

# Digestive ripening: a synthetic method *par excellence* for core–shell, alloy, and composite nanostructured materials

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**Abstract.** The solvated metal atom dispersion (SMAD) method has been used for the synthesis of colloids of metal nanoparticles. It is a top-down approach involving condensation of metal atoms in low temperature solvent matrices in a SMAD reactor maintained at 77 K. Warming of the matrix results in a slurry of metal atoms that interact with one another to form particles that grow in size. The organic solvent solvates the particles and acts as a weak capping agent to halt/slow down the growth process to a certain extent. This as-prepared colloid consists of metal nanoparticles that are quite polydisperse. In a process termed as *digestive ripening*, addition of a capping agent to the as-prepared colloid which is polydisperse renders it highly monodisperse either under ambient or thermal conditions. In this, as yet not well-understood process, smaller particles grow and the larger ones diminish in size until the system attains uniformity in size and a dynamic equilibrium is established. Using the SMAD method in combination with digestive ripening process, highly monodisperse metal, core–shell, alloy, and composite nanoparticles have been synthesized. This article is a review of our contributions together with some literature reports on this methodology to realize various nanostructured materials.

**Keywords.** Nanoparticles; core shell; alloy.

## 1. Introduction

In recent years, distinct structures and properties exhibited by materials belonging to the nanometer size regime has stimulated a lot of research interest. The versatile applications of these materials enriched the field of biomedicine,<sup>1</sup> optoelectronics,<sup>2</sup> and catalysis<sup>3</sup> to a great extent due to their unique properties. The property of a nanoparticle strongly depends on its size, shape, interparticle distance and the surrounding environment.<sup>4</sup> These properties could be tuned precisely by controlling the particle size of the material keeping the other parameters unchanged. The size effect is much more pronounced when the particle size is in the range of 1–10 nm.<sup>5</sup> Size dependent property that stems from a polydisperse sample will show an average effect due to different sizes present in the system. In the case of a monodisperse sample, the displayed property could be identified as emerging from a single entity. Hence, tight control over size and size distribution is indispensable for attaining a desired property. In this respect, much attention is focused on developing synthetic strategies

leading to monodispersity and those that are simple to manipulate, easy to scale up and highly reproducible.

We discuss here how digestive ripening, a post synthetic approach is exploited for achieving monodispersity of nanoparticles. An even more remarkable feature of digestive ripening exemplified here is, it could be exercised as a synthetic method towards various heterostructured materials like core–shell particles, nanoalloys, and nanocomposites in combination with the synthetic method, solvated metal atom dispersion (SMAD).

## 2. Solvated metal atom dispersion: A top-down approach

The SMAD set-up for the synthesis of colloidal nanoparticles is comprised of a high vacuum line typically operating at pressures of  $10^{-3}$  to  $10^{-4}$  torr, a pair of water-cooled copper electrodes with a tungsten crucible (works for most materials) in which the material to be vapourized is placed and a suitable power supply to resistively heat the crucible. The fundamental reactor design was given by Skell, Wescott, Golstein and Engel in 1964.<sup>6</sup> The modified SMAD set-up is described in detail elsewhere.<sup>7</sup> The basic approach of the SMAD

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synthesis involves the growth of atomic/molecular clusters at low temperature starting from the corresponding bulk material. The synthesis involves co-evaporation of the bulk material and stabilizing solvent followed by their co-condensation on the walls of a reactor maintained at 77 K. Warm up of the frozen matrix under argon upon completion of the evaporation results in a slurry of atoms/molecules that interact to form particles that may further grow in size. The solvent can act as a weak capping agent to prevent the growth to some extent. Optionally, an organic ligand/surfactant can be incorporated in the reaction to arrest the growth process and thereby to stabilize the nanoparticles. First report on this approach was from Klabunde and coworkers on the preparation of non-aqueous gold colloid.<sup>8</sup> From then on, synthesis of a number of metal nanoparticles has been reported by the SMAD method. Apart from metals, the same method has been extended to other systems like metal sulphides, metal halide, etc.<sup>9</sup> The supremacy of SMAD synthesis over other methodologies is apparent because of its high reproducibility, easy scale up, avoidance of tedious purification processes and high yield. Moreover, this is exceptionally suitable for the synthesis of highly air and moisture sensitive materials which are difficult to prepare by other methods.

### 3. The issue of size control: Digestive ripening

In general, the as-prepared SMAD colloid is quite polydisperse in nature. It can be transformed into a monodisperse sample in a remarkable one-step process termed as digestive ripening which involves refluxing of a polydisperse sample at or near the boiling point of the solvent in the presence of a capping agent and is limited to nanoparticles. In this, not-fully understood process, smaller particles grow in size and larger ones shrink until the system attains uniformity in size. The optimum size obtained for a particular nanoparticle depends on various factors like capping agent, solvent, temperature, etc. The first tentative manifestation of this process was provided by Klabunde and coworkers in 1999.<sup>10</sup> In this work, Au nanoparticle surface was ligated by dodecane thiol by heating under reflux which resulted in narrow distribution of size. Subsequent studies on Au nanoparticles provided more insight into the digestive ripening process.<sup>11</sup> Apart from the reduction in average particle size and polydispersity, digestive ripening also prompted the formation of 2D and 3D superlattices. In addition to thiols, amines, silanes, and phosphines were also found to be effective in digestive ripening.<sup>12</sup> It was

noted that refluxing of the as-prepared colloid should be done only with digestive ripening agent without surfactants and other impurities. In this context, SMAD provides an excellent starting material for digestive ripening.

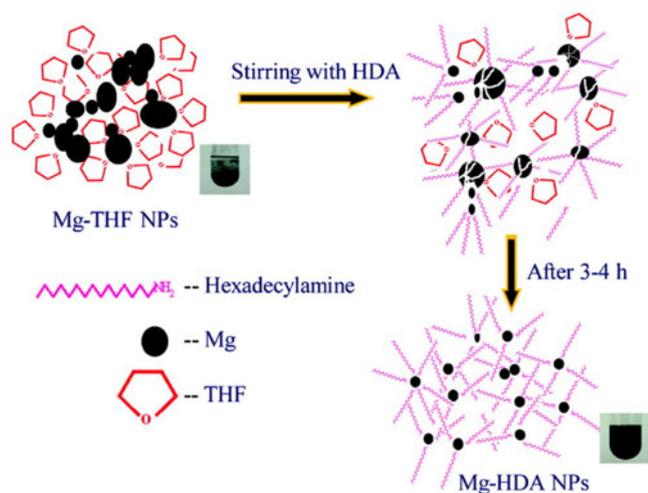
Digestive ripening of SMAD prepared colloid was first reported by Stoeva *et al.*<sup>13</sup> In this work a highly polydisperse Au-toluene-thiol colloid containing particles of size ranging from 1 to 40 nm was subjected to digestive ripening. Upon heating under reflux for 1.5 h, transformation to nearly monodisperse colloid with particle size of about 4–4.5 nm took place. Digestive ripening of silver nanoparticles with different ligands also led to monodispersity.<sup>14</sup> The monodisperse particles formed during digestive ripening of SMAD colloid showed large tendency to form extensively ordered superlattices.

Following the same protocol we also made similar kind of observation with copper and zinc.<sup>15</sup> In the earlier reports on the SMAD synthesis of Cu nanoparticles, particle agglomeration took place to form spongy ensembles. In our case, the as-prepared Cu colloid by the SMAD method resulted in broad distribution of well-separated nanoparticles having size in the range of 2.5–8.0 nm. Digestive ripening of this Cu colloid in the presence of hexadecyl amine (HDA) gave rise to a very narrow size distribution of  $2.1 \pm 0.3$  nm. Self-assembly into 2D superlattice was also shown by these stabilized Cu nanoparticles. Similar to this, digestive ripening of the SMAD prepared agglomerated zinc butanone colloid in the presence of HDA resulted in a narrow size distribution of  $3.9 \pm 0.3$  nm with well-separated nanoparticles. However, rather strange behaviour was shown by palladium upon digestive ripening.<sup>16</sup> The as-prepared Pd-butanone-4-tert-butyl toluene-dodecanethiol colloid showed spherical particles of mean size  $2.8 \pm 0.1$  nm. Even though the colloids were stable against precipitation under Ar, a Pd-thiolate complex formation started slowly with time at room temperature. This disintegration of colloid is attributed to the ligand exchange occurring between 2-butanone and dodecanethiol. Digestive ripening of this colloid simply accelerated the thiolate formation. Recently, digestive ripening of indium nanoparticles prepared by the SMAD method under mild condition was reported by Klabunde *et al.*<sup>17</sup> Ripening was done in a low boiling solvent methylene chloride at 38 °C. Motivated by the success of the SMAD method followed by the digestive ripening process, this methodology has been extended to binary systems e.g., CdSe also.<sup>18</sup> In all the above mentioned works, refluxing at the boiling point of solvent is an essential condition for the digestive ripening process.

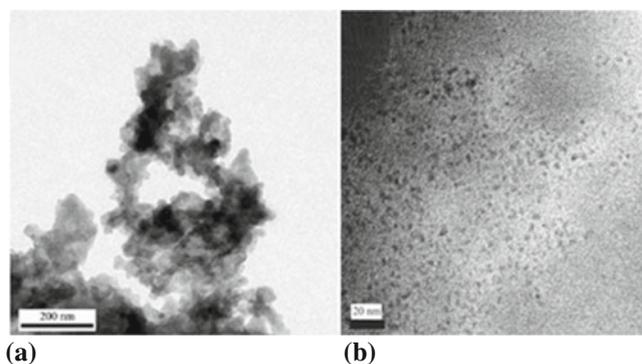
Contrary to this, we found that highly monodisperse colloidal Mg nanoparticles could be obtained by room temperature digestive ripening.<sup>19</sup> In this work, Mg–THF nanoclusters of 25 nm size undergo a drastic size reduction to  $2.8 \pm 0.2$  nm upon mere stirring with HDA ligand. The schematic representation of this process is given in figure 1. The TEM images of the as-prepared Mg–THF and the ripened Mg–HDA nanoparticles are shown in figure 2.

Pileni *et al.* reported room temperature ripening of worm-like palladium nanoparticles by stirring with large amount of dodecane thiol.<sup>20</sup> They showed the transformation of worm-shaped structures to spherical particles revealing shape selectivity of this process. Here, no size reduction is observed since the particle diameter of both the worm-like and the spherical structures remained similar.

In a very recent work, we reported the synthesis of calcium nanoparticles by the SMAD method.<sup>21</sup> The synthesis of calcium nanoparticles by conventional methods turned out to be a difficult task because of its high reactivity and pyrophoric nature. In our work, the as-prepared, nearly spherical nanoparticles were free standing but quite polydisperse in nature with an average particle size of  $8.3 \pm 1.0$  nm. As evident from the case of Mg nanoparticles, here also we observed room temperature ripening by stirring Ca nanoparticles with HDA taken at bottom of the SMAD reactor. The digestive ripening of the as-prepared Ca nanoparticles in the presence of HDA was apparent from the TEM micrographs showing monodispersity with well-separated spherical nanoparticles of size 2–3 nm. Based



**Figure 1.** Room temperature digestive ripening of Mg–THF nanoparticles in the presence of HDA. Reproduced with permission from the American Chemical Society [ref. 19].



**Figure 2.** TEM image of (a) Mg–THF nanoparticles and (b) Mg–HDA nanoparticles after room temperature digestive ripening. Reproduced with permission from the American Chemical Society [ref. 19].

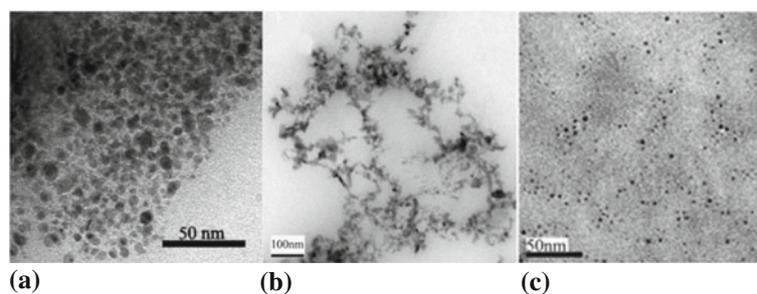
on the obtained experimental evidences to date, refluxing need not be a necessary condition atleast in case of certain nanoparticles.

#### 4. Towards the heterostructures

Bimetallic nanosystems like core–shell structures, nanocomposites, and nanoalloys have been attracting much attention because of their versatile applications, especially in the field of catalysis.<sup>22</sup> This is due to the fact that the physicochemical properties of these systems originate from the collective interactions of the constituents and that can be enhanced or extended significantly compared to the individual entity. Numerous methods have been suggested for their synthesis, even though most of the methods suffer from certain limitations associated with scale up, reproducibility, monodispersity of particle size and reaction conditions.

Prompted by the advantages of the SMAD method followed by digestive ripening, we explored this combination for realizing bimetallic core–shell structures. The synthetic protocol involves digestive ripening of a mixture of separately prepared as-prepared colloids together with a capping agent at the boiling point of the solvent. Following this protocol, we reported the synthesis of nearly monodisperse Cu@ZnO core–shell structure of average particle size of  $3.0 \pm 0.7$  nm by refluxing Cu and Zn colloids with HDA in butanone solvent at 80 °C (figure 3).<sup>15</sup>

Under this mild experimental condition, there was a reduction in the size distribution of both Cu and Zn nanoparticles as well as transfer of atoms from one particle to the surface of the other with different elemental composition to form a core–shell structure. The ZnO shell was formed on the surface of Cu–Zn particle due to the preferential oxidation of the Zn surface.



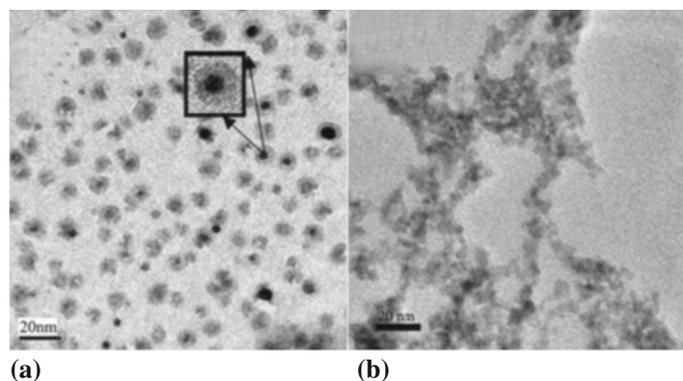
**Figure 3.** TEM image of (a) as-prepared Cu-butanone colloid and (b) as-prepared Zn-butanone colloid and (c) Cu@ZnO core-shell nanoparticles. Reproduced with permission from the American Chemical Society [ref. 15].

By the same method, we prepared Au@Pd core-shell nanoparticles which established the reproducibility of this method further.<sup>16</sup> As mentioned before, rather than leading to monodispersity, refluxing of the Pd-thiol colloid resulted in the rapid formation of Pd-thiolate which was slow at room temperature. The expected competition between formation of thiolate and the core-shell structure is largely suppressed upon mixing Au and Pd colloids. Here the core-shell structure formation is initiated even before the mixture is refluxed. Upon refluxing, free Pd particles bound to thiol get attached to the surface of an Au core hindering the thiolate formation. This core-shell particle was found to be kinetically stable and showed no tendency to form an Au-Pd alloy even at higher temperatures. In a similar fashion, Ag@Pd core-shell particles were realized by the digestive ripening process of a mixture of as-prepared dodecanethiol capped Ag and Pd colloids.<sup>23</sup> During refluxing, polydisperse dodecanethiol-capped Ag nanoparticles transformed into monodisperse Ag seeds along with small amount of Ag thiolate. These Ag seeds favour the breakdown of the Pd clusters into smaller

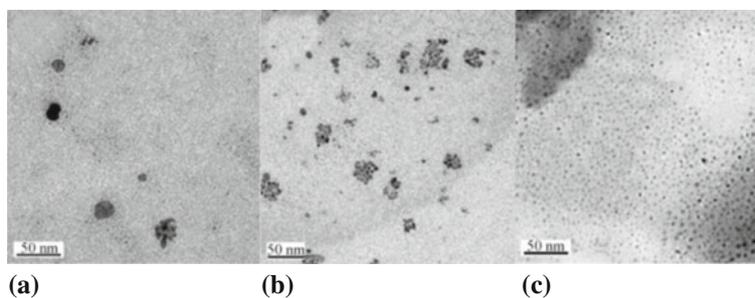
particles which in turn get deposited on the surface of Ag seeds. This process limited the formation of Pd thiolate complex.

It is interesting to mention that we also reported the synthesis of Cu@Cu<sub>2</sub>O and Cu<sub>2</sub>O (figure 4) nanoparticles using only the SMAD method and studied their catalytic activity in generating hydrogen from ammonia-borane.<sup>24</sup> The core-shell structure was achieved by the controlled oxidation of SMAD prepared Cu nanoparticles whereas purging of oxygen for 30 min resulted in Cu<sub>2</sub>O nanoparticles. The TEM image of Cu@Cu<sub>2</sub>O core-shell nanoparticles revealed the formation of more or less monodisperse spherical nanoparticles of average size  $7.7 \pm 1.8$  nm.

Recently, the synthesis of Cu/Mg nanocomposite was realized by the digestive ripening process.<sup>25</sup> A physical mixture of Mg and Cu-HDA-mesitylene colloids was subjected to digestive ripening near the boiling point of mesitylene around 170 °C. The Cu nanoparticles first underwent narrowing of size distribution with already ripened Mg nanoparticles, eventually leading to Cu/Mg nanocomposite of less than 5 nm size (figure 5).



**Figure 4.** TEM image of (a) Cu@Cu<sub>2</sub>O nanoparticles and (b) Cu<sub>2</sub>O nanoparticles. Reproduced with permission from the Royal Society of Chemistry [ref. 24].



**Figure 5.** TEM image of (a) physical mixture of Mg/Cu nanoparticle before reflux, (b) after 1 h of reflux and (c) after 6 h reflux. Reproduced with permission from Wiley-VCH [ref. 25].

Annealing of this Cu/Mg nanocomposite resulted in the formation of Cu/MgO nanocomposite. The advantage of this procedure is that the difficulty in synthesizing Cu/Mg and Cu/MgO nanocomposite by conventional method based on the high energy solid state reactions is overcome by simple and mild reaction conditions.

It has been observed in certain cases that by providing sufficient energy dissolution of the core-shell structure leading to formation of an alloy takes place via diffusion of surface atoms of the shell into the bulk of the core. Hodak *et al.* showed the conversion of Au@Ag core-shell structure into an Au-Ag alloy by laser-induced heating.<sup>26</sup> Under this high energy condition, melting and consequent erosion of the core-shell structure took place to form a homogeneous alloy. Digestive ripening process also has been demonstrated to be effective for nano-alloy formation. Klabunde *et al.* used this synthetic methodology to prepare alloys of Cu and Ag nanoparticles with Au nanoparticles.<sup>27</sup> The reaction was carried out in 4-tert-butyl toluene at 198 °C. It was suggested that at this temperature, interparticle diffusion of atoms from the surface to the centre of nanoparticle brought about the formation of an alloy. Prompted by this, further studies are being carried out in this direction to accomplish different bimetallic nano-alloys.

## 5. Conclusions

Digestive ripening is a well-established process to obtain highly monodisperse nanoparticles. Based on the experimental evidence, we put forward the combination of SMAD and digestive ripening as a powerful and promising technique for realizing core-shell nanoparticles, nanocomposites and nanoalloys. It is also emphasized here that the SMAD method offers propitious solution over the synthetic challenges existing over the synthesis of air sensitive materials. The mechanistic

aspects of this coveted process are largely unknown; efforts are in progress in our laboratories to unravel the mechanistic details of the digestive ripening process.

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