TEMPO-mediated, room temperature synthesis of pure CoO nanoparticles†

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Treatment of dicobalt octacarbonyl with TEMPO in THF at room temperature, in the presence of oleic acid as the sole additive, leads to the formation of monodisperse nanoparticles (*ca.* 3.0 nm diameter) of CoO; the particles agglomerate in solution at room temperature into aggregates, and this property has been used for the controlled preparation of hybrid materials.

Transition metal oxide nanoparticles possess important applications, due to their electric[1] and magnetic[2] properties, as well as their size and high specific surface, in catalysis,[3] as chemosensors,[4] or as specific adsorbents.[5] Among these materials, cobalt(II) oxide is particularly interesting, and its synthesis as monodisperse nanoparticles has only been disclosed very recently.[6] It is difficult, however, to prepare CoO nanostructured materials in pure form since they are biased to overoxidation to the more stable Co_3O_4 form or to contain Co(0) impurities. These problems arise from the harsh reaction conditions needed to prepare CoO, and highlight the need for mild procedures for selective nanoparticle synthesis. In fact, the mildest method available for the synthesis of CoO nanoparticles has been the room temperature oxidation of cobalt(0) nanoparticles in air, but the need for up to sixty days to drive the reaction to pure CoO and to avoid the formation of Co_3O_4 makes it impractical.[6g]

Herein we wish to present a practical and extremely mild procedure to form aggregates of monodisperse, *ca.* 3 nm CoO nanoparticles through the controlled oxidation of $Co_2(CO)_8$ with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in THF, with oleic acid as the sole stabilizer. By this procedure the CoO nanoparticles can be easily prepared within minutes at room temperature.

TEMPO is a mild organic oxidizing agent[7] that has been used to trap the $Co(CO)_4$ radical from dicobalt octacarbonyl.[8] More interestingly, it has been recently shown to promote the decarbonylation of dicobalt hexacarbonyl complexes of alkynes, opening a new pathway to Pauson–Khand reaction.[9] Inspired by this result, we envisioned that under appropriate experimental conditions, it could also promote the decarbonylation of $Co_2(CO)_8$[10] to CoO nanoparticles.

In line with these expectations, we were pleased to find that the addition of TEMPO to solutions of $Co_2(CO)_8$ in different solvents, in the presence of oleic acid (OA) and trioctylphosphine oxide (TOPO),[10a] leads to complete decarbonylation at room temperature or below, while the metal is oxidized to Co^{2+} to yield CoO nanoparticles.[11]

A thorough optimization of the experimental conditions (solvent, temperature, and additives), monitored by *in situ* FT-IR spectroscopy and TEM showed that the solvent had a major effect on the size of the aggregates, while the role of TOPO appears to be limited to a better control of the aggregation process. Its presence results in a narrower size distribution of the aggregates, similarly to what is observed for nanoparticle size in the purely thermal process.[10c] The most practical conditions found in terms of nanoparticle yield and ease of isolation involved the reaction of $Co_2(CO)_8$ with TEMPO (4 equivalents) in THF at room temperature for 15 min, with oleic acid (1 equivalent) as the sole stabilizer (Scheme 1).
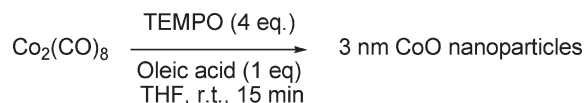
The chemical nature of the nanoparticles and its core crystal structure was determined by energy dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED), energy-loss spectroscopy (EELS), and X-ray photoelectron spectroscopy (XPS). The EDS and EELS spectra indicated that oxygen and cobalt are the only elements present in the specimen; moreover, the oxidation state of the cobalt atoms could be confirmed by XPS with the presence of two peaks at 780.8 and 796.0 eV and two satellites at 786 and 802 eV which are characteristic of high spin Co^{2+},[12] and the absence of a peak at 778.1 eV, which is characteristic of Co(0).[13] In addition to that, SAED of individual particles (see ESI†) showed that this material is made of crystalline, cubic CoO.

The determination of the size of the nanoparticles prepared by this procedure posed an important challenge; efforts in this direction, however, unveiled a most interesting aggregation behaviour. TEM micrographs of the nanoparticles taken at different times reveal that the aggregation process takes several hours at room temperature until an equilibrium is reached, and can be accelerated by heating (Fig. 1). The final size of the aggregates depends on the solvent, and size dispersion is efficiently controlled by the presence of TOPO.[14]

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$$Co_2(CO)_8 \xrightarrow[\substack{\text{Oleic acid (1 eq)} \\ \text{THF, r.t., 15 min}}]{\text{TEMPO (4 eq.)}} \text{3 nm CoO nanoparticles}$$

Scheme 1 Optimized preparation of CoO nanoparticles.
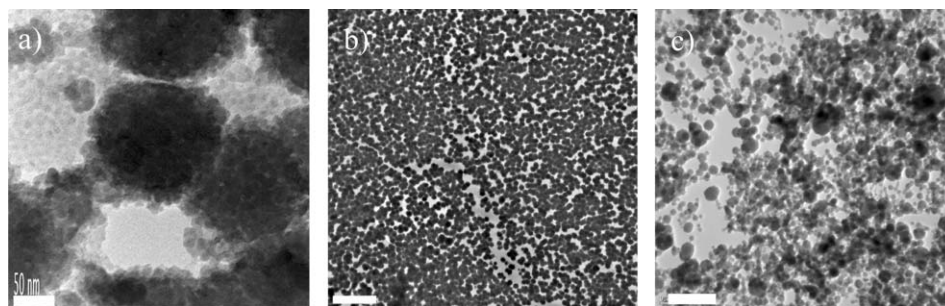
Fig. 1 TEM micrographs of CoO nanoparticle aggregates prepared under different reaction conditions: (a) in o-$C_6H_4Cl_2$, 4 equiv. TEMPO, 1 equiv. oleic acid, 0.2 equiv. TOPO, rt for 30 min. Scale bar: 50 nm. (b) In o-$C_6H_4Cl_2$, 8 equiv. TEMPO, 1 equiv. oleic acid, 0.2 equiv. TOPO, rt for 15 min plus 1 h aging at 50 °C. Scale bar: 1 μm. (c) In THF, 4 equiv. TEMPO, 1 equiv. oleic acid, rt for 1 h. Scale bar: 400 nm.
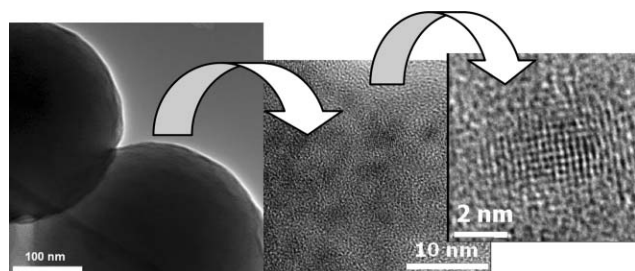
High resolution TEM confirmed that the final material was an aggregate of the smaller nanoparticles: by focusing on the aggregates' limits, darker spots with a *ca.* 3 nm diameter can be easily distinguished (Fig. 2).

Magnetic studies,[15] provided independent, yet global information on particle nature and size. The material exhibited the behavior of small nanoparticles as predicted by Néel.[16] In addition, its nature as CoO is strongly supported by a spontaneous magnetization of the particles (M_S) of 17 $\pm$ 1 emu g^{-1} (Co: 161 emu g^{-1}; Co_3O_4: 6 emu g^{-1}; CoO: 17 emu g^{-1}). More importantly, the ZFC–FC magnetization *vs.* T curves agreed well with monodisperse, energetically non-interacting *ca.* 3 nm nanoparticles (see Fig. 3).[17]

Simple mathematical treatment (see ESI†) showed that *ca.* 736 cobalt atoms should be present in a fcc CoO particle of this diameter, 42% of them being at the surface. On the other hand, a thermogravimetric analysis of the nanoparticles indicated a CoO/oleic acid molar ratio of 1.8 (67.5% weight of oleic acid), in reasonable agreement with the expected value (2.4) for a Co(surface)/oleic acid ratio of 1.

Thus, all the available information indicates that we are dealing with small CoO nanoparticles surrounded by a very important amount of organic matter, and this particular nature is probably relevant to the observed aggregation behavior. Most likely, the self-assembly of the individual particles takes place by interpenetration of the aliphatic chains of the oleic acid molecules.[18]
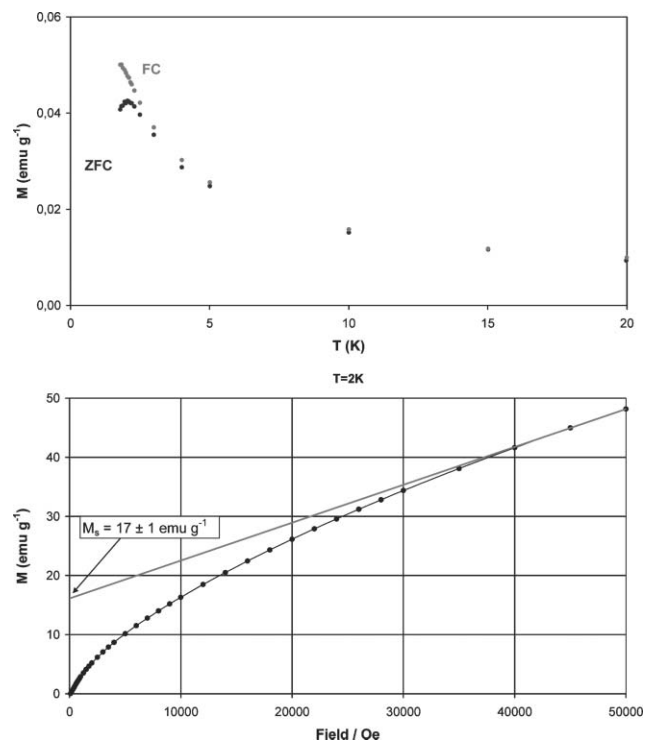
It is worth mentioning that by the present method *crystalline* nanoparticles are obtained in the absence of a thermal treatment. We reasoned that the very special characteristics of this method, where small particles are formed in a fast manner at low temperature and their aggregation is then induced by aging or

by thermal treatment, could be the basis for a simple method of nano- or microfabrication.

Thus, if the aging of the CoO nanoparticles was done in the presence of an appropriate microporous substrate, so that aggregation took place inside the pores, hybrid materials could be very easily prepared. As a proof of principle, CoO nanoparticles were prepared by reacting $Co_2(CO)_8$ with TEMPO at room temperature in o-DCB solution, and then treated with a porous polystyrene–divinylbenzene resin at 50 °C for 1 h. Very interestingly, the material recovered from the experiment was constituted by resin beads of unchanged size uniformly decorated at the surface by deposits of CoO (Fig. 4) which appear to fill the surface pores. XPS analysis confirmed the presence of CoO on the polymer beads.

Fig. 2 From left to right, TEM zoom in sequence into an aggregate showing the CoO nanoparticles of *ca.* 3 nm diameter.

Fig. 3 Top, magnetic susceptibility of the CoO samples. Zero field cooled and field cooled curves measured at 10 Oe. Bottom, magnetization *vs.* applied field plot at 2 K.
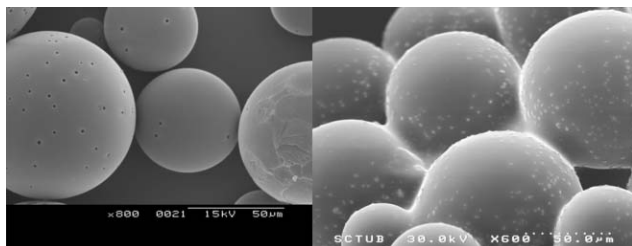
Fig. 4 SEM micrographs showing the adsorption of CoO nanoparticles (right image) onto the pores of a PS–DVB resin (left image).

In conclusion, an extremely mild methodology for the synthesis of cobalt oxide nanoparticles has been developed. The material prepared by this method is free of metallic cobalt and/or Co^{3+}, very small in size, and is surrounded by an important shell of coordinated oleic acid. The particles experience a controllable aggregation process, and this unique behavior should allow the systematic study of co-aggregation phenomena between different CoO and other micro- or nanosized entities as a new nanofabrication method. Work devoted to this endeavour, and to the preparation of metal oxide nanoparticles of different types by TEMPO-mediated decarbonylation of different metal carbonyls is underway in our laboratory.

Notes and references

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