

# A safe sonochemical route to iron, cobalt and nickel monoarsenides

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In this paper, we report a safe method for the preparation of transition metal arsenides. At room temperature, well-crystallized and monodispersed arsenides particles were successfully obtained under high-intensity ultrasonic irradiation for 4 h from the reaction of transition metal chlorides, arsenic (which is the least toxic arsenic feedstock) and zinc in ethanol. Characterization by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), electron diffraction (ED), and X-ray photoelectron spectroscopy (XPS) shows that the product powders consist of nanosize particles. The ultrasonic irradiation and the solvent are both important in the formation of the product.

## Introduction

In recent years, nanocrystalline semiconductors have been of great research interest due to their unusual physical properties. The quantum size effects of nanomaterials may induce unique electronic,<sup>1</sup> optical<sup>2</sup> and magnetic properties<sup>3</sup> compared with those in traditional bulk materials. Their nanometer-scale dimensions may allow new structures that could serve as potential building blocks for field-emission electron sources,<sup>4</sup> electronic<sup>5</sup> and optoelectronic<sup>6</sup> devices. In the following years, many methods have been explored to produce various nanomaterials, such as gas-liquid precipitation,<sup>7</sup> molecular beam epitaxy (MBE),<sup>8</sup> metalorganic chemical vapor deposition (MOCVD),<sup>9</sup> organometallic vapor phase epitaxy (MVPE),<sup>10</sup> electrochemical methods,<sup>11</sup> solvothermal methods,<sup>6a</sup>  $\gamma$ -radiation synthesis,<sup>12</sup> microwave assisted preparation,<sup>13</sup> and sonochemical synthesis,<sup>14</sup> *et al.* Among these methods, sonochemical synthesis has been paid more extensive attention due to its special potential applications. Currently, the sonochemical process has been proved to be a useful technique for generating novel materials with unusual properties,<sup>15</sup> since it results in particles of a much smaller size and high surface area than those produced by other methods. The chemical effects of ultrasound, which arise from acoustic cavitation, formation growth and implosive collapse of a bubble in a liquid, will produce unusual chemical and physical environments.

Metal pnictide semiconductors have a wide variety of applications. For example, they can be used in compact disc players,<sup>16</sup> satellite TV receivers<sup>17</sup> and as optical fibers.<sup>18</sup> Transition metal pnictides have many special electrical, mechanical and anticorrosion properties<sup>19</sup> compared with III-V semiconductors. Among them, iron arsenides have attracted much attention for a long time because of their technological importance as semiconductors,<sup>20</sup> secondary high-temperature batteries<sup>21</sup> and catalysts.<sup>22</sup>

To produce transition metal arsenides, the most straightforward way, as we know, is the direct combination of elemental metal and arsenic.<sup>19</sup> However, this method requires elevated temperature, inert atmosphere protection and a relatively long duration. Furthermore, it is difficult to obtain nanoscale materials by this traditional solid-state reaction. Recently, Parkin<sup>23</sup> and co-workers synthesized a series of metal arsenides by a solid state metathesis (SSM) reaction with alkaline metal arsenides and metal halides as precursors at a temperature of

500 °C, however they only obtained a mixture of FeAs and Fe<sub>2</sub>As.

In order to decrease the reaction temperature and alleviate the reaction time and energy cost, several new strategies have been introduced to prepare arsenides, such as dehalosilylation and related reactions,<sup>24</sup> organometallic synthesis,<sup>25</sup> chemical conversion of monometric arsenogallane,<sup>26</sup> solution-liquid-solid (SLS) growth method,<sup>27</sup> and solvothermal method.<sup>28</sup> All of these methods are much more useful and milder than the traditional element combination reaction, but there are some limitations to their utilities because very toxic arsenic sources, such as AsCl<sub>3</sub> and AsH<sub>3</sub>, have usually been used. It is well known that the use of AsCl<sub>3</sub> and AsH<sub>3</sub> is of particular concern due to their carcinogenic and mutagenic properties. Thus, it is very challenging to seek a less toxic arsenic feedstock in the process of preparing arsenides. One can clearly see that elemental arsenic powder is a perfect arsenic feedstock considering the order of toxicity given by Penrose:<sup>29</sup> R<sub>3</sub>As (R = H, Me, Cl, *etc.*) > As<sub>2</sub>O<sub>3</sub> (As(III)) > (RAsO)<sub>n</sub> > As<sub>2</sub>O<sub>5</sub> (As(V)) > R<sub>n</sub>AsO(OH)<sub>3-n</sub> (n = 1, 2) > R<sub>4</sub>As<sup>+</sup> > As(0). Herein, we report a safe, new and simple technique for the sonochemical synthesis of nanocrystalline transition metal arsenides (FeAs, CoAs and NiAs) by using elemental arsenic powder as the arsenic source at room temperature.

The use of ultrasound to enhance chemical reactions in liquid-solid heterogeneous systems has become increasingly widespread. Ohtani<sup>30</sup> reported that ultrasonic irradiation can accelerate reactions, and Gedanken<sup>14a-d</sup> and Suslick<sup>14e,f</sup> have used sonochemical irradiation to produce a variety of nanostructured materials, but they are often amorphous. Based on previous research, our group have successfully expanded this method to prepare nanoscale metal chalcogenides.<sup>31</sup> Here, we successfully obtained transition metal arsenides in ethanol solutions by using the ultrasound irradiation method under ambient conditions. To our knowledge, this is the first time that arsenides have been prepared by ultrasound irradiation. Furthermore, we successfully avoid very toxic arsenic sources such as AsCl<sub>3</sub> and AsH<sub>3</sub> in the process.

## Experimental

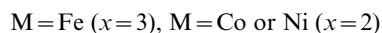
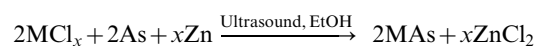
All reagents were of analytical grade. In a typical experimental procedure, FeAs can be prepared from a stoichiometric mixture of arsenic (0.450 g, 6.00 mmol), zinc (0.390 g,

6 mmol) and FeCl<sub>3</sub> (0.975 g, 6.00 mmol). The reagents were loaded into a 100 mL reactor, which was designed to ensure that the horn tip was immersed into the solution consistently to the same depth (10 mm). Then absolute ethanol was added up to 85% of the total volume. The solution was purged with nitrogen for 30 min, and then the container was sealed. The sealed reactor was kept in a circulating water bath to maintain the temperature of the bulk solution at 20 ± 5 °C and irradiated with a high-intensity ultrasonic probe (Model, 1.5 cm Ti horn, 20 kHz, 100 W cm<sup>-2</sup>) for 4 hours. The products were filtered out, washed with 1 M HCl, distilled water and absolute ethanol in sequence to remove the byproducts. Finally, the products were dried under vacuum at 40 °C for 3 h. For the preparation of CoAs and NiAs, the procedure was analogous to that for FeAs with the use of CoCl<sub>2</sub> or NiCl<sub>2</sub> with the molar ratio MCl<sub>2</sub>:As:Zn = 1:1:1 (M = Co, Ni). The yields of FeAs, CoAs, and NiAs based on arsenic were about 92%, 87%, and 93%, respectively.

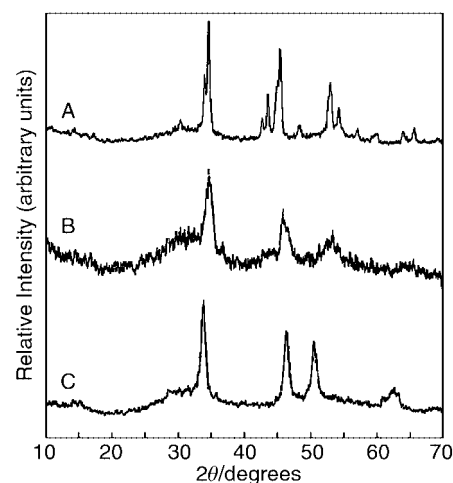
The phases and the crystallographic structures of the products were determined by X-ray powder diffraction (XRD) using a Japan Rigaku D/max-γA X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The scan rate of 0.05° s<sup>-1</sup> was applied to record the pattern in the 2θ range of 10°–70°. Transmission electron microscopy (TEM) images, which were obtained using a Hitachi Model H-800 at an acceleration voltage of 200 kV, were used to observe the morphology and size of the prepared products. The products purity and composition were examined by X-ray photoelectron spectroscopy (XPS) on an ESCALab MKII instrument with Mg Kα radiation as the excitation source. The atomic ratios of the samples were measured using inductively coupled plasma (ICP) spectroscopy with a Seiko Electronics SPD 1200A ICP emission analyzer with a pump flow of 1.85 ml min<sup>-1</sup> and the flow rate of auxiliary gas (Ar 99.99%) 0.5 l min<sup>-1</sup>. The samples were dissolved in a heated dilute HNO<sub>3</sub> solution and further elemental analysis was carried out. Elemental Co and Ni are similar to Fe in some aspects of their chemical properties, therefore the atomic ratios of CoAs and NiAs were analyzed in our experiments.

## Results and discussion

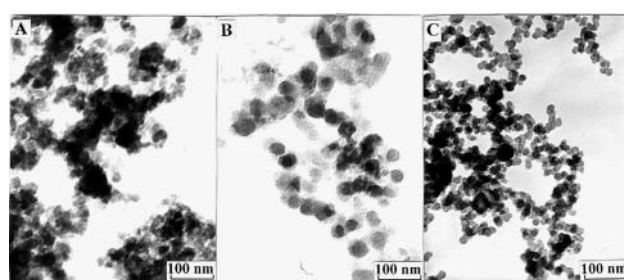
Reaction of arsenic powders, zinc powders and MCl<sub>x</sub> (M = Fe, Co and Ni) under ultrasound irradiation in absolute ethanol resulted in black precipitates. In this process, zinc reduces the dissolved MCl<sub>x</sub> to the corresponding active metal element under ultrasonic irradiation. Ultrasonic waves, which are intense enough to produce cavitation, can provide sufficient energy for the reaction of arsenic and the newly formed transition metals to form the corresponding arsenide nanocrystals. The reaction can be formulated as follows:



The XRD patterns for FeAs (A), CoAs (B) and NiAs (C) are



**Fig. 1** XRD patterns of as-prepared nanocrystalline arsenides: (A) FeAs, (B) CoAs, and (C) NiAs.



**Fig. 2** TEM images of typical samples of nanocrystalline arsenides: (A) FeAs, (B) CoAs, and (C) NiAs.

shown in Fig. 1. All their reflection peaks were indexed. The cell parameters calculated after refinement were close to those in the JCPDS files. The average sizes of particles for all samples were calculated by using the Scherrer formula.<sup>32</sup> The results are in good agreement with the observations from TEM images (Fig. 2). All the reflection peaks were used to calculate the cell parameters in each XRD pattern. The characterization data of the as-prepared products are listed in Table 1. Fig. 2 shows the transmission electron microscopy (TEM) microphotographs of the samples. It is apparent that all products possess monodisperse spherical morphology. The average sizes from the TEM images are also listed in Table 1.

The product purity and elemental composition were detected by X-ray photoelectron spectroscopy (XPS). As an example, XPS spectra for NiAs are shown in Fig. 3. A survey spectrum is shown in Fig. 3a, which indicates the presence of Ni and As, as well as C and O (from reference absorbed gaseous molecules, respectively). There are no peaks for chloride ion and elemental arsenic (from the starting materials) in the survey spectrum. Higher resolution spectra shown in Fig. 3b and c were also taken of the As 3d and Ni 2p regions. The binding energy is

**Table 1** Characterization of as-prepared products

Product	Cell constants/Å		Phase	Morphology	JCPDS	TEM size/nm
	Observed	Reported				
FeAs	<i>a</i> = 5.445 <i>b</i> = 6.032 <i>c</i> = 3.354	<i>a</i> = 5.436 <i>b</i> = 6.024 <i>c</i> = 3.372	Orthorhombic	Spherical	No. 12-799	18
CoAs	<i>a</i> = 3.472 <i>b</i> = 5.876 <i>c</i> = 5.306	<i>a</i> = 3.458 <i>b</i> = 5.869 <i>c</i> = 5.292	Orthorhombic	Spherical	No. 9-94	20
NiAs	<i>a</i> = 3.629 <i>c</i> = 5.018	<i>a</i> = 3.622 <i>c</i> = 5.013	Hexagonal	Spherical	No. 31-900	12

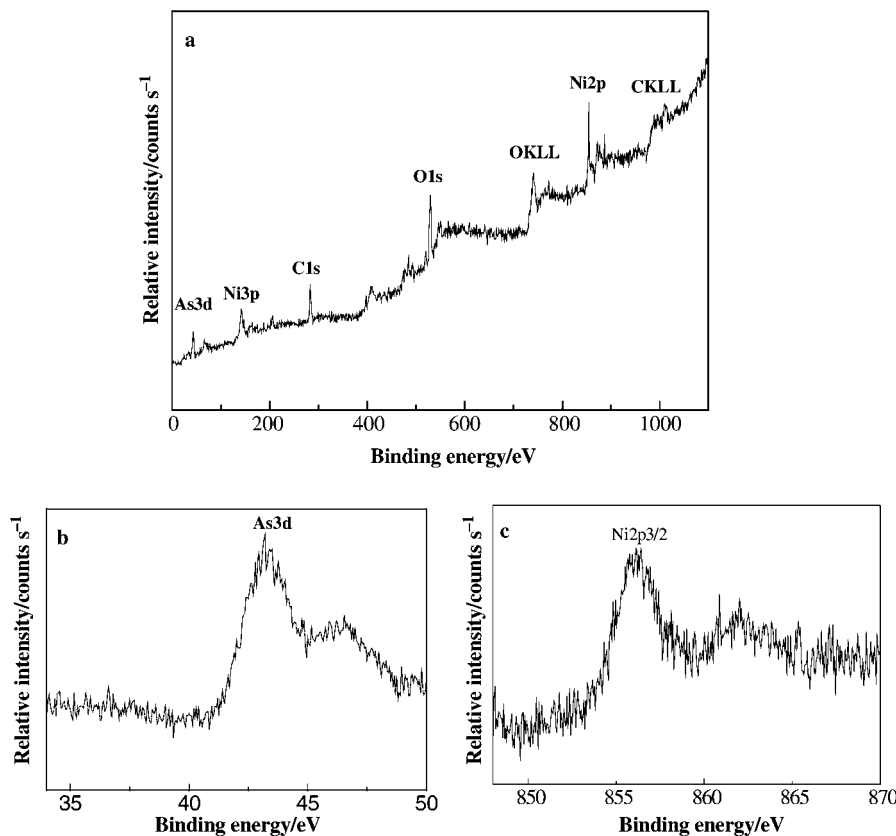


Fig. 3 XPS analysis of as-prepared nanocrystalline NiAs.

41.9 eV for As 3d and 855.85 eV for Ni 2p, respectively, which is in agreement with the literature.<sup>33</sup> The As 3d core also shows another peak at about 45.0 eV corresponding to oxidized As species. Similar results have been observed by other authors in InP nanocrystals.<sup>34</sup> Peak areas of these high-resolution scans were measured and used to calculate the Ni-to-As ratio for the nanocrystals. Quantification, in which only the As 3d peak corresponding to NiAs was used, gives the ratio of Ni to As of 1.034 : 1, which is almost consistent with the formula of NiAs. This result is in agreement with the quantitative composition analysis *via* energy-dispersive X-ray (EDX) analysis, which is 1.027 : 1. For FeAs and CoAs, similar results were obtained. The results are also nearly consistent with those obtained from ICP elemental analysis (Fe<sub>1.07</sub>As, Co<sub>1.14</sub>As and Ni<sub>1.04</sub>As).

In the processes of producing arsenides, ultrasonic irradiation plays a crucial role. Ultrasonic irradiation, which can drive chemical reactions, such as reduction, oxidation, dissolution, decomposition<sup>15</sup> and polymerization<sup>35</sup> to proceed under ambient conditions, is a novel energy source differing from traditional energy sources (for example, heat, light, or ionizing radiation) in duration, pressure, and energy per molecule. The XRD patterns (Fig. 1) of sonochemically prepared transition metal arsenides reflect that these nanoparticles are well crystallized, which is markedly different from the general result that products prepared by high-intensity ultrasonic irradiation are often amorphous.<sup>36</sup> In our processes, transition metal chlorides can dissolve into ethanol and form a complex. So in the present process, the reaction is conducted in a heterogeneous system. This heterogeneous process provides the possibility of annealing of the products. In addition, when the reactions were carried out at room temperature with low-intensity (such as produced by a commercial ultrasonic cleaner) or without ultrasonic irradiation, the XRD measurements showed that no arsenides could be obtained even for very long reaction times. That is to say, the high-intensity ultrasonic irradiation is necessarily fully responsible for these reactions. Because of the effects of interparticle collisions, microjets and

shockwaves, this new process is also helpful in the preparation of well-dispersed particles as shown in Fig. 2.

In the liquid–solid (LS) heterogeneous system, the use of ultrasound can enhance the reaction.<sup>30</sup> It has been known that some reactions can not proceed due to limited surface areas, such as where a passive surface oxide coating exists on the solid. The effects of interparticle collisions, microjets and shockwaves can drive high-speed jets of liquid to impinge upon the surface which act to remove this coating and create a localized erosion to produce a newly exposed and highly reactive surface. At the same time, the ultrasound improves mass transport, and causes particle fragmentation which can substantially increase the surface area of arsenic as a brittle solid. So, the reaction can take place easily at room temperature.

There are three regions of sonochemical activity reported by Suslick:<sup>37</sup> (I) the inner environment (gas phase) of the collapsing bubble, where elevated temperature (several thousands of degrees) and pressure (hundreds of atmospheres) are produced; (II) the interfacial region where the temperature is lower than that in the gas-phase region but still high enough to induce a sonochemical reaction; and (III) the bulk solution, which is at ambient temperature. Among the above-mentioned three regions, it appears that the current sonochemical reaction occurs within the interfacial region, yielding nanocrystals, because of the not very high quenching rate experienced by the product. If the reaction takes place inside the collapsing bubble, the product is amorphous as a result of the cooling rates ( $> 10^{10} \text{ K s}^{-1}$ ),<sup>38</sup> whereas if the reaction takes place at the interface, one expects to obtain crystalline products. These results can also be proved by the XRD patterns from which we can clearly observe that the products have high crystallinity.

In the processes of preparing transition metal arsenides, selecting ethanol as the solvent is another important step in the formation of arsenides. Transition metal chlorides can dissolve in ethanol. This favors the formation of the liquid–solid heterogeneous system. When using benzene as solvent, because

of the insolubility of transition metal chlorides in benzene the metal ion can not be reduced by Zn, nor can the formation of arsenides take place. Another advantage of using ethanol as the solvent is that ethanol is a low toxic solvent in comparison with other organic solvents, such as ethylenediamine (en) and heptane, etc.

## Conclusion

In summary, a simple and safe route to nanocrystalline transition metal arsenides under ultrasound irradiation at room temperature has been developed. The use of ultrasound has dramatically reduced the temperature and pressure requirements for these materials and the reaction conditions in our route are easy to maintain. High-intensity ultrasound sources are inexpensive, available from commercial sources and extremely reliable. In this work, the goals to lower the processing temperature, to avoid the use of toxic arsenic sources and extreme operational conditions have all been realized, compared with considerable efforts on the synthesis of arsenides in recent years. This method can also be extended to the preparation of III–V arsenides, such as InAs and GaAs, which are important semiconductors.

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