

## Chapter 2

# A General Phase Transfer Approach for Metal Ions and Nanoparticles

**Abstract** This chapter introduces a general protocol to transfer metal ions from aqueous solution to an organic medium, which involves mixing the aqueous solution of metal ions with an ethanolic solution of dodecylamine (DDA), and extracting the coordinating compounds formed between metal ions and DDA into toluene. This protocol could be applied toward transferring a wide variety of transition metal ions with efficiency higher than 95 % and allows the synthesis of a variety of metallic and semiconductor nanocrystals to be performed in organic medium using relatively inexpensive water-soluble metal salts as starting materials. This protocol could also be extended to transfer a variety of noble metal nanoparticles from aqueous phase to nonpolar organic media. As shown in latter sections, the phase transfer of metal ions and nanoparticles offers necessary solvent surroundings for the wet chemistry-based synthesis of nanomaterials and is an important step preceding the fabrication of noble metal-based nanocomposites with multiple functionalities.

**Keywords** Phase transfer • Dodecylamine • Metal ions • Noble metal • Nanoparticles • Wet chemistry • Nanomaterials • Nanocomposites

## 2.1 Introduction

We are currently witnessing impressive advances in nanoscience and nanotechnology. A variety of recipes have been developed to synthesize, assemble, and package nanomaterials/nanostructures into forms more amenable to applications. After close to a decade of intense effort, a large number of metal nanoparticles with different geometries can be routinely synthesized by solution chemistry methods in polar (for example, water) and nonpolar environments. Each method has its own unique advantages and disadvantages (Sastri 2003; Yang et al. 2011). There is also an increased interest in the synthesis of more complex nanostructures such as core-shell, hollow, or composite particles consisting of components with distinctly different physicochemical properties because of the promise of tunable properties

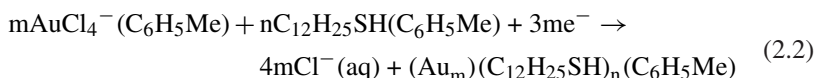
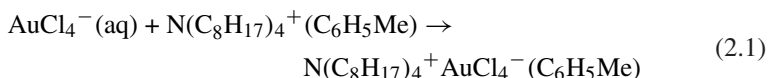
for a new generation of technology-driven applications in catalysis (Kim et al. 2002; Zhang et al. 2005; Alayoglu et al. 2008; Luo et al. 2008; Mani et al. 2008; Liu et al. 2009; Zhang et al. 2009; Yang and Ying 2011; Liu et al. 2012, 2014), chemical and biological sensing (Talon et al. 2000; Krasteva et al. 2002; Gao et al. 2008; Liang et al. 2009; Shin et al. 2009), and optics (Lei and Chim 2005; Gobin et al. 2007; Bao et al. 2007; Lessard-Viger et al. 2009). Specific applications often require the transfer of newly formed nanoparticles from a polar environment to a nonpolar environment, or vice versa, in order to maximize the advantages of these environments based on some processing considerations. This makes phase transfer an important technique in the development of nanoscience and nanotechnology.

Metal nanoparticles of different shapes and sizes can be obtained in the organic phase by preparing them there or by transferring nanoparticles from the aqueous phase to the organic phase. The latter has the advantage of leveraging upon many existing methods for preparing the metal nanoparticles in the aqueous phase (Zhou et al. 2002; Carotenuto and Nicolais 2003). Phase transfer of metal nanoparticles from the aqueous solution to the organic phase is often accomplished by capping the nanoparticles with thiols and amines (Wang et al. 1998), or by using surfactants to improve the solubility of nanoparticles in the organic phase (Lala et al. 2001). The applications of phase transfer in metal nanoparticle synthesis and in the surface modifications of quantum dots have recently been reviewed by a number of nice works (Sastri 2003; Medintz et al. 2005; Yang et al. 2011). Herein, we prefer to devote this chapter to a general protocol for the transfer metal ions from aqueous solution to an organic medium after a brief update of the literature (Yang et al. 2009). This strategy involves mixing an aqueous solution of metal salts with an ethanol solution of dodecylamine (DDA) and then extracting the metal ions into an organic layer (toluene, hexane, or other nonpolar solvents). It could be successfully applied toward the synthesis of a variety of metallic, alloy, and semiconductor nanoparticles. Compared with other general approaches (Cushing et al. 2004; Wang et al. 2005), this protocol allowed metal or semiconductor nanocrystals to be synthesized in organic medium using aqueous soluble metal salts as starting materials, which are relatively inexpensive and easily obtained. In addition, this protocol could also be extended to transfer a variety of noble metal nanoparticles from aqueous phase to nonpolar organic media and therefore creates favorable solvent surroundings for the wet chemistry-based synthesis of noble metal-based nanocomposites with multiple functionalities.

## 2.2 Brust–Schiffrin Method

The often cited Brust–Schiffrin method is the earliest phase transfer approach to prepare thiol-stabilized nanoparticles (Brust et al. 1994, 1995). In this method, gold metal ions from an aqueous solution are extracted to a hydrocarbon (toluene) phase using tetraoctylammonium bromide (TOAB) as the phase transfer agent. Subsequent reduction takes place in the organic solution using an aqueous  $\text{NaBH}_4$

solution in the presence of an alkanethiol, yielding Au particles with average diameter of ~2.5 nm. The overall reaction is summarized as Eqs. (2.1) and (2.2), where the source of electrons is NaBH<sub>4</sub> (Brust et al. 1994):



Here, the nucleation and growth of the gold particles and the attachment of the thiol molecules occur simultaneously in a single step.

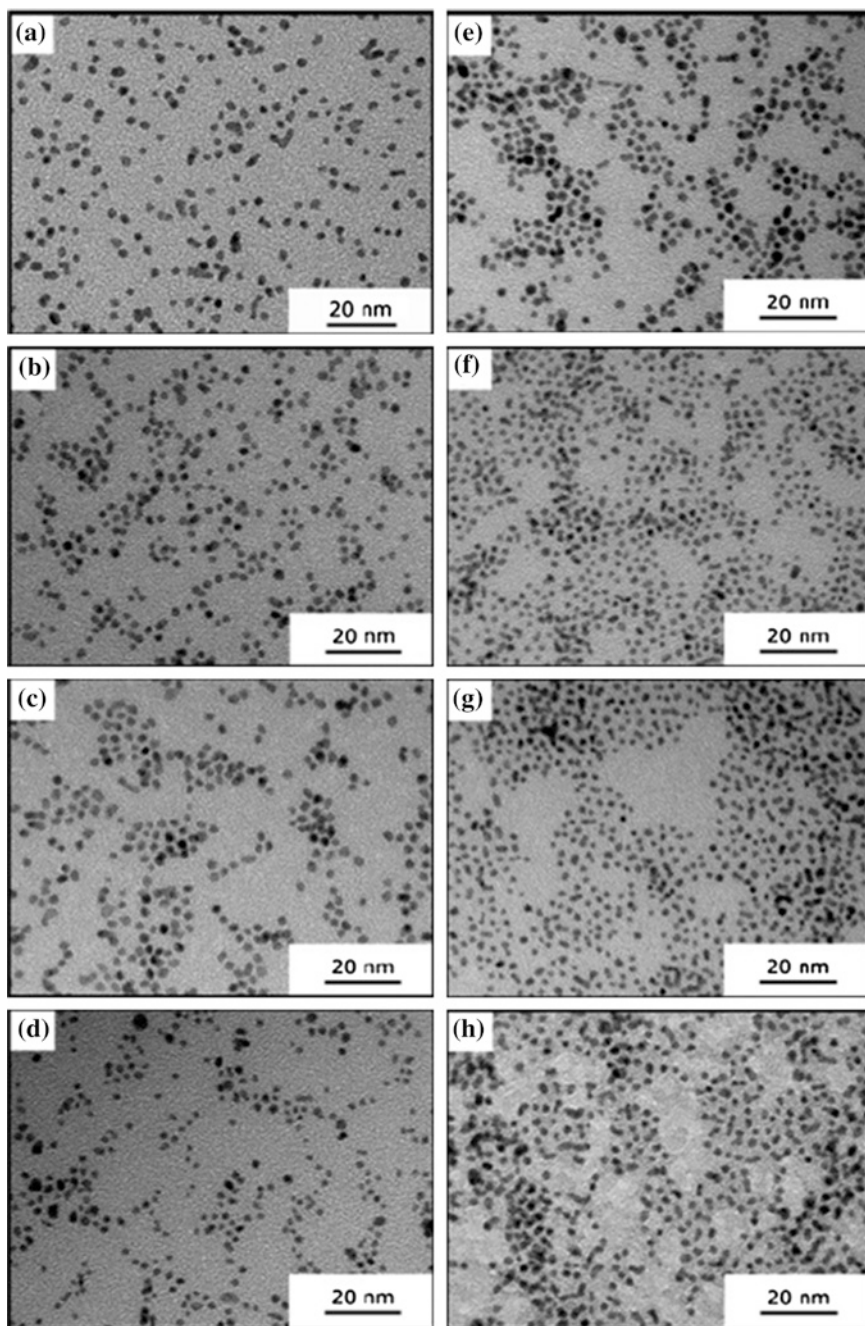
It should be noted that we emphasize the thiol stabilization in Brust–Schiffrin method. Actually, early in 1988, Meguro et al. (1988) have reported the extraction of H<sub>2</sub>PtCl<sub>6</sub> into organic solvents from an aqueous solution using dioctadecyldimethylammonium chloride, trioctylmethylammonium chloride, or trioctylphosphine oxide as extractants. The Pt<sup>4+</sup> ions after extraction were reduced by formaldehyde or benzaldehyde in the presence of sodium hydroxide for several hours at 65 °C. The Pt particles obtained in CHCl<sub>3</sub>, cyclohexane, or methylisobutylketone were very stable with diameters of 1.5–2.5 nm. Subsequently in 1989, they extended this extraction method for the preparation of organogold nanoparticles. The relationship between Au particle size and preparative condition was also discussed (Meguro et al. 1988/1989).

The Brust–Schiffrin method provides ready access to functionalized nanomaterials with properties analogous to those of large molecules, as they exhibit remarkable stability in both solution and dry forms, allowing characterization using standard analytical approaches and further chemical modification by introducing a wide variety of structural groups onto the particles (Hostetler et al. 1998, 1999; Templeton et al. 2000). Considerable subsequent work with modifications to this classic method ensued, including use of alkanethiol of different chain lengths (Terrill et al. 1995; Hostetler et al. 1998; Donkers et al. 2004; Jimenez et al. 2004), aromatic thiol (Johnson et al. 1998), dialkyl disulfides (Porter et al. 1998), and various thiol/Au reactant ratios (Whetten et al. 1996), for the synthesis of monolayer-protected clusters (MPCs). In 1998, the Murray group employed hexanethiol instead of dodecanethiol as stabilizer in a 3:1 thiol/Au ratio and chilled the reaction to yield a solution of clusters with an mean diameter of 1.6 nm and average Au<sub>145</sub>(S(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>)<sub>50</sub> composition (Hostetler et al. 1998). In the subsequent work (Chen et al. 2000), the same group addressed specific issues of particle growth and monodispersity issues in the preparation of hexanethiol-protected Au clusters by monitoring the size evolution of the particles over the course of 125 h. The researchers found that the average diameter of Au core gradually increases over the first 60 h of reaction and then remains largely unchanged afterward (out to 125 h) at ~3 nm. The results support the findings that MPCs of the smallest core size could be best obtained by quenching the reaction at relatively early time

(Whetten et al. 1996; Schaaff et al. 1997; Schaaff and Whetten 1999) and are important to understand how MPC core size evolves in the Brust–Schiffrin cluster synthetic reaction.

The discussions above have been focused on gold nanoparticles, but further insight can be derived from similar treatment of platinum, lending greater understanding to the preparation of other noble metal nanomaterials. Early in 1999, the Brust–Schiffrin method has already been extended by Horswell et al. (1999) for the synthesis of isocyanide-protected platinum nanoparticles. The authors follow every step of Brust–Schiffrin method to prepare tetraoctylammonium-stabilized Pt nanoparticles, which were further functionalized by dodecylisocyanide via a ligand exchange process. Transmission electron microscopy (TEM) shows the Pt particles of 1–3 nm in diameter with well-defined crystalline structure were obtained this way. The use of isocyanide as ligands for transition metal nanoparticles offers the possibility for extending the range of metals from which stable nanosized materials could be prepared and manipulated as simple chemical compounds, thus broadening the established use of thiols in nanoparticle synthesis.

The Brust–Schiffrin method of nanoparticle synthesis has been extended to generate amine-stabilized nanoparticles by simply substituting an appropriate amine for the thiol. Leff et al. (1996) first reported the synthesis of amine-stabilized Au nanoparticles using Brust–Schiffrin method by substituting the dodecanethiol with DDA or oleylamine. Larger Au nanoparticles having diameters up to 7 nm can be accessed by this modified Brust–Schiffrin method. Although the broad dispersity of the size range, the extension characterizations of the particles including infrared spectroscopy (IR), UV–vis, nuclear magnetic resonance spectroscopy (NMR), mass spectroscopy (MS), X-ray photoelectron spectroscopy (XPS), TEM, XRD (powder X-ray diffraction), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and element analysis lead to several important conclusions to facilitate the understanding of the interaction between primary amine and Au nanoparticle surface: (1) the amine/gold surface interaction is charge neutral and is best described by a weak covalent bond; (2) particle stability is predominantly kinetic, rather than thermodynamic, in nature. This contrasts with the system of thiol-capped Au nanocrystals, which are shown to possess thermodynamic stability with respect to ligand desorption and subsequent particle agglomeration; (3) the stability of the nanoparticles is finite-size effect from a comparison of the amine-capped gold nanoparticle system to amines adsorbed onto bulk Au surfaces. In a later work, Wikander et al. use tetrakisdecylammonium bromide instead of TOAB to transfer platinum(IV) chloride from aqueous solution to toluene and then reduce the platinum ions using  $\text{NaBH}_4$  in the presence of alkylamine of different chain lengths. This research demonstrates that the length of the primary amine chains used to coat the platinum nanoparticles induces control of the nanoparticle size (Fig. 2.1). The calculated average diameter indicates that there is an inverse relationship between the size of the nanoparticles and the length of alkylamine. Inspection of TEM images reveals that Pt nanoparticles are more spherical in shape when short-chain alkylamine are used rather than their longer-chain homologs (Wikander et al. 2006).



**Fig. 2.1** TEM images of platinum nanocrystals obtained by the phase transfer method using different alkylamines as stabilizing agents: **a**  $\text{C}_6\text{NH}_2$ , **b**  $\text{C}_7\text{NH}_2$ , **c**  $\text{C}_8\text{NH}_2$ , **d**  $\text{C}_9\text{NH}_2$ , **e**  $\text{C}_{10}\text{NH}_2$ , **f**  $\text{C}_{12}\text{NH}_2$ , **g**  $\text{C}_{16}\text{NH}_2$ , and **h**  $\text{C}_{18}\text{NH}_2$ . Reproduced from Wikander et al. (2006) with permission from the American Chemical Society

The extension of Brust–Schiffrin method for the syntheses of nanomaterials is still very active in recent years. In addition to continue to be a useful tool to prepare Au, Ag, or Pt nanoparticles with controlled size and improved dispersity (Selvakannan et al. 2004; Grace and Pandian 2007; Chen and Wang 2008), with suitable choice of the phase transfer agent, the Brust–Schiffrin method was also employed to produce Cu (Song et al. 2004), CoPt alloy (Demortiere and Petit 2007), Ag<sub>2</sub>S (Schaaff and Rodinone 2003; Shi et al. 2006a), and PbS (Song et al. 2008). As the phase transfer agent and the stabilizer for particles in Brust–Schiffrin synthesis were chemically different, the nanoparticles so obtained were found to contain nitrogenous surface impurities due to the phase transfer agent. Besides this contamination problem, the greatest limitation of the Brust–Schiffrin preparation is that the stabilizing ligands, such as thiol or amine, must be compatible with all of the reagents, including reducing (NaBH<sub>4</sub>) and the phase transfer agents, thus sidestepping adverse influences on the reaction chemistry. For example, the thiol or amine cannot interact with the phase transfer agent in such a way that leads to products that are inseparable from the reaction mixture. To this end, Brust–Schiffrin-type reactions have been performed in other solvents such as water and THF, permitting a single-phase synthesis of organic soluble metal nanoparticles while eliminating the need for phase transfer reagents (Dahl et al. 2007).

## 2.3 Ethanol-Mediated Phase Transfer

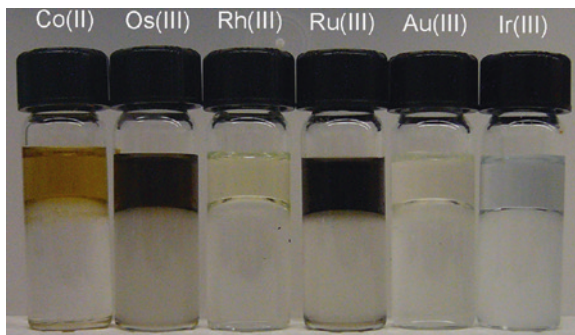
Notwithstanding the contamination issue, the Brust–Schiffrin method should be recognized for its ability to produce finer metallic nanoparticles. An ethanol-mediated protocol, in which alkylamine is used as a stabilizer cum phase transfer agent, has been developed to realize the distinctive advantage of Brust–Schiffrin method without its associated problem of impurity contamination (Yang et al. 2009). It was also generic enough for the transition metal ions and could be easily extended to the preparation of metallic and semiconductor nanocrystals with finer sizes.

### 2.3.1 Ethanol-Mediated Phase Transfer of Metal Precursors

The transfer of metal precursors from aqueous to hydrocarbon layer is a two-step approach (Yang et al. 2009). Typically, the aqueous solution of metal ions was mixed with equal volume of ethanol containing DDA and the mixture was stirred for 3 min. Then, toluene was added and stirring continued for 1 more minutes before the transfer to a separating funnel. The formation of two immiscible layers occurred within minutes. The transfer of metal salts from the aqueous phase to toluene was complete, leaving behind a colorless aqueous solution. Ethanol is important for the transfer of metal precursors. Metal ions would not be transferred to the organic phase by direct mixing of an aqueous metal precursor solution with



**Fig. 2.2** Photographs showing the successful transfer of Co(II), Os(III), Rh(III), Ru(III), Au(III), and Ir(III) metal ions from aqueous phase to toluene. Reproduced from Yang et al. (2009) with permission from Nature Publishing Group



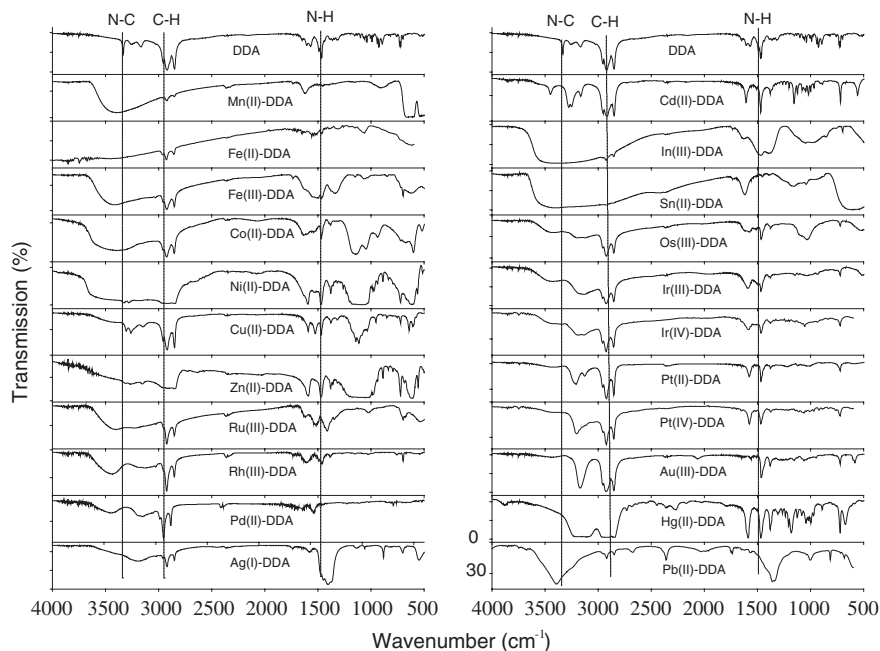
an organic solvent containing DDA. Prolonged agitation would only result in a turbid mixture of metal salt solution and organic solvent, but no transfer of metal ions took place after the mixture was settled down into two immiscible layers in a separating funnel. However, the transfer of metal ions could occur using ethanol as an intermediate solvent based on the fact that water and ethanol are miscible, and this would ensure the maximum contact between the metal ions and DDA. Figure 2.2 illustrates the complete bleaching of the aqueous phase as the metal ions were successfully transferred from water to toluene.

The mechanism of this protocol was different from that of Brust–Schiffrin method, whereby the gold ions from an aqueous solution were directly transferred to a hydrocarbon phase (toluene) based on electrostatic interaction with tetraoctylammonium bromide (Brust et al. 1994, 1995). A metal complex between metal ions and DDA was hypothesized to have formed in the process, which could be more easily extracted by toluene. This was verified by the Fourier transform infrared (FTIR) spectra of the compounds recovered from the organic layer after phase transfer (Fig. 2.3). Compared to pure DDA, differences were observed in the N–C and N–H stretching regions, demonstrating that DDA was bound to the metal ions by its  $\text{NH}_2^-$  group. The XPS analyses of N 1 s spectra of pure DDA and several types of metal ion–DDA complexes indicated that metal ions coordinated with DDA through sharing the electron pair of  $\text{NH}_2^-$  group. The electron donating effect from  $\text{NH}_2^-$  to metal ions resulted in appreciable shift of N 1 s binding energy to a higher value, as shown in Fig. 2.4. By combining the FTIR analyses with XPS spectra, the mechanism of the ethanol-mediated transfer of metal precursors could be summarized by the scheme in Fig. 2.5. After coordinating with metal ions, the nonpolar tail of DDA enabled the compounds to dissolve easily in nonpolar organic solvents, such as toluene or hexane.

The transfer efficiency (TE) and the distribution ratio (DR) were calculated using the following equations:

$$\text{TE (\%)} = 100([M^{n+}]_i - [M^{n+}]_f) / [M^{n+}]_i$$

$$\text{DR} = \text{TE} / (100 - \text{TE})$$

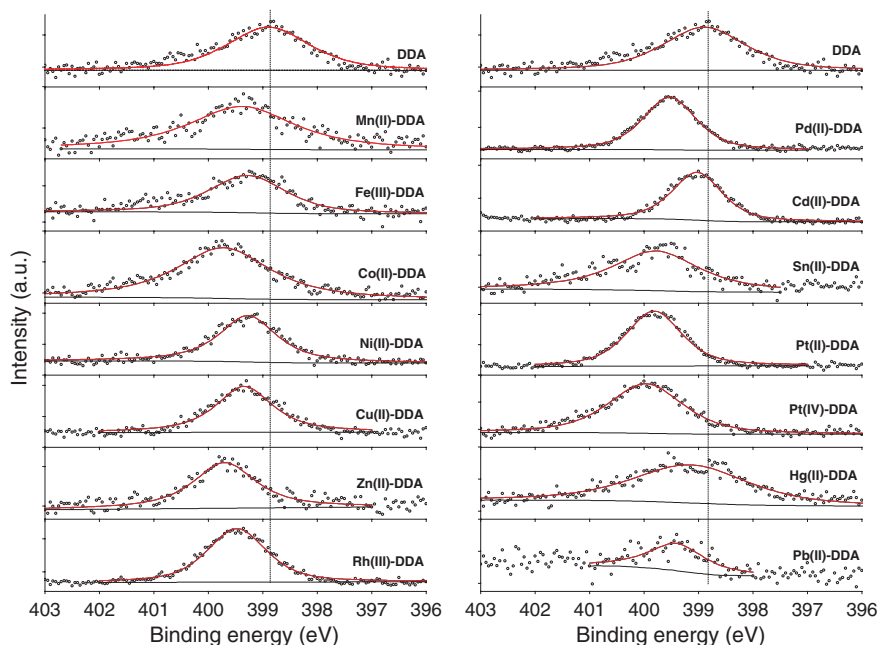


**Fig. 2.3** FTIR spectra of pure DDA and metal ion-DDA complexes. Reproduced from Yang et al. (2009) with permission from Nature Publishing Group

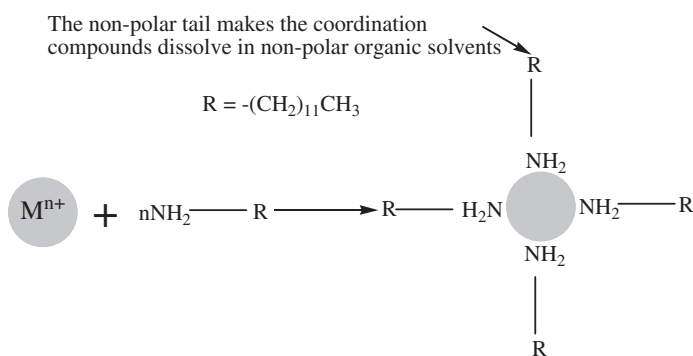
where  $[M^{n+}]_i$  and  $[M^{n+}]_f$  were the initial and final metal ion concentrations in aqueous phase, respectively. Analyses by inductively coupled plasma atomic emission spectrophotometry (ICP-AES) indicated that the phase transfer efficiencies for a wide variety of metal ions were higher than 95 % (Table 2.1).

After transfer into organic solvent, a large number of commonly used methods, e.g., wet chemistry reduction, seed-mediated growth, coreduction, and solvothermal approaches could be adopted to fabricate metal or semiconductor nanoparticles with different structures or morphologies. The synthesis of noble metal nanoparticles could be served as a typical example to demonstrate the extension of this transfer protocol to the nanomaterial preparation. At 100 °C, the reducing agent solution (toluene solution of hexadecanediol, tetrabutylammonium borohydride, or aqueous solution of  $\text{NaBH}_4$ ) was added to the toluene solution of noble metal precursor ( $\text{Ru}^{3+}$ ,  $\text{Rh}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Os}^{3+}$ ,  $\text{Ir}^{3+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Pt}^{4+}$ , or  $\text{Au}^{3+}$ ), and the mixture was agitated for several minutes. The noble metal colloids thus obtained were highly stable, with no sign of agglomeration even after weeks of storage. The synthesis was easily scaled up by increasing the volumes of the metal ion aqueous solution, the DDA ethanolic solution, and toluene proportionately. The nanoparticles and nanostructures synthesized upon this phase transfer protocol include monometallic, bimetallic alloy and core-shell, and semiconductors (Fig. 2.6). Compared with other general approaches (Cushing et al. 2004; Wang et al. 2005), this protocol allows the synthesis of nanocrystals to be performed in





**Fig. 2.4** N 1s XPS spectra of pure DDA and metal ion-DDA complexes. Reproduced from Yang et al. (2009) with permission from Nature Publishing Group



**Fig. 2.5** Schematic illustration to show the phase transfer of metal precursors from aqueous to an organic medium using ethanol as mediating solvent

organic medium using aqueous soluble metal salts as starting materials, which are relatively inexpensive and easily obtained. As demonstrated in later chapters, a notable advantage is this transfer protocol could be easily extended to synthesize a large number of semiconductor–noble metal composite nanomaterials, an important challenge in current materials synthesis (Mokari et al. 2004; Shi et al. 2006b; Yang and Ying 2009, 2011; Yang et al. 2011). Thus, this universal phase

**Table 2.1** The phase transfer efficiency of metal ions from water to toluene

Metal precursor	C <sub>B</sub> <sup>a</sup> (mg/L)	C <sub>A</sub> <sup>b</sup> (mg/L)	TE (%) <sup>c</sup>	DR <sup>d</sup>	Relative standard deviation (%)
Mn(II) <sup>e</sup>	54.94	0.06	99.89	908.09	3.56
Fe(II) <sup>e</sup>	55.85	0.24	99.57	231.56	5.84
Fe(III) <sup>e</sup>	55.85	0.32	99.43	174.44	6.19
Co(II)	58.93	0.33	99.44	177.57	4.16
Ni(II)	58.69	0.12	99.80	499.00	7.24
Cu(II)	63.55	0.50	99.21	125.58	3.09
Zn(II)	65.39	1.67	97.44	38.06	4.28
Ru(III)	101.07	0.56	99.45	180.82	7.46
Rh(III)	102.91	1.88	98.17	53.64	3.58
Pd(II)	106.42	0.32	99.70	332.33	4.86
Ag(I)	107.87	0.17	99.84	624.00	0.52
Cd(II) <sup>e</sup>	112.41	3.20	97.15	34.09	6.59
In(II)	114.82	0.74	99.36	155.25	5.62
Sn(II)	118.71	5.44	95.42	20.83	8.47
Os(III)	190.20	1.86	99.02	101.04	8.97
Ir(III)	192.22	2.40	98.75	79.00	4.56
Ir(IV)	192.22	1.98	98.97	96.09	4.32
Pt(II)	195.08	1.58	99.19	122.46	4.93
Pt(IV)	195.08	1.36	99.30	141.86	2.46
Au(III)	196.97	2.24	98.86	86.72	0.65
Hg(II)	200.59	2.57	98.72	77.12	2.84
Pb(II) <sup>e</sup>	207.20	1.41	99.32	146.06	5.30

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<sup>a</sup>Concentration of aqueous metal ion solution before transfer

<sup>b</sup>Concentration of aqueous metal ion solution after transfer

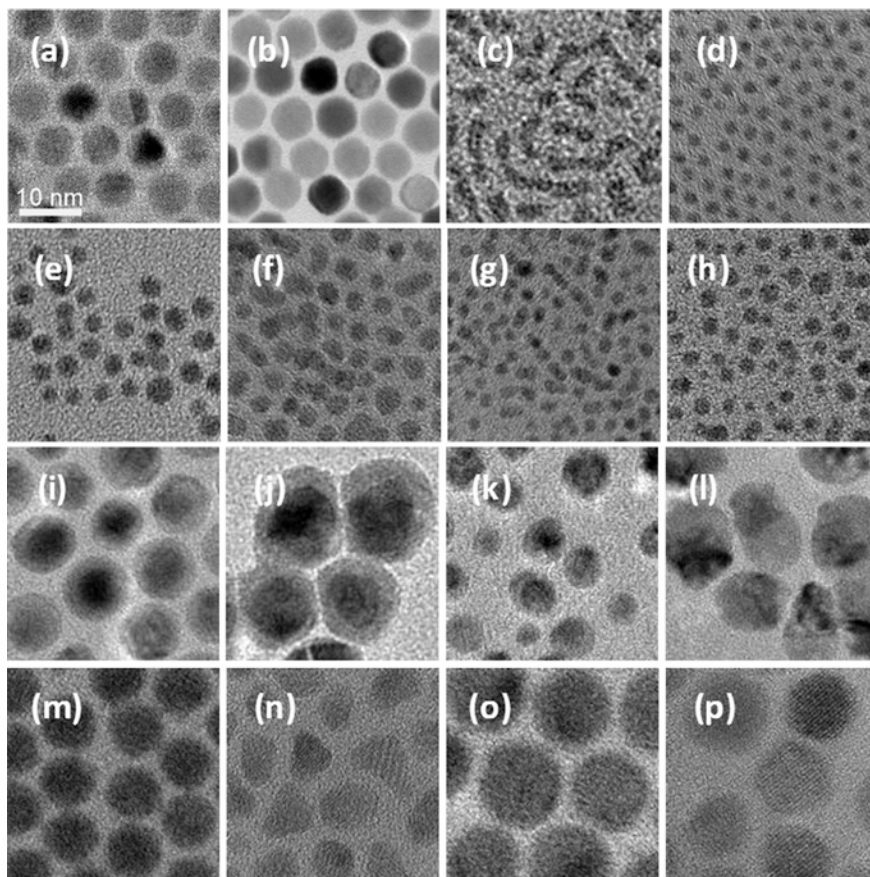
<sup>c</sup>TE (transfer efficiency) = 100 ([M<sup>n+</sup>]<sub>i</sub> - [M<sup>n+</sup>]<sub>f</sub>)/[M<sup>n+</sup>]<sub>i</sub>

<sup>d</sup>DR (distribution ratio) = TE/(100 - TE), where [M<sup>n+</sup>]<sub>i</sub> and [M<sup>n+</sup>]<sub>f</sub> are the initial and final metal ion concentrations in aqueous phase, respectively

<sup>e</sup> Some coordination compounds remained at the water/toluene interface

transfer approach represents a simple and flexible route for fabricating nanostructured materials with novel structures and multiple functionalities.

In addition to the application in nanomaterials synthesis, our phase transfer protocol possesses the following advantages: (1) good ion uptake by the complexing agent, allowing for fast binding with the metal ion, (2) high stability against hydrolysis, (3) selective ion complexation of heavy metals, along with no affinity for alkali or alkaline earth ions whose concentrations are usually high in water and soil, (4) sufficiently high binding strength for the metal ions to be extracted, and (5) preference of the metal complex derived for the organic phase over the aqueous phase, which would be of interest for applications in environmental remediation, e.g., extraction of heavy metals from water and soil (Roundhill 2001).



**Fig. 2.6** TEM images of metal nanoparticles. **a** Ag derived with HDD, **b** Au, **c** worm-like Pd, and **d** Pt from Pt(IV), derived with TBAB. Alloy nanoparticles of **e** Ag–Au, **f** Pd–Pt, **g** Pt–Rh, and **h** Pt–Ru, synthesized by coreduction of the metal precursors with TBAB. Core–shell nanoparticles of **i** 7.4-nm Au@Ag, **j** 12.7-nm Au@Ag, **k** 3.9-nm Pt@Ag, and **l** 9.2-nm Pt@Ag, synthesized by seed-mediated growth. Semiconductor nanocrystals of **m** Ag<sub>2</sub>S, **n** CdS, **o** HgS, and **p** PbS. Reproduced from Yang et al. (2009) with permission from Nature Publishing Group

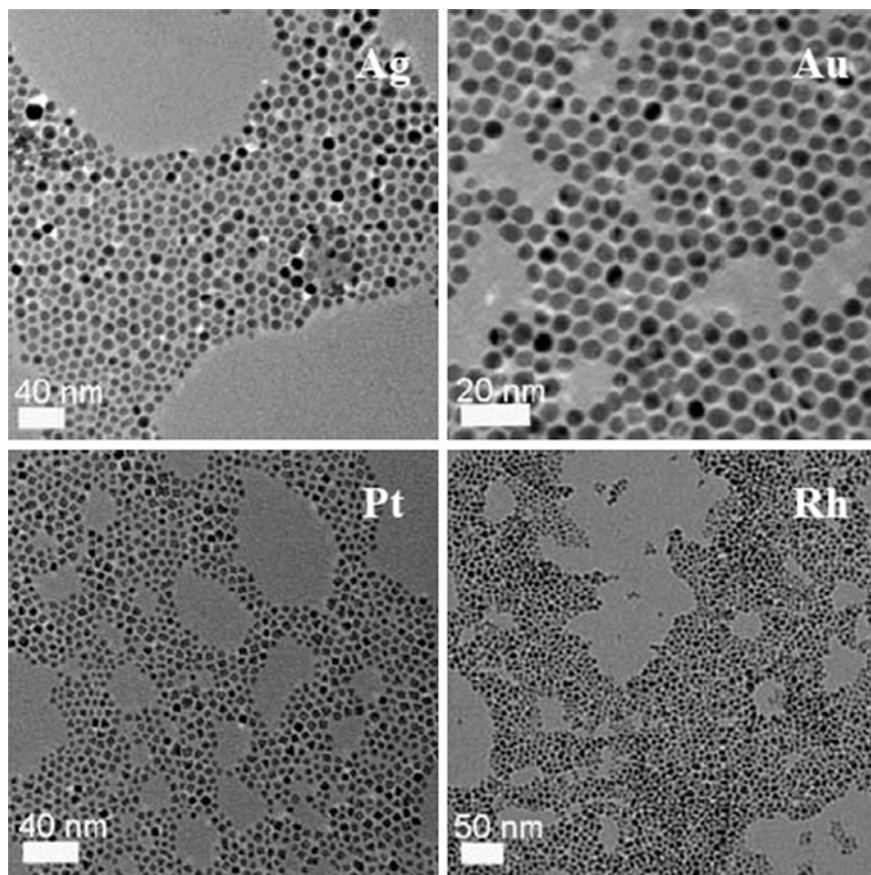
### 2.3.2 Ethanol-Mediated Phase Transfer of Metal Nanoparticles Already Formed

The ethanol-mediated phase transfer method described in the previous section was also applicable for the transfer of the noble metal nanoparticles from aqueous phase to a hydrocarbon layer (Yang et al. 2004, 2007, 2011). The direct phase transfer by mixing the metal hydrosol and alkanethiol or alkylamine in toluene only can work for limited metals in their “unprotected” forms. For example, ruthenium nanoparticles cannot be transferred from the aqueous environment to

a hydrocarbon layer by directly mixing the unprotected Ru hydrosol and toluene containing dodecanethiol or DDA. In addition, the direct transfer procedures involving a ligand exchange process often fail to transfer metal nanoparticles in the presence of external stabilizers, such as sodium citrate, which are often used as temporary capping agent for further assembly (Mirkin et al. 1996; Mucic et al. 1998; He et al. 2000), into a hydrocarbon layer containing thiol or amine. It was also found that the direct extraction of short-chain thiol-capped semiconductor nanocrystals from an aqueous solution by the use of long-chain aliphatic thiols is not possible (Gaponik et al. 2002). In the direct phase transfer process, as the exchange between the incoming ligands and initial stabilizers could only occur at the interface between water and organic phase, the failure in transferring the nanoparticles was possibly a consequence of the poor interfacial contact between the two immiscible phases. On the basis of this consideration, ethanol, which is water miscible and a good solvent for DDA, was used in lieu of toluene to increase the interfacial contact between citrate-stabilized metal nanoparticles and alkylamine, and this ethanol-mediated phase transfer protocol can be used to transfer metal nanoparticles capped by a variety of stabilizers from the aqueous phase to an organic medium with the efficiency of ~100 %. Analogous to the formation of metal ion–DDA complexes, the ethanol-mediated transfer for noble metal nanoparticles is primarily based on the formation of uniform alkylamine-stabilized metal nanoparticles through a stabilizer exchange process that involves firstly the mixing of the metal hydrosol and an ethanol solution of DDA, and then extracting the DDA-stabilized metal nanoparticles into toluene.

The typical experiment follows every step for transferring metal ions from aqueous phase to a nonpolar organic medium. For example, citrate-stabilized metal hydrosol prepared by  $\text{NaBH}_4$  reduction of metal precursors was mixed with equal volume of ethanol containing DDA and the mixture was stirred for 2 min. Then toluene was added, and stirring continued for 3 more minutes. DDA-stabilized metal nanoparticles were extracted into the toluene layer rapidly, leaving behind a colorless aqueous solution (Yang et al. 2004).

Citrate-stabilized metal nanoparticles could not be transferred directly to toluene by mixing the metal hydrosol together with a toluene solution of DDA. Prolonged stirring only produced a milky mixture of metal hydrosol and toluene, but the particles were aggregated at the interface of two immiscible layers instead of being transferred into toluene after the mixture was settled down into in a separating funnel. Instead, after stirring the ethanol–metal hydrosol mixture for about two minutes, the initially transparent hydrosol turned turbid, and suspending deep brown (for Ru, Pd, Pt, Ir, Os), purple (for Au), or yellowish brown-colored (for Ag) liquid droplets began to appear near the top of the mixture or on the container walls. This indicates that DDA has displaced citrate from the surface of the metal nanoparticles. The brown-, or purple-, or yellowish brown-colored liquid could be easily extracted into toluene by adding toluene and stirring the mixture briefly. Figure 2.7 shows the representative TEM images of Ag, Au, Pt, and Rh nanoparticles in toluene. The particle size distribution was fairly narrow, and the self-assembly of alkylamine-stabilized metal nanoparticles is also evident from these images.

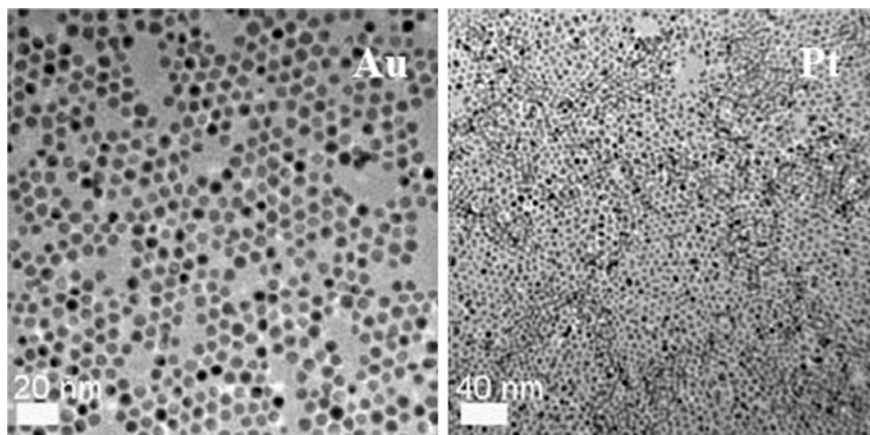


**Fig. 2.7** TEM images of alkylamine-stabilized Ag nanoparticles ( $d = 7.09$  nm), Au nanoparticles ( $d = 7.89$  nm), Pt nanoparticles ( $d = 4.43$  nm), and Rh nanoparticles ( $d = 6.89$  nm). Reproduced from Yang et al. (2004, 2007) with permission from Elsevier

The yields of all alkylamine-stabilized metal nanoparticles were estimated to be more than 90 % (Yang et al. 2004). The losses were likely caused by centrifugation and nanoparticle attachment to the container walls. On the other hand, the actual yields could also be lower due to surface oxidation of the metal particles during drying and the residual presence of DDA; both of them would add to the measured product weights.

For Pt, Au, Rh, Ir, and Os, the ethanol-mediated phase transfer method could also be extended to the preparation of alkanethiol-stabilized metal nanoparticles (Yang et al. 2004, 2007). The detailed procedures followed nearly every step in the alkylamine-stabilized metal nanoparticle preparation except that dodecanethiol was used instead of DDA. Figure 2.8 shows the TEM images of alkanethiol-stabilized Au and Pt nanoparticles thus obtained. The self-assembly is again evident in





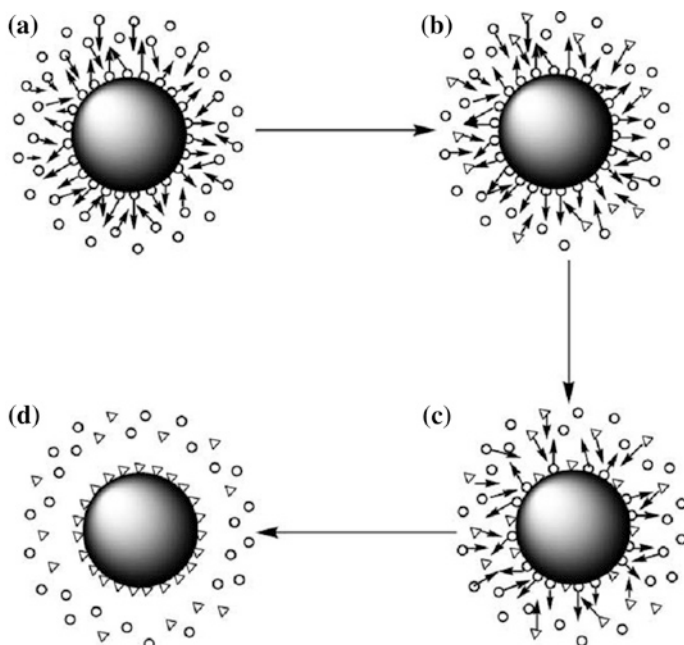
**Fig. 2.8** TEM images of alkanethiol-stabilized Au nanoparticles ( $d = 6.24$  nm) and Pt nanoparticles ( $d = 4.82$  nm). Reproduced from Yang et al. (2004) with permission from Elsevier

these images. On the other hand, the alkanethiol stabilization of Ru, Ag, and Pd nanoparticles was not as successful by this method. It was experimentally found that nanoparticles of Ru, Ag, and Pd would stay at the interface of the water and toluene or on the container walls instead of being transferred into toluene.

These experimental findings show that amine or thiol could displace citrate ions from the surface of metal nanoparticles in a hydrosol, provided that there was close contact between the amine or thiol molecules and the metal nanoparticles. Experimentally, the citrate-stabilized metal nanoparticles could not be re-dispersed in water after several rounds of washing and centrifugation. This could be easily explained by the progressive loss of the citrate ions as fresh solvent (water) was used in each re-dispersion attempt. The need to re-establish equilibrium between free and adsorbed citrate ions would slowly but eventually deplete the adsorbed citrate ions to a level inadequate to maintain the particles in suspension. The process of displacing citrate from the metal nanoparticle surface by DDA or dodecanethiol can be depicted as the scheme in Fig. 2.9.

The failure to directly transfer citrate-stabilized metal nanoparticles from the hydrosol to the toluene solution of DDA (or dodecanethiol) could also be understood from simple adsorption principles. Dissolved DDA (or dodecanethiol) in toluene was unable to exchange sufficiently with the citrate ions because of inadequate contact between the metal nanoparticles and these molecules. The mechanism shown in Fig. 2.9 also satisfactorily interprets the change in the size of nanoparticles coupled with ligand exchange process (Lala et al. 2001; Brown and Hutchison 1997, 1999). The dynamic equilibrium between free and adsorbed capping agents would sometimes result in the exposure of nanoparticle surface, which offers the contact points for particle agglomeration in the absence of sufficient exchanging ligands, a case usually occurred in direct ligand exchange.





**Fig. 2.9** Schematic illustration to show the process of displacing citrate from nanoparticle surface by  $\text{NH}_2^-$  (or  $\text{SH}^-$ ). *Open circle* citrate ions; *triangle*  $\text{NH}_2^-$  (or  $\text{SH}^-$ ). Reproduced from Yang et al. (2004) with permission from Elsevier

This ethanol-mediated transfer method could be used to transfer metal nanoparticles capped by a variety of surfactants, such as sodium acetate, polyvinylpyrrolidone (PVP), bis(p-sulfonatophenyl)phenylphosphine (BSPP), or Triton X-100 (Yang et al. 2005, 2006). It is also applicable to transfer the nanoparticles prepared by the  $\text{NaBH}_4$  reduction of metal precursors without a stabilizer and to transfer Cu and Ni nanoparticles from aqueous environment to hydrocarbon layer, but the latter need to be performed in inert atmosphere to prevent these metals from oxidation. In comparison with the procedure reported by Sarathy and coworkers (Sarathy et al. 1997a, b), where concentrated HCl has to be used to facilitate the nanoparticle transfer, the ethanol-mediated method is much gentler. Besides its generic applicability, it offers ease of operation and is compatible with the transfer of metals which are reactive toward concentrated HCl.

## 2.4 Summary

In summary, this chapter demonstrated a general protocol for transferring metal ions and nanoparticles from water to organic medium, which involved mixing an aqueous solution of metal ions or metal hydrosol with an ethanolic solution of

DDA, and extracting the metal ions or metal nanoparticles into a toluene layer. This protocol could be applied to transfer a wide variety of transition metal ions from water to toluene with an efficiency of >95 %. It led to the successful synthesis of a wide range of metallic, alloy, and semiconductor nanocrystals. Thus, this approach represents a simple and flexible route for fabricating nanostructured materials with novel structures and multiple functionalities and would create favorable solvent surroundings for the wet chemistry-based synthesis of noble metal-based nanocomposites with multiple functionalities.

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