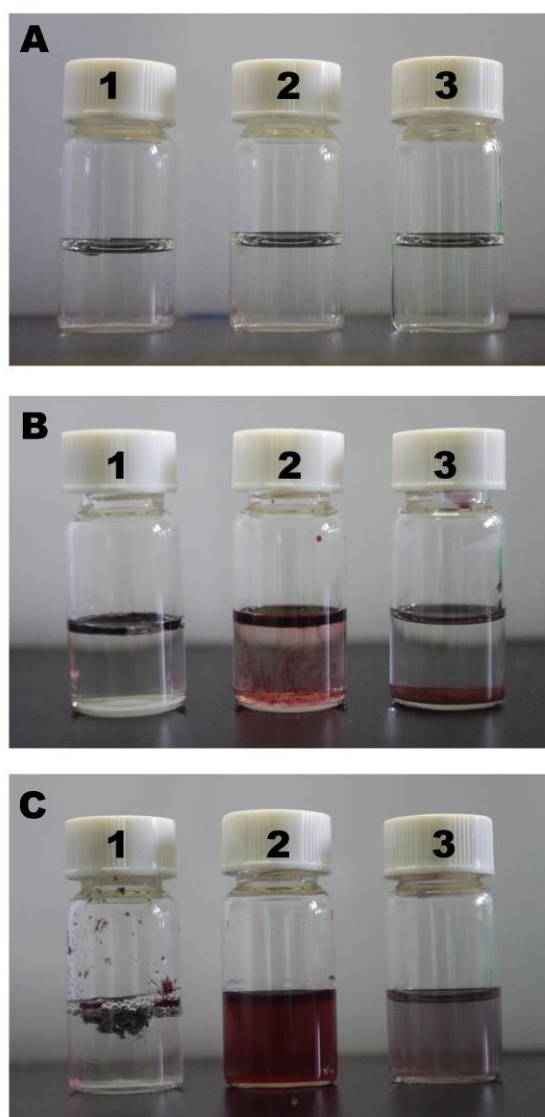


Figure S5. Photographs showing (A) sodium oleate (0.025 M) in (1) pure H₂O, (2) H₂O/EtOH (1:1 by volume) and (3) pure EtOH, respectively. (B) OAm-capped Au nanocrystals were injected into the solution. (C) After gentle shaking, the Au nanocrystals was (1) insoluble in pure water, (2) soluble in the H₂O/EtOH solution, and (3) aggregation in pure ethanol.

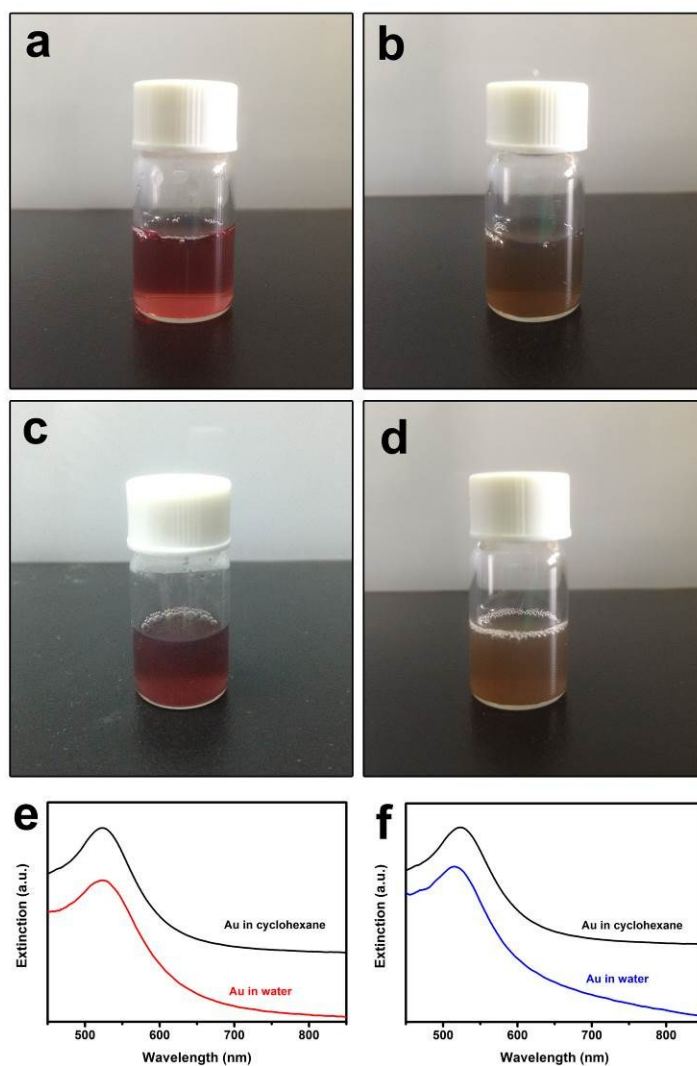


Figure S6. (a) Au NCs in a solution that contains sodium oleate, isopropanol and water (the volume ratio between H₂O and isopropanol is 3:1). (b) Fe₃O₄ NCs in a solution that contains sodium oleate, isopropanol and water (the volume ratio between H₂O and isopropanol is 3:1). (c) Au NCs in a solution that contains sodium oleate, DMF and water (the volume ratio between H₂O and DMF is 3:1). (d) Fe₃O₄ NCs in a solution that contains sodium oleate, DMF and water (the volume ratio between H₂O and DMF is 3:1). The concentration of sodium oleate is 0.025 M. (e) and (f) are the corresponding UV-vis spectra of (a) and (c), respectively.

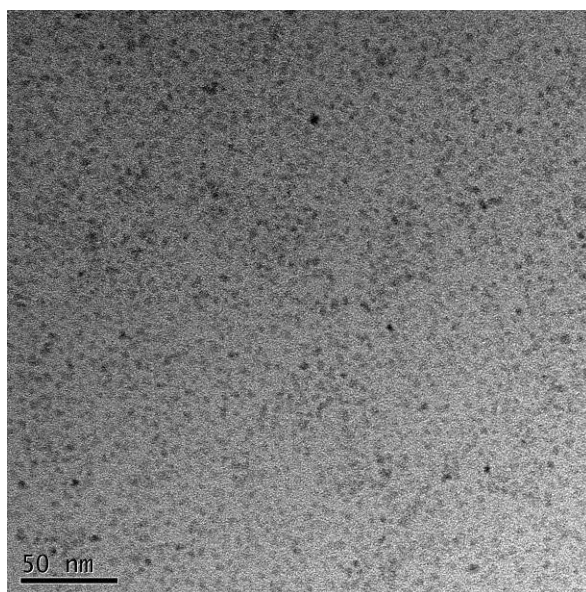


Figure S7. Low magnification TEM image of TiO₂ nanodots after phase transfer.

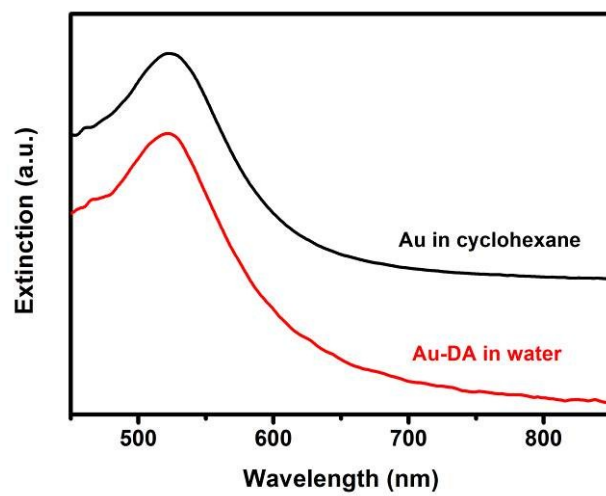


Figure S8. UV-vis spectra of Au NPs in cyclohexane (black) and water (red).

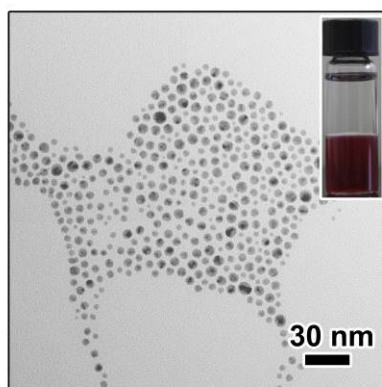


Figure S9. TEM image of Au NCs transferred into water by using CTAB as the capping ligand. The inset is the photograph showing that AuNCs can be well dispersed in water (bottom layer).

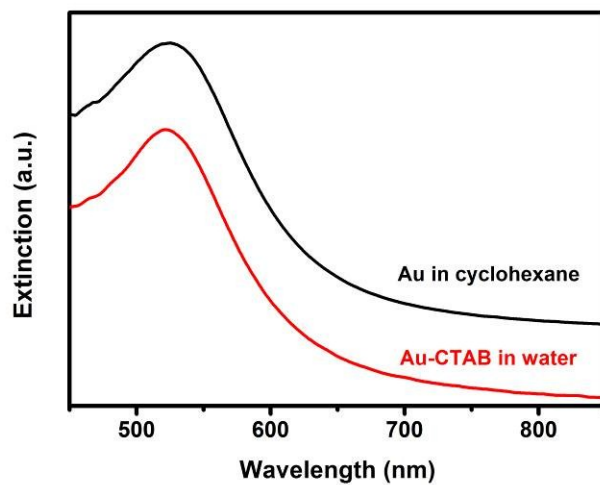


Figure S10. UV-vis spectra of Au NPs in cyclohexane (black line) and water (red line).

References

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