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# Synthesis and characterization of reduced transition metal oxides and nanophase metals with hydrazine in aqueous solution

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**Abstract**

Reduction of the first row (3d) transition metal complexes in aqueous solution using hydrazine as the reducing agent has been investigated systematically. Nanoscale reduced metal oxides such as $VO_2$(B), $Cr_2O_3$ were obtained through hydrazine reduction followed by proper thermal treatments. Nanocrystalline $\gamma$-$Mn_2O_3$ was synthesized directly through aqueous phase reduction at room temperature. Nanoclusters of cobalt, copper and the one-dimensional single crystal nickel nanowhiskers were synthesized by direct reduction without post-annealing process. All the products were characterized on their structure and micro-morphology. The reaction details and features were described and discussed.


*Keywords:* Inorganic compounds; Nanostructure; Chemical synthesis

## 1. Introduction

Low temperature soft chemistry preparative techniques recently attract increasing interests in the synthesis of technologically important transition metal oxides and nanophase metals due to their unique advantages over the conventional high temperature solid state reactions in approaching novel metastable phases and controlling homogeneity, grain size and micro-morphology of products [1,2]. It is of great significance to turn down the reaction temperature, which creates new chances in synthetic chemistry techniques [3], including sol–gel method [4], hydrothermal process [5], solverthermal process [6]and molten salts process [7]. Recently, a great deal of work has been done on using new reducing agents for preparing reduced metal oxides. These oxides are important for many applications such as catalysts [8], high-energy-density battery cathodes [9], magnetic materials [10] and so on.

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Manthiram and coworkers reported that alkali borohydrides can be used as the reducing agent to generate binary oxides $VO_2$, $MoO_2$, $MnO_{2-\delta}$, $Cr_2O_3$ and some ternary oxides like the tungsten bronze $Na_xWO_3$ [11–15]. Goodenough and coworkers made use of the hydroxyamine hydrocloride ($NH_2OH{\cdot}HCl$) to produce reduced transition metal oxides such as $Fe_3O_4$, $VO_2$, and $MoO_2$ at relatively low temperatures [16,17]. Ultrafine particles of the metal Fe, Ni, Co and their alloys were prepared by the reduction of $Fe^{2+}$, $Co^{2+}$ and $Ni^{2+}$ in the aqueous solutions using alkali borohydrides [18].

Hydrazine is an important reducing agent in organic synthesis. Recently, it was demonstrated useful for preparing II–VI group semiconductor nanorods [19], and layered $MoE_2$ (E = S, Se) [20]. Gibson and Putzer reported that anisometric cobalt nanoclusters were obtained by sonication of aqueous $Co^{2+}$ and hydrazine [21]. Ultrafine nickel particles were prepared by Li et al. [22] through the hydrothermal reduction of aqueous Ni salts with hydrazine assisted by a selected surfactant.

In the present work, we systematically studied the reduction of the first row (3d) transition metal complexes in aqueous solutions at low temperature with hydrazine as the reducing agent. Nanoscale oxides of $VO_2$, $Cr_2O_3$, $\gamma$-$Mn_2O_3$, nanoparticles of Co, Cu and one-dimensional single crystal Ni nanowhiskers were obtained.

## 2. Experimental

A given amount of analytically pure transition metal source compounds (e.g. $NH_4VO_3$, $K_2Cr_2O_7$, and $KMnO_4$) were dissolved in distilled water and then more distilled water was added until its total volume reached up to 50 ml. After that, the hydrazine ($N_2H_4{\cdot}H_2O$) solution (85 vol.%) was slowly dripped into the solution under constant stirring until precipitates formed. In the case of vanadium oxides, hydrochloric acid should be pre-added to adjust the pH value of the solution to the weak acidic condition. The precipitates were allowed to settle overnight and collected by washing and filtration. Thermal treatment of the chromium and vanadium products, thermal treatment at elevated temperatures is leads to crystallization.

For the synthesis of Ni nanowhiskers, 50 ml of 0.1 M $Ni(CH_3COO)_2$ aqueous solution and 5 ml of ammonia solution (28%) were added into a beaker to give a dark blue $[Ni(NH_3)_4]^{2+}$ solution. Then 5 ml of 17 M hydrazine solution was dripped into this above solution slowly. This solution is pretty clear and no solid formed at this stage. Here pH value of the solution was around 10.5. When this solution was heated up to 100 °C, it can be observed that some black solid formed. The hot plate was removed immediately after the initiation of the reaction. This reaction generated a great deal of heat, which drove the reaction to proceed ahead and therefore, is shown to be self-sustained. After 30 min of reacting the resulting solids, many of which were floating on the surface of the solution, were collected by filtration and washing.

For the synthesis of Co nanoclusters, 0.01 mol of analytically pure $Co(CH_3COO)_2{\cdot}6H_2O$ was dissolved in 5 ml of distilled water and directly dripped into 50 ml of 17 M (85%) hydrazine ($N_2H_4{\cdot}H_2O$) solution under heating and constant stirring. The pH value of the resulting solution is 12. Gray precipitate formed slowly after the solution was heated to boiling temperature and held for 40 min.

For the synthesis of nanometer Cu metal, the surfactant of sodium dodecyl sulphonate (SDS) is needed to confine the product size. Hydrazine was dripped into the solution of $CuSO_4$/SDS to produce a black precipitate at room temperature.

All products were collected after filtration, washed with water and absolute alcohol, then dried in vacuum at 80 °C for 5 h and stored in a desiccator. X-ray powder diffraction (XRD) analysis was conducted on a Rigaku D/Max X-ray diffractometer with graphite monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) to verify the formation of products. Transmission electron microscopy (TEM) images of the samples were collected on Hitachi H-800 electron microscope operated at 200 keV. High-resolution electron microscopy (HREM) images and X-ray energy dispersion spectrum (EDS) analysis were recorded on a JEOL 2010 operated at 200 keV.

## 3. Results and discussion

The optimum reaction conditions and the products obtained are listed in Table 1. The as-prepared $VO_2$ directly from room temperature reduction shows no Bragg reflections in the X-ray diffraction pattern. For further characterization of phase transformation of the as-prepared $VO_2$, it was heated in a flowing $N_2$ atmosphere at various temperatures for 24–48 h and then analyzed by X-ray diffraction. The results as shown in Fig. 1(a–d) reveal that only the metastable $VO_2$(B) is present in the product obtained below 300 °C, while the monoclinic rutile $VO_2$(R) begins to form at around 350 °C. This conversion completes at around 650 °C that is much higher than the phase transition temperature of $VO_2$(B) to $VO_2$(R) reported in the previous literature [23]. When the as-prepared $VO_2$ was exposed in air atmosphere for 2 weeks, and then heated in a flowing $N_2$ atmosphere at 650 °C, only $V_2O_5$ was obtained. This suggests that the as-prepared $VO_2$ is easily oxidized by oxygen in the air at room temperature. The nanocrystalline $VO_2$(B) we prepared has the potential application as a cathode for lithium cells. The chromium oxide obtained from room temperature reduction shows no discernible Bragg reflections in the XRD pattern; when it was annealed at 500 °C in a flowing $N_2$ atmosphere for 24 h, X-ray powder diffraction pattern shows that the product is hexagonal $Cr_2O_3$ after annealing at 500 °C, in (Fig. 2a). TEM images (Fig. 3a and b) for the samples of $VO_2$(B) and $Cr_2O_3$ after annealing show that they are quasi-spherical particles with the average diameter of 35 nm for $VO_2$(B) and 30 nm for $Cr_2O_3$, respectively.

It is interesting that the sample of manganese oxides directly from room temperature reduction is found to be crystalline γ-$Mn_2O_3$ as shown in Fig. 2b. To our knowledge, this is the first report that the

Table 1
The starting materials, reaction conditions and the products obtained

| Metal sources | | Hydrazine ($N_2H_4 \cdot H_2O$) | | pH | Additament | Crystal temperature (°C) | Final products |
|---|---|---|---|---|---|---|---|
| Concentration | Volume (ml) | Concentration (M) | Volume (ml) | | | | |
| 0.2 M $NH_4VO_3$ | 50 | 3.4 | 1.5 | 3.5 | | 300 | $VO_2$(B) |
| 0.2 M $K_2CrO_7$ | 50 | 17 | 5 | | | 500 | $Cr_2O_3$ |
| 0.2 M $KMnO_4$ | 50 | 17 | 5 | | | | γ-$Mn_2O_3$ |
| 0.2 M $CuSO_4$ | 50 | 17 | 2 | | SDS[a] | | Cu |
| 0.1 M $NiAc_2$ | 50 | 17 | 3 | 10.5 | $NH_3H_2O$ | | Ni |
| 2 M $CoAc_2$ | 5 | 17 | 50 | 12 | | | Co[b] |

[a] SDS: sodium dodecyl sulfonate.
[b] During this experiment, aqueous $CoAc_2$ was dripped into 50 ml of 85% hydrazine solution under stirring.

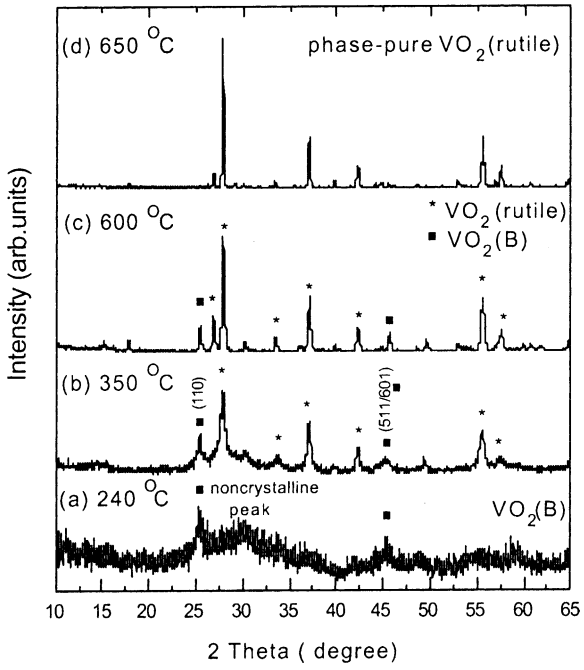


Fig. 1. XRD patterns of $VO_2$ upon heating at (a) 240, (b) 350, (c) 600 and (d) 650 °C for 36 h.

crystalline γ-$Mn_2O_3$ can be directly synthesized through a simple redox method at room temperature. Manthiram et al. [13] obtained amorphous $Mn_2O_3$ by reduction of $KMnO_4$ with $KBH_4$ in aqueous solutions, but a high temperature thermal treatment was needed to obtain a crystalline product. The reducing agent $N_2H_4$ may play a complex role in the formation of the crystalline product and the confinement of crystal size. From the TEM image as shown in Fig. 3c, the γ-$Mn_2O_3$ obtained comprises homogenous nanoparticles with an average diameter of 8 nm. The surface self-organization of these particles results in the monolayer film of nanocrystallites [25].

The reduction of $[Ni(NH_3)_4]^{2+}$ by hydrazine is found to be an interesting self-sustained reaction initiated by short time heating. Significant exotherm effect drives the reaction to proceed forward completely. A black sponge-like solid formed and floated on the solution surface. XRD pattern as shown in Fig. 2c indicates it is the face-centered cubic (fcc) structure of nickel. SEM images (Fig. 3d) show that the as-prepared black Ni comprised of an intercrossed framework, which is highly porous and is of low density, just like sponge. After ground and dispersed by ultrasound, this sample is observed to consist of crystal whiskers typically with a width of 10–20 nm and a length 200–300 nm indicated by TEM image in Fig. 3e. Fig. 3f is the high-resolution election microscopy (HERM) image for Ni nanowhiskers. The unambiguous continuous fringes continuously in the individual whiskers indicate that each Ni whisker is a single crystal. Compositional analysis of the individual Ni nanowhiskers carried out by X-ray electron dispersive spectroscopy shows that Ni is pure. The growth of one-dimensional nanowhiskers of nickel may attribute to the coordination effect of $NH_3$ ligand. $NH_2CH_2CH_2NH_2$(en) has been reported to be the solvent molecular coordination template agent assisting the growth of CdS nanorods due to the assembly of square-planar coordinated $[Cd(en)_2]^{2+}$ along the perpendicular direction [24]. In our work $[Ni(NH_3)_4]^{2+}$ also adopts square-planar

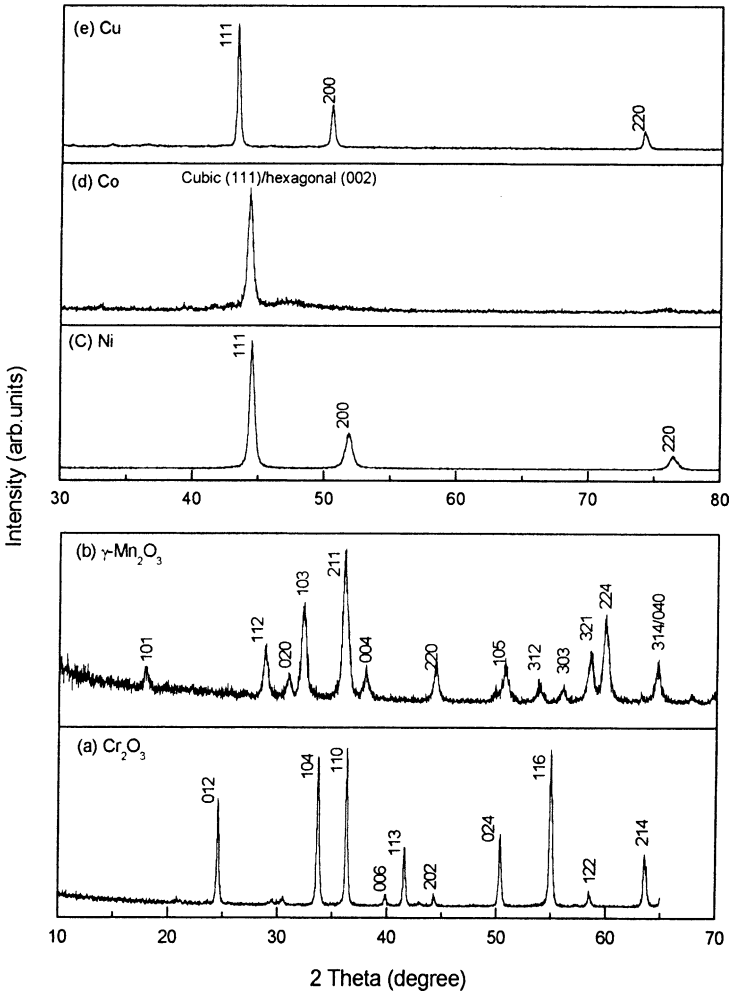


Fig. 2. XRD patterns for the products of (a) $Cr_2O_3$, (b) $Mn_2O_3$, (c) Ni, (d) Co, and (e) Cu.

coordination and is structurally anisotropic. Therefore, the crystal growth used as a building block may lead to the formation of one-dimensional nanostructure. To our knowledge, this is the first simple synthesis of single crystal Ni nanowhiskers through a chemical reduction.

For cobalt, only one peak can be observed in the XRD pattern (Fig. 2d); it could be indexed either to (1 1 1) in cubic Co (fcc) or as (0 0 2) in hexagonal Co (hcp). However, electron diffraction in Fig. 3h reveals the coexistence of fcc and hcp cobalt. The disappearance of corresponding peaks in XRD pattern may result from the formation of stacking faults, which lead to the collapse of periodicity along some directions. The sample of cobalt comprises homogenous nanoclusters with an average diameter of 20 nm, as shown in the TEM image of Fig. 3g. Gibson and Putzer pointed out that the nanoclusters of cobalt cannot be prepared by direct reduction of $Co^{2+}$ with hydrazine, while a sonication process is necessary for obtaining Co nanoclusters [21]. We also found that dripping hydration to $Co^{2+}$ solution did not generate cobalt metal, instead some kind of cobalt hydroxides were formed. But, gray

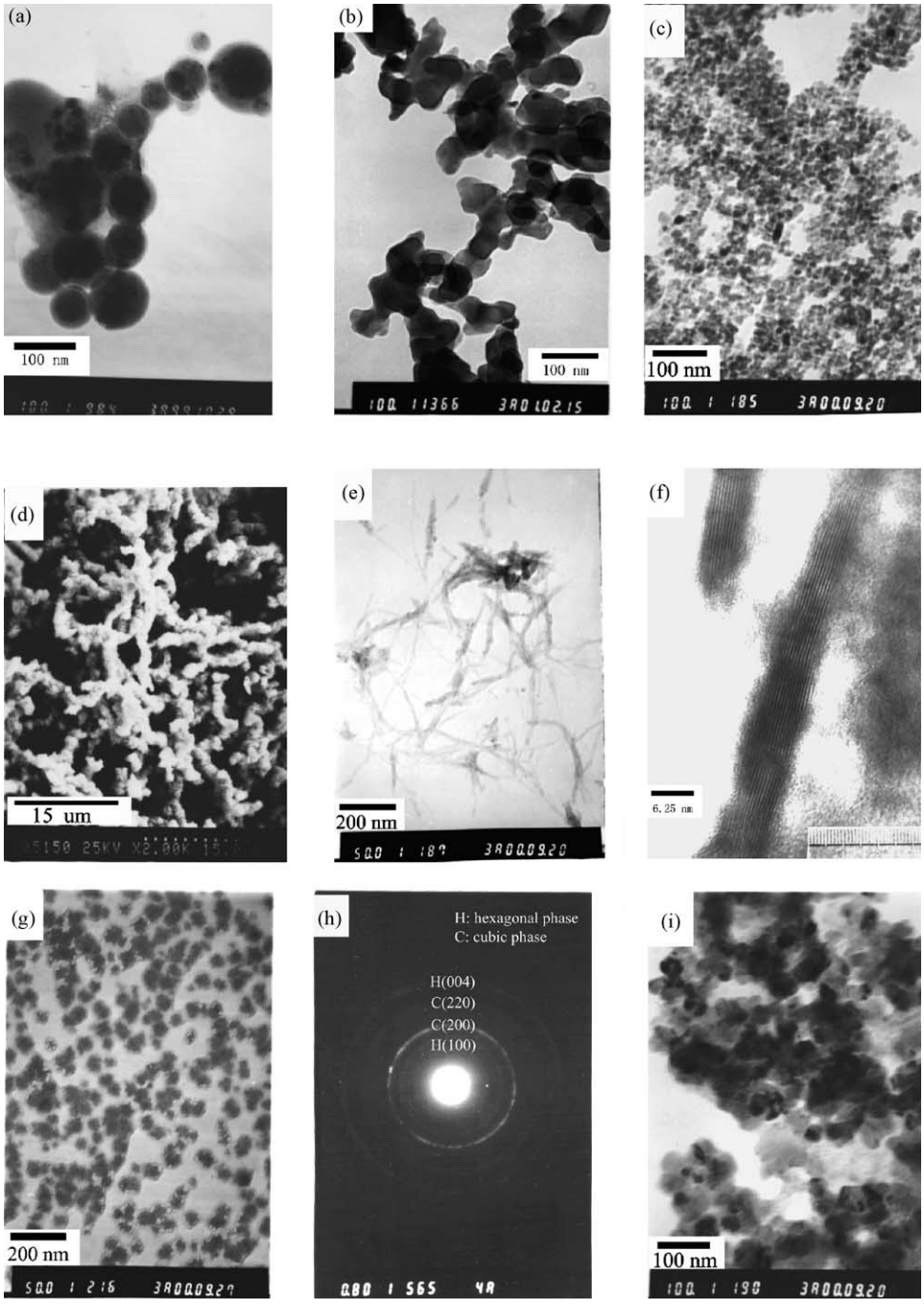


Fig. 3. TEM images for the products of (a) $VO_2$, (b) $Cr_2O_3$, (c) $Mn_2O_3$, (e) Ni, (g) Co, and (i) Cu; (d) SEM image for sponge Ni; (h) ED pattern of Co nanocluster; (f) HREM image for Ni nanowhiskers.

precipitate forms slowly when $Co^{2+}$ solution is directly dripped into 85% hydrazine under heating near boiling. In addition when the ligand $N_2H_4 \cdot H_2O$ was also pre-added to $CoAc_2$ solution, one-dimensional Co nanowhisker cannot be obtained. This is different from the synthesis of Ni nanowhiskers. The preparation of Co nanoclusters is a reduction reaction in high concentration hydrazine solution, while the formation of Ni nanowhiskers is a slow self-sustained process, which allows the possibility of the gradual growth of one-dimensional whiskers.

The reduction of $Cu^{2+}$ solution with hydrazine produced golden colored Cu particles without the assistance of any surfactant. By surfactant assisted (SDS) reduction, black nanophase copper particles were obtained. The XRD pattern for the as-prepared Cu nanoparticles as shown in Fig. 2d can be indexed to face-centered cubic structure. TEM image of Fig. 3i indicates that the obtained Cu sample is comprised of nanoparticles with an average diameter of 35 nm. It is found that the choice of starting materials is important: if $CuCl_2$ is used instead of $CuSO_4$ as the starting agent, keeping other experimental variables unchanged, the product is a mixture of Cu and CuCl. That is, because of the formation of undissolvable CuCl, which prohibits the further reduction of Cu(I) to Cu(0).

## 4. Conclusion

We have systematically studied the low temperature chemical reduction of 3d transition metal cations or metalates using hydrazine as the reductant in aqueous solution. Nanoscale reduced oxides $VO_2$(B), $Cr_2O_3$ and $\gamma$-$Mn_2O_3$ and metals (Co, Ni, and Cu) have been obtained. The structure and micromorphology of the products were well characterized. It is of special interest that the nanocrystalline $\gamma$-$Mn_2O_3$ could be prepared by a direct reduction at room temperature without post-thermal treatment for crystallization, and one-dimensional single crystal Ni nanowhiskers have been obtained by a simple direct chemical reduction with the aid of $NH_3$ ligand. The nanophase reduced transition metal oxides are technologically important for catalysts. The magnetic metal (Co, Ni) nanoclusters or whiskers have great significance in fabricating single-domain magnetic devices.

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