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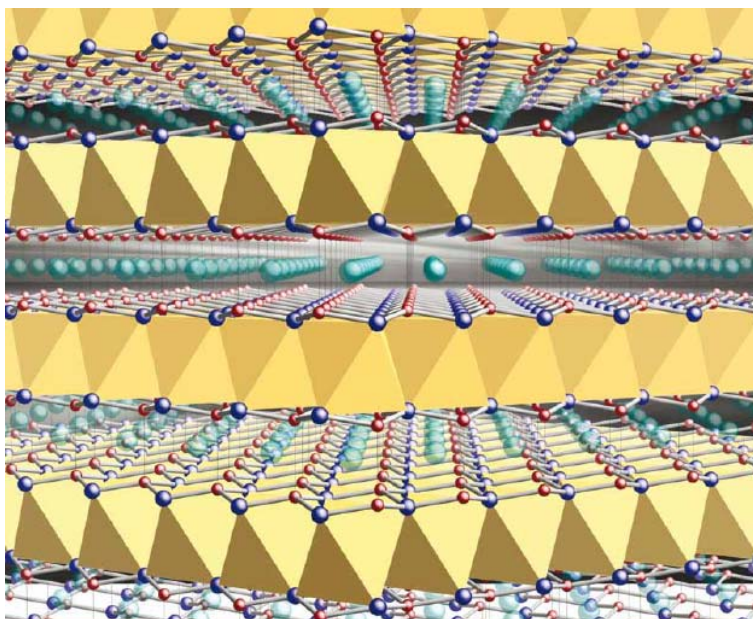


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One-step synthesis of high-purity fluorous-capped inorganic nanoparticles†

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Making use of the fact that perfluorohydrocarbon, and hydrocarbon solvents become miscible at high temperatures, highly pure inorganic nanoparticles capped with fluorous labels have been generated in a one-step synthesis. The procedure involves taking the reactants in a hydrocarbon+perfluorohydrocarbon mixture along with a fluorous reagent and carrying out the reaction at elevated temperatures. On cooling the reaction mixture, fluorous-capped inorganic nanoparticles dispersed in the perfluorohydrocarbon are obtained.

Fluorous chemistry is a novel method employed for the synthesis and purification of organic materials.¹ In this method, one attaches a fluorous reagent label such as a perfluoroalkanethiol or amine to a substrate and extracts the adduct into a perfluorohydrocarbon. Such separation is favored by fluorine-fluorine interaction between the fluorous reagent and the perfluorohydrocarbon, perfluorohydrocarbons being immiscible with water as well as hydrocarbons at room temperature. There are a few reports in the literature related to the preparation of nanoparticles capped with fluorous capping agents.^{2,3} Such fluorous-capped nanoparticles tend to be highly pure because of the method employed. Fluorous separation is generally employed as a post-synthetic technique for the purification of materials. The method generally employed requires two steps, one involving the synthesis of the desired product in a hydrocarbon or an aqueous medium and the second involving the transfer to a fluorocarbon medium after attaching the fluorous-label to the product (nanoparticles). Fluorous-capped nanoparticles are of special interest due to their high purity as well as the superhydrophobic nature.^{2c,4} Furthermore, the perfluorohydrocarbon medium with a very low refractive index of 1.23 enables the generation of inorganic nanomaterial in the most nonpolar medium possible. In this communication, we describe a novel fluorous chemical procedure for the one-step synthesis cum purification of inorganic nanoparticles. For this purpose, we have made use of the fact that perfluorohydrocarbons (PFC) and hydrocarbons become miscible at high temperatures and become biphasic only on cooling to room temperature.¹ We have prepared inorganic nanoparticles in a boiling mixture of a hydrocarbon and a PFC in the presence of a fluorous reagent which acts as the capping agent. The reaction mixture, on cooling, becomes biphasic with the PFC layer containing the fluorous-capped nanoparticles as shown in Fig. 1. By employing this procedure, we have prepared

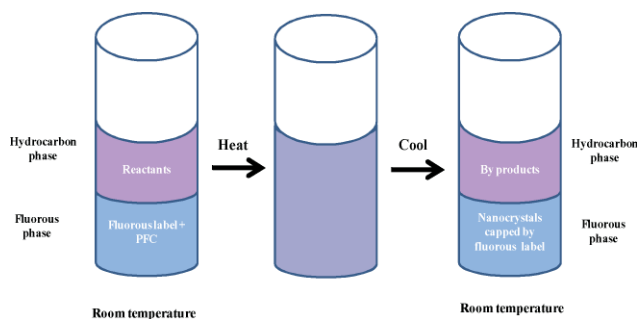


Fig. 1 Schematic showing the thermomorphic nature of fluorous and hydrocarbon solvents. (Note that colors of different phase are given for visualization purpose only).

nanoparticles of metal chalcogenides such as CdSe, CdS, PbSe, ZnSe, of metal oxides such as γ -Fe₂O₃ and ZnO and of bimetallic FePt.

A TEM image of perfluorodecanethiol-capped CdSe nanoparticles dispersed in perfluorohexane obtained by the procedure reported in the synthesis part† is shown in the Fig. 2a. The TEM image shows a narrow size distribution of nanoparticles, the average diameter of nanoparticles being around 4 nm. The photograph shown as an inset of Fig. 2a reveals a reddish brown solution of the fluorous-capped CdSe nanoparticles in the perfluorohexane layer. Fig. 3a shows the UV-visible absorption spectrum and the photoluminescence spectrum of the 4 nm CdSe nanoparticles. The absorption spectrum shows a band at 545 nm and the PL spectrum shows a band at 554 nm (excitation at 430 nm) characteristic of the 4 nm particles.⁵ The narrow PL band reflects the nearly monodisperse nature of the sample. The absorption and PL bands of the CdSe nanoparticles are red-shifted due to the highly nonpolar nature of the perfluorohydrocarbon.

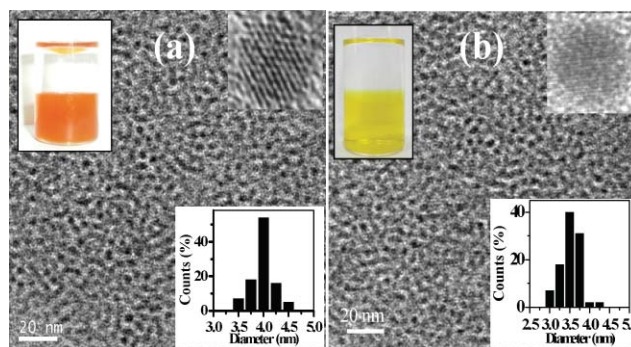


Fig. 2 TEM images of (a) 4 nm CdSe and (b) 3.5 nm CdS nanoparticles with size distribution histograms as inset. Photographs of the dispersions of the nanoparticles in PFC are also given as insets. HRTEM images are also shown as insets.

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† Electronic supplementary information (ESI) available: X-ray diffraction patterns of nanoparticles. See DOI: 10.1039/b927355g

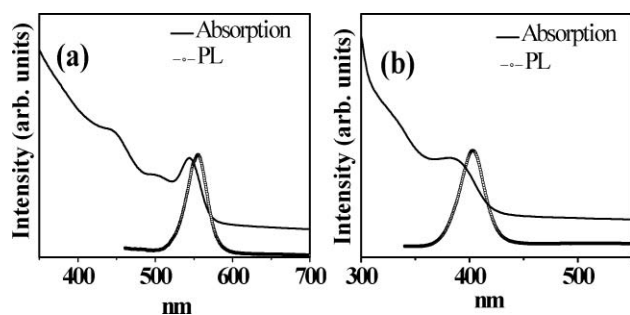


Fig. 3 UV-visible absorption and photoluminescence spectra of (a) 4 nm CdSe and (b) 3.5 nm CdS nanoparticles.

A TEM image of CdS nanoparticles capped with perfluorodecanethiol, prepared by a procedure similar to that of CdSe \ddagger is shown in Fig. 2b. The average diameter of the nanoparticles is around 3.5 nm. The photograph of the solution in perfluorohexane in the inset of Fig. 2b reveals the yellow color of the dispersion. The UV-visible absorption spectrum and the PL spectrum of the CdS nanoparticles are shown in Fig. 3b. The absorption spectrum, characteristic of 3.5 nm CdS particles, shows a band at 395 nm while the PL spectrum shows a band at 403 nm (excitation at 320 nm).⁶

We have obtained 12.5 nm PbSe and 5 nm ZnSe nanoparticles by employing a procedure similar to those for the Cd chalcogenide nanoparticles. \ddagger The absorption spectrum of the PbSe nanoparticles shows a first exciton peak around 1680 nm.⁷ The UV-visible absorption spectrum of the 5 nm ZnSe nanoparticles shows a band at 400 nm and a photoluminescence band at 407 nm.⁸

By the thermal decomposition of Fe(CO)₅, we have obtained perfluorodecanoic acid-capped γ -Fe₂O₃, dispersed in perfluorohexane. \ddagger A TEM image of the nanoparticles is shown in Fig. 4(a). The as prepared γ -Fe₂O₃ nanoparticles are monodisperse

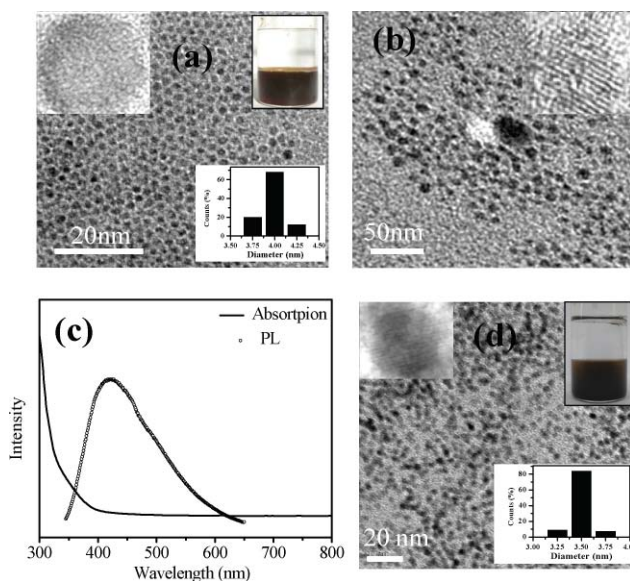


Fig. 4 (a) TEM image of 4 nm γ -Fe₂O₃. (b) TEM and (c) UV-visible absorption and photoluminescence spectra of 8 nm ZnO nanoparticles. (d) TEM image of 3.5 nm FePt nanoparticles. Photographs of the dispersions of the nanoparticles in PFC are also given as insets in PFC are given as insets in (a) and (d). HRTEM images are also shown as insets.

with a diameter around 4 nm. Magnetic susceptibility measurements show divergence between field-cooled (FC) and zero field-cooled (ZFC) measurements with a blocking temperature of 23 K (at 100 Oe) as shown in the Fig. 5(a).⁹ Below the blocking temperature, the particles show magnetic hysteresis.

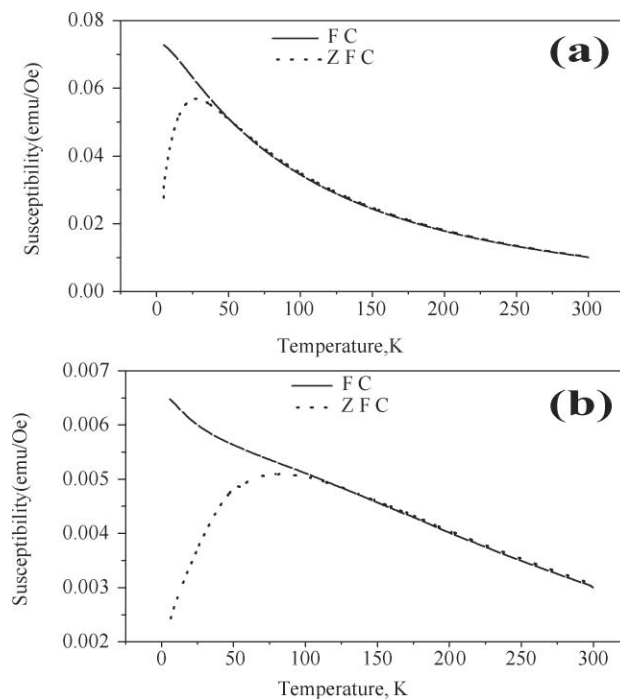


Fig. 5 Zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibility data as a function of temperature for (a) Fe₂O₃ and (b) FePt nanoparticles.

Heptadecafluorodecylamine-capped ZnO nanoparticles were prepared by the nonhydrolytic decomposition of zinc acetyl acetonate. \ddagger In Fig. 4b we show a TEM image of ZnO nanoparticles with an average diameter of 8 nm dispersed in perfluorohexane. The UV-visible absorption spectrum in Fig. 4c shows an absorption band edge around 330 nm.¹⁰ The PL spectrum shows a broad blue-green emission band at above 430 nm. A broad blue-green emission band above 430 nm is attributed to a singly charged oxygen vacancy, which results from the recombination of a photogenerated hole with a charge state of the specific defect, such as oxygen vacancies, or resulted from the surface deep traps.

In Fig. 4d, we show a TEM image of 3.5 nm Heptadecafluorodecylamine-capped FePt nanoparticles. \ddagger FePt nanoparticles show superparamagnetic behavior at room temperature and divergence between FC and ZFC measurements with a blocking temperature of 75 K (at 100 Oe) as shown in Fig. 5(b) in agreement with the literature value.¹¹ The particles show magnetic hysteresis below the blocking temperature.

All the nanoparticles were characterized by X-ray diffraction (see Figs. S1 and S2 in the electronic supplementary information, ESI \ddagger). The patterns of CdSe, CdS and ZnSe were indexed on the cubic zinc blende structure where as PbSe was indexed on the rock salt structure. The XRD pattern of iron oxide was indexed as magahmite. The FePt nanoparticles show XRD patterns corresponding to the FCC structure where as ZnO nanoparticles had the wurtzite structure

In conclusion, it has been possible to synthesize pure fluorocapped inorganic nanoparticles by a one step procedure. This procedure conveniently uses the fact that hydrocarbons and perfluorohydrocarbons become fully miscible at high temperatures. This feature has enabled us to extract fluorocapped inorganic nanoparticles in perfluorohydrocarbons, having prepared them in mixture of hydrocarbon and perfluorohydrocarbon at high temperatures. It is noteworthy that the nanoparticles are nearly monodisperse and highly pure. The purity is assured because only the nanoparticles which are capped by the fluorocarbon label get extracted by the fluorocarbon. The fluorocarbon label gets attached to only the desired products in the synthesis. The method can be used for the synthesis of variety of fluorocapped inorganic nanostructures dispersed in perfluorohydrocarbons.

Notes and references

‡ Synthesis: The synthetic procedure involves first taking appropriate metal precursors and other reagents in a hydrocarbon solvent such as toluene. To this mixture, the required quantity of the fluorocarbon label (which caps the product) is added along with perfluorohexane. The reaction is carried out under solvothermal or refluxing conditions. We have used perfluorodecanethiol as the capping agent for metal chalcogenides, heptadecafluorodecylamine for ZnO, and perfluorodecanoic acid for γ -Fe₂O₃ and FePt.

In a typical procedure to prepare fluorocapped metal chalcogenides (CdSe, CdS, PbSe and ZnSe), the metal cupferronate or acetylacetonate (0.07 mmol) is taken along with selenium or sulfur (0.07 mmol), tetralin (7.5 μ L) and a small quantity of perfluorodecanethiol (200 μ L) in a mixture of 10 ml toluene and 10 ml perfluorohexane.¹² The reaction mixture which was biphasic at room temperature was sealed in a stainless steel 30 ml teflon-lined autoclave and placed in an air oven preheated to 250 °C for 5 h. After the reaction was complete, the autoclave was allowed to cool to room temperature and the contents were then transferred to a vial. The resulting product consisted of two layers with the perfluorodecanethiol-capped nanoparticles present in the perfluorohexane layer (Fig. 1).

Synthesis of fluorocapped γ -Fe₂O₃ nanoparticles was carried out by the following procedure.⁹ Around 0.2 ml of Fe(CO)₅ (1.5 mmol) was added to a mixture of 10 ml of dioctyl ether, 10 ml of perfluorohexane and 1 g of perfluorodecanoic acid at 100 °C. The resulting mixture was heated to 250 °C and kept at that temperature for 2 h. During this time, the initial orange color turned black. The reaction mixture was allowed to cool to room temperature. The iron nanoparticles in perfluorohexane upon exposure to air got oxidized to γ -Fe₂O₃ nanoparticles.

Fluorocapped ZnO nanoparticles¹⁰ were prepared starting with a mixture of 7.5 mg of Zn(acac)₂ with 150 mg of heptadecafluorodecylamine in the presence of 7.5 ml toluene and 10 ml perfluorohexane. The mixture was sealed in a stainless steel 25 ml teflon-lined autoclave placed for 20 h in an air oven preheated to 250 °C. On cooling, ZnO nanoparticles capped with heptadecafluorodecylamine dispersed in the denser fluorocarbon medium were obtained.

Fluorocapped FePt nanoparticles were prepared as follows.¹¹ Under a flow of nitrogen, Pt(acac)₂ (0.5 mmol) was mixed with benzyl ether (10 ml) and heated to 100 °C. To this mixture, Fe(CO)₅ (1 mmol), heptadecafluorodecylamine (5 mmol, 500 μ L) perfluorodecanoic acid (5 mmol) and perfluorohexane (10 ml) were added under a flow of nitrogen. The mixture was heated to 250 °C at a heating rate of -15 °C min⁻¹ to assure complete decomposition of Fe(CO)₅, and then mixture was refluxed for 1 h. The reaction mixture was then cooled to room temperature to obtain pure FePt particles capped with heptadecafluorodecylamine and perfluorodecanoic acid dispersed in perfluorohexane.

All the fluorocapped nanoparticles were characterized by transmission electron microscopy (TEM) by employing a JOEL JEM 3010 instrument. Photoluminescence spectra were recorded with a Fluorolog-22 (Horiba-Jobin Yvon) spectrofluorometer fitted with a Xenon lamp excitation source while the absorption spectra were recorded with UV/VIS/NIR Perkin-Elmer spectrometer. Magnetic measurements were carried out with a vibrating sample magnetometer option in the Physical Properties Measuring System (PPMS, Quantum Design, USA). The samples were examined by X-ray diffraction using Cu-K α radiation ($\lambda = 1.54056$ Å) using a Rigaku-99 instrument.

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