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Preparation and characterization of uniform coated particles (Cobalt compounds on cadmium compounds)

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Uniformly dispersed particles of $CdCO_3$ were prepared by homogeneous precipitation from aqueous solutions of cadmium sulphate and urea at the elevated temperatures. These particles were then employed as cores for coating with $2CoCO_3{\cdot}Co(OH)_2{\cdot}H_2O$ from cobalt nitrate and urea solutions at 85 °C. In the absence of cores, when heated under similar conditions, the coating solutions produced nearly uniform particles of $2CoCO_3{\cdot}Co(OH)_2{\cdot}H_2O$. On calcination at 700 °C, the core [$CdCO_3$], coated [$CdCO_3/2CoCO_3{\cdot}3Co(OH)_2$], and coating precursor [$2CoCO_3{\cdot}Co(OH)_2{\cdot}H_2O$] particles transformed into CdO, CdO/Co_3O_4, and Co_3O_4, respectively. No sintering occurred during calcination and the particles preserved their morphological features to a significant extent.

1. Introduction

Fine powders of inorganic compounds are widely used in the fabrication of superconductors [1, 2], sensors [3, 4], adsorbents [5, 6], advanced ceramic products [7, 8], etc. In recent years, scientists have tried a number of techniques, such as sol-gel [9], spray pyrolysis [10], induced plasma synthesis [11], and homogeneous precipitation [12], for the preparation of various types of fine powders. Among these techniques, the homogeneous precipitation appears to be the most versatile method, since it has been adopted by many researchers for the preparation of fine powders, comprised of simple and coated particles of various morphological features and chemical compositions [13–24].

This work describes the preparation of cadmium carbonate particles and their coating with cobalt basic carbonate by homogeneous precipitation method. The as prepared particles are transformed to their respective oxides by controlled calcination at high temperatures without sintering and significant change in the morphology.

2. Experimental procedures

2.1. Materials

Reagent grade cadmium (II) sulphate, cobalt (II) nitrate, and urea were used without further purification. All the stock solutions were prepared with doubly distilled water and were filtered through membrane filters before use.

2.2. Particles preparation

Particles of cadmium carbonate were prepared by aging aqueous solutions, containing 0.04–0.09 mol dm^{-3} cadmium sulphate and 0.1–0.9 mol dm^{-3} urea for different periods of time [30–150 min] and temperatures [70–90 °C] in a preheated thermostated water bath. Teflon coated capped 50 cm^3 Pyrex glass tubes were employed as reaction vessels. The dispersions resulted at the end of the aging periods were quenched to room temperature in the ice water bath in order to stop the thermal decomposition of urea, and then the solids were separated by centrifugation, washed with doubly distilled water, and finally kept in a desiccator for drying.

2.3. Coating of particles

Uniform particles of cadmium carbonate were employed as cores for the coating purposes. For this purpose, aqueous dispersions containing 0.2–1 g dm^{-3} cores, 0.01–0.05 mol dm^{-3} cobalt nitrate, and 0.5–1.5 mol dm^{-3} urea were aged at different temperatures [75–90 °C] for different periods of time [25–90 min] with and without stirring. 500 cm^3 double-walled Pyrex glass container was used as a reaction vessel and magnetic stirrer was used for stirring, whenever desired. In some cases, the above mentioned coating mixtures were treated under similar conditions in the absence of cores which also produced dispersed solids. In all cases, the solids were separated from the mother liquors by centrifugation, washed with

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sufficient amount of distilled water and then stored in desiccator for drying.

2.4. Calcination

Calcination of the selected powder samples was carried out in a tube furnace, equipped with a programmable controller, at 700 °C for 1 h at the heating rate of 5 °C min^{-1}.

2.5. Characterization

All the powder samples were characterized by scanning electron microscopy [SEM, JEOL, JSM-6300, combined with a Noran Voyager x-ray microanalysis system], x-ray diffractometry [Siemens D500, with using Ka radiations], and thermogravimetry [TGA, Perkin-Elmer 7]. Metal content of the desired samples was estimated by atomic absorption spectrometry [Pye-Unicam, SP-190]. For this purpose, known amount

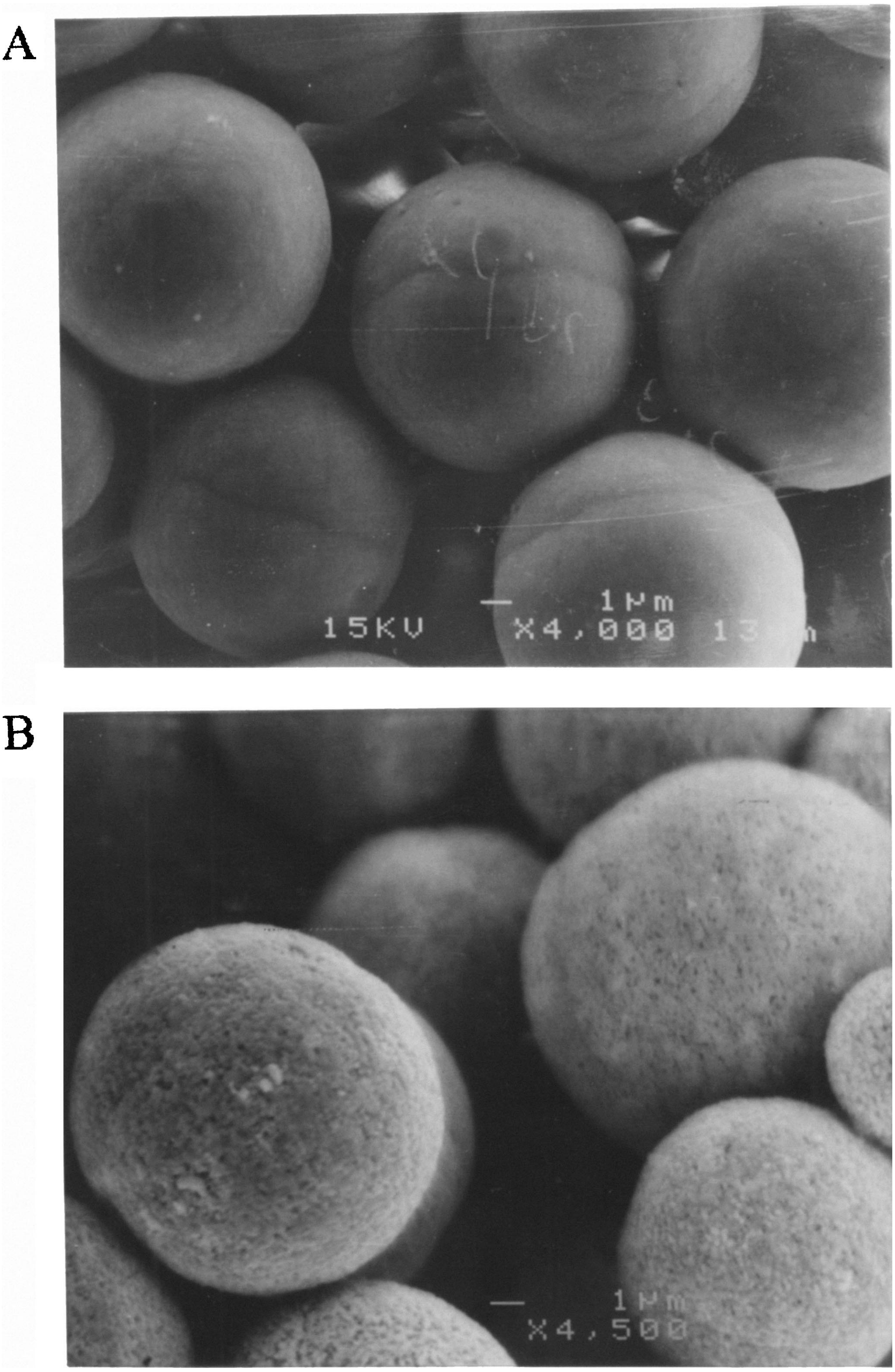

Figure 1 Scanning electron micrographs (SEM) of particles obtained, when (A) an aqueous solution containing 0.04 mol dm^{-3} $CdSO_4$ and 0.4 mol dm^{-3} urea was aged for 1 h at 85 °C, (B) particles in A were calcined at 700 °C.

[250–400 mg] of the solid was dissolved in $\sim$10 cm^3 aqua regia and then diluted to 100 cm^3 with doubly distilled water before analysis. The carbonate content of the desired samples was estimated from the weight difference by dissolving a known weight of the dry powder in a weighed sample of nitric acid. Similarly, the base content of the desired samples was estimated by dissolving a known quantity [400–800 mg] of the sample in hydrochloric acid (0.4 mol dm^{-3}) and back titrating the excess acid against standard solution of sodium hydroxide.

3. Results and discussion

3.1. Core particles

A systematic study was carried out to produce uniform particles of cadmium carbonate by homogeneous precipitation. Following this method, aqueous solutions containing various amounts of urea and cadmium sulphate were heated at the elevated temperatures for various periods of time which produced the precipitated solids. The precipitation reaction was launched by the progressive increase in pH and carbonate content of the reactant solutions, caused by the thermal decomposition of urea [22]. It was observed that the precipitation reaction was sensitive to the experimental conditions, i.e., temperature, heating time, composition of the reactant mixtures, etc. In most of the trials, described in the experimental Section 2.2, gelatinous or agglomerated solids were generated. Particles with uniform morphological features were obtained only under limited experimental conditions. For example, the particles displayed in Fig.1A were produced when aqueous solution, containing 0.04 mol dm^{-3} cadmium sulphate, and 0.4 mol dm^{-3} urea was heated at 85 °C for 1 h. In this case, pH of the reactant mixture increased from 5.37 to 6.24. These particles were identified by XRD analysis [Fig. 2A] to be crystalline $CdCO_3$. It is worth mentioning that $CdCO_3$ was precipitated out in cubic morphology from aqueous solutions of cadmium chloride and urea under different experimental conditions [22]. Thus these findings clearly pointed to the dependence of morphological features of the resulting particles on the composition of the reactant mixtures, nature of the starting materials, and other experimental parameters.

Thermogravimetric analysis [Fig. 3a] demonstrated that the $CdCO_3$ particles, displayed in Fig. 1A, lost significant weight in the temperature range 300–350 °C, beyond which temperature the weight loss became small, and in the vicinity of 700 °C, it was nearly constant. The observed weight loss was ascribed to the phase transformation, which apparently completed at 700 °C. As such, these particles were then calcined at 700 °C at the rate of 5 °C min^{-1} and held them at this temperature for 1 h in a tube furnace. The calcined particles [SEM, Fig. 1B] were identified by XRD [Fig. 2B] as CdO.

The phase transformation of the $CdCO_3$ particles was described by the following reaction:

$$CdCO_3 \xrightarrow{25.5\%} CdO + CO_2 \quad (1)$$

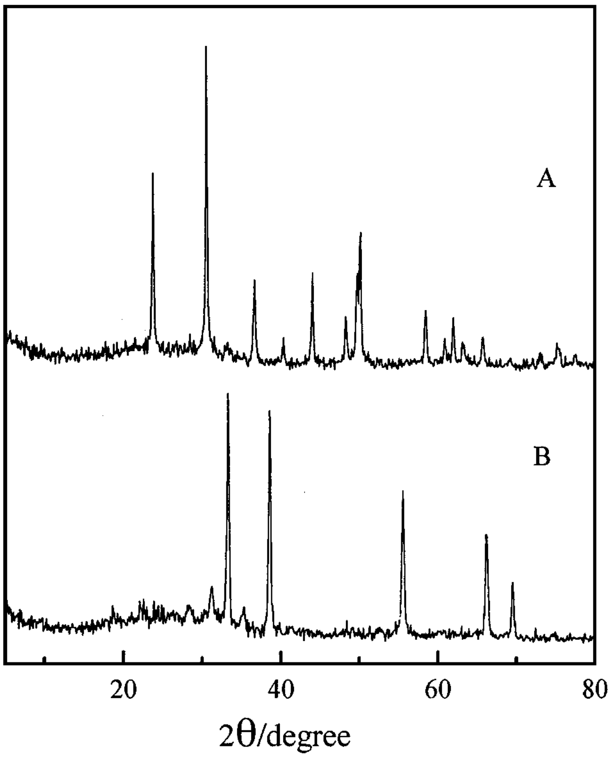

Figure 2 X-ray diffraction (XRD) patterns of the particles shown in Fig. 1A (A), and in Fig. 1B (B).

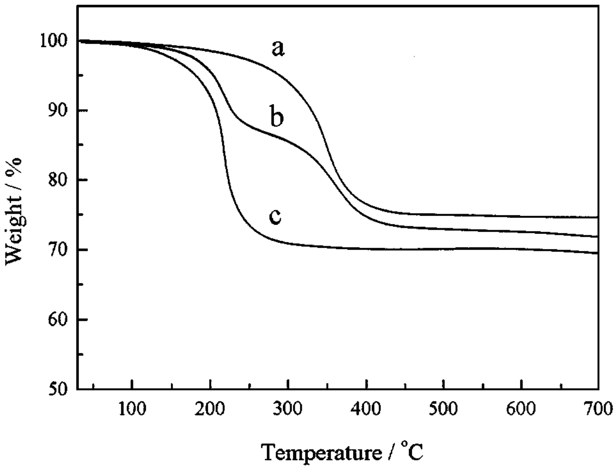

Figure 3 Thermogravimetric analysis (TGA) curves obtained with particles shown in Fig. 1A (a), Fig. 4A (b), Fig. 7A (c).

since the indicated theoretical weight loss [Equation 1] agreed with the practical loss of 26.1%. Moreover, the calcined particles acquired rather rough surfaces due to the loss of material while preserving their morphology [SEM, Fig. 1B]. Similarly, these particles were redispersable in aqueous medium and stayed as CdO with the same shape and size for nearly two months. This pointed to the absence of (a) sintering during calcination and (b) interaction with water. In contrast to (b), in aqueous dispersion the CdO particles, reported elsewhere [22], interacted with water and transformed into $CdCO_3$ particles with irregular morphology. In fact, the precursor particles [$CdCO_3$] of CdO [22] were produced instantly by mixing the reactant solutions at room temperature, while in this study they were generated by aging the reactant mixture for 1 h at 85 °C

[Fig. 1A]. As such, it is believed that in this study due to the elevated temperature and relatively long aging period, the precipitated particles of $CdCO_3$ might have acquired sufficient structural stability in the growth process and which on calcination ended with rather stable CdO particles.

3.2. Coated particles

$CdCO_3$ particles, depicted in Fig. 1A were employed as cores for the coating purposes. Different experimental strategies were adopted for obtaining uniformly coated particles. In these attempts, varying amounts of core particles were dispersed in aqueous solutions, containing cobalt nitrate and urea and then heated at the elevated temperatures for different periods of time, with and without stirring. Finding appropriate conditions for uniform coating were in fact difficult because in most of these trials cobalt compound precipitated out independently and ended with the mixture of cores and coating precursors. The inception of coating appeared to be effective only in case of stirred dispersions, composed of the starting materials in the limited amounts. As such, experimental parameters were then changed

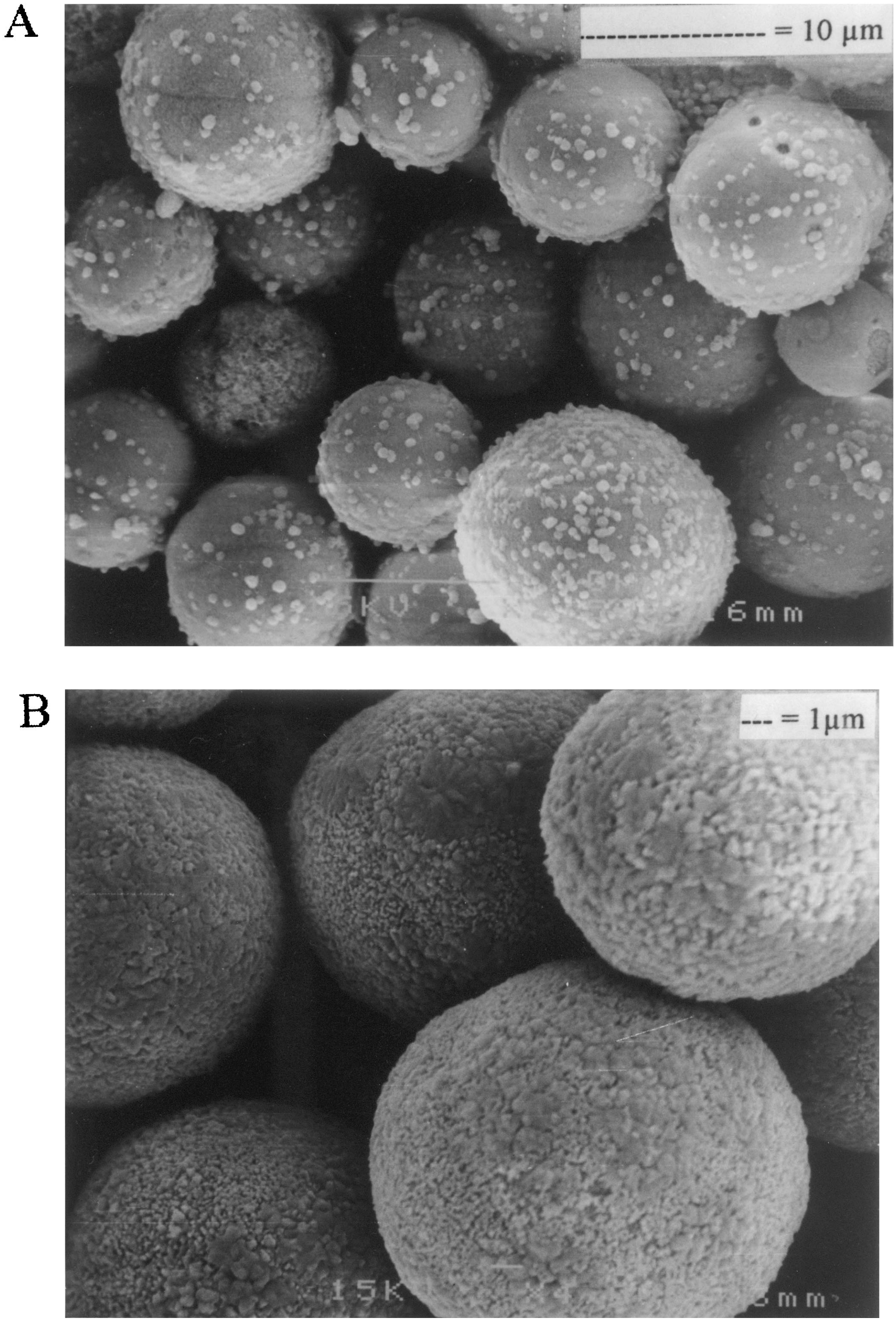

Figure 4 Scanning electron micrographs (SEM) of the particles obtained, when (A) an aqueous dispersion, 0.8 g dm^{-3} in $CdCO_3$ cores (Fig. 1A), 0.8 mol dm^{-3} urea, and 0.04 mol dm^{-3} $Co(NO_3)_2$, was aged for 40 min at 85 °C; (B) particles in A were calcined at 700 °C.

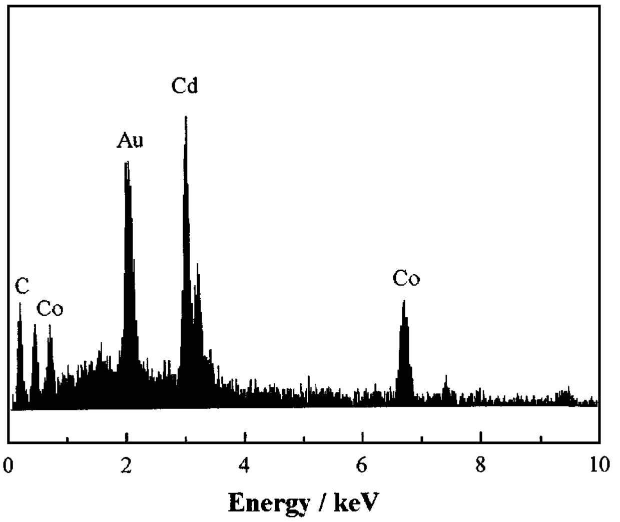

Figure 5 Energy-dispersive X-ray (EDX) analysis pattern of the particles, shown in Fig. 4A.

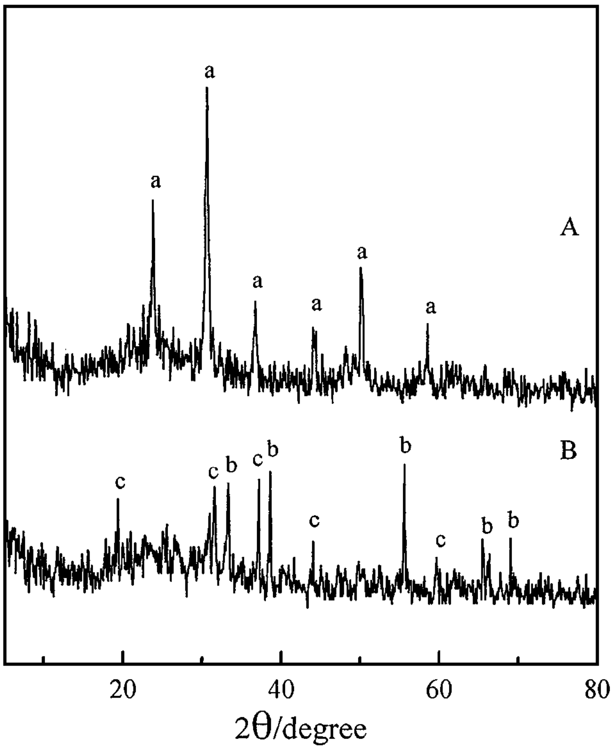

Figure 6 X-ray diffraction (XRD) patterns of the particles shown in Fig. 4A (A), and Fig. 4B (B). Symbols: a, $CdCO_3$; b, CdO; c, Co_3O_4.

systematically in order to establish conditions for uniform and reproducible coating. In fact, shells of variable thickness were generated on the dispersed cores when the aqueous dispersions, 0.7–1 g dm^{-3} in cores, 0.03–0.06 mol dm^{-3} in cobalt nitrate, and 0.3–0.6 mol dm^{-3} in urea were heated at 85 °C for different periods of time [25–40 min] with constant stirring. Fig. 4A showed a typical example of the coated particles obtained, when a dispersion 0.8 g dm^{-3} in cores, 0.04 mol dm^{-3} in cobalt nitrate, and 0.8 mol dm^{-3} in urea, was heated at 85 °C for ~30 min with constant stirring. In this case, cores acquired 40.5% increase in weight as a result of coating.

Inspection of Fig. 4A revealed that coating apparently took place by two consecutive processes, i.e. surface precipitation which produced uniform skin and heterocoagulation in which the tiny particles of the precipitated cobalt compound coagulated with the formed coated particles. Energy-dispersive x-ray analysis [Fig. 5] showed the presence of cadmium and cobalt in the coated particles. The peak, assigned to Au in Fig. 5, corresponded to gold sputtered on the powder sample before microscopic examination. Chemical analysis revealed that the coating materials composed of $2CoCO_3\cdot Co(OH)_2\cdot H_2O$ which resulted [Co]/[Cd] molar ratio of 0.6 in these particles.

XRD analysis showed that coating of the coated particles [Fig. 4A] was amorphous, since their XRD pattern [Fig. 6A] was identical to that of the cores [XRD, Fig. 2A]. The amorphous nature of the coating on crystalline cores pointed to the possibility of the fact that the deposition of the coating precursor monomeric species on the cores was too fast for the surface nuclei to acquire proper orientation of their own or like the core crystal lattice and grew as crystalline phase.

Thermogravimetric analysis [Fig. 3b] demonstrated prominent weight losses around 200 and 350 °C, which was attributed to the phase transition of the coating and core materials, respectively.

On calcination at 700 °C, the coating and core materials transformed independently into Co_3O_4 and CdO, respectively [XRD, Fig. 6B] without any interaction, which showed the absence of chemical association of core and coating materials in the precursor solid. It is likely to mention that during calcination, core and coating materials also stayed mutually inert in the coated systems, described elsewhere [14, 18].

Similarly, the surfaces of the calcined coated particles [SEM, Fig. 4B] turned out rather smooth which was obviously due to the loss of material during calcination.

3.3. Coating precursor particles

In the absence of cores, the reactant mixture described in Fig. 4A, produced particles [SEM, Fig. 7A] when heated under similar experimental conditions. These particles were found to be amorphous cobalt (II) basic carbonate [XRD, Fig. 8A] and composed of $2CoCO_3\cdot Co(OH)_2\cdot H_2O$, as confirmed by chemical analysis. Cobalt (II) basic carbonate particles were precipitated in needle-type morphology from cobalt sulphate and urea solutions under different experimental conditions [24].

Thermogravimetric analysis [Fig. 3c] of these particles demonstrated significant weight loss at ~200 °C, which was attributed to the loss of water contents and phase transition. The weight loss became nearly constant around 700 °C which indicated the completeness of the transition process. When calcined at 700 °C for 1 h at the rate of 5 °C min^{-1}, these particles transformed into Co_3O_4 [XRD, Fig. 8B] without sintering and significant change in the particle morphology [SEM, Fig. 7B]. The phase transformation was described as,

$$2CoCO_3\cdot Co(OH)_2\cdot H_2O \xrightarrow{30.96\%} Co_3O_4 + CO_2 + CO + 2H_2O \qquad (2)$$

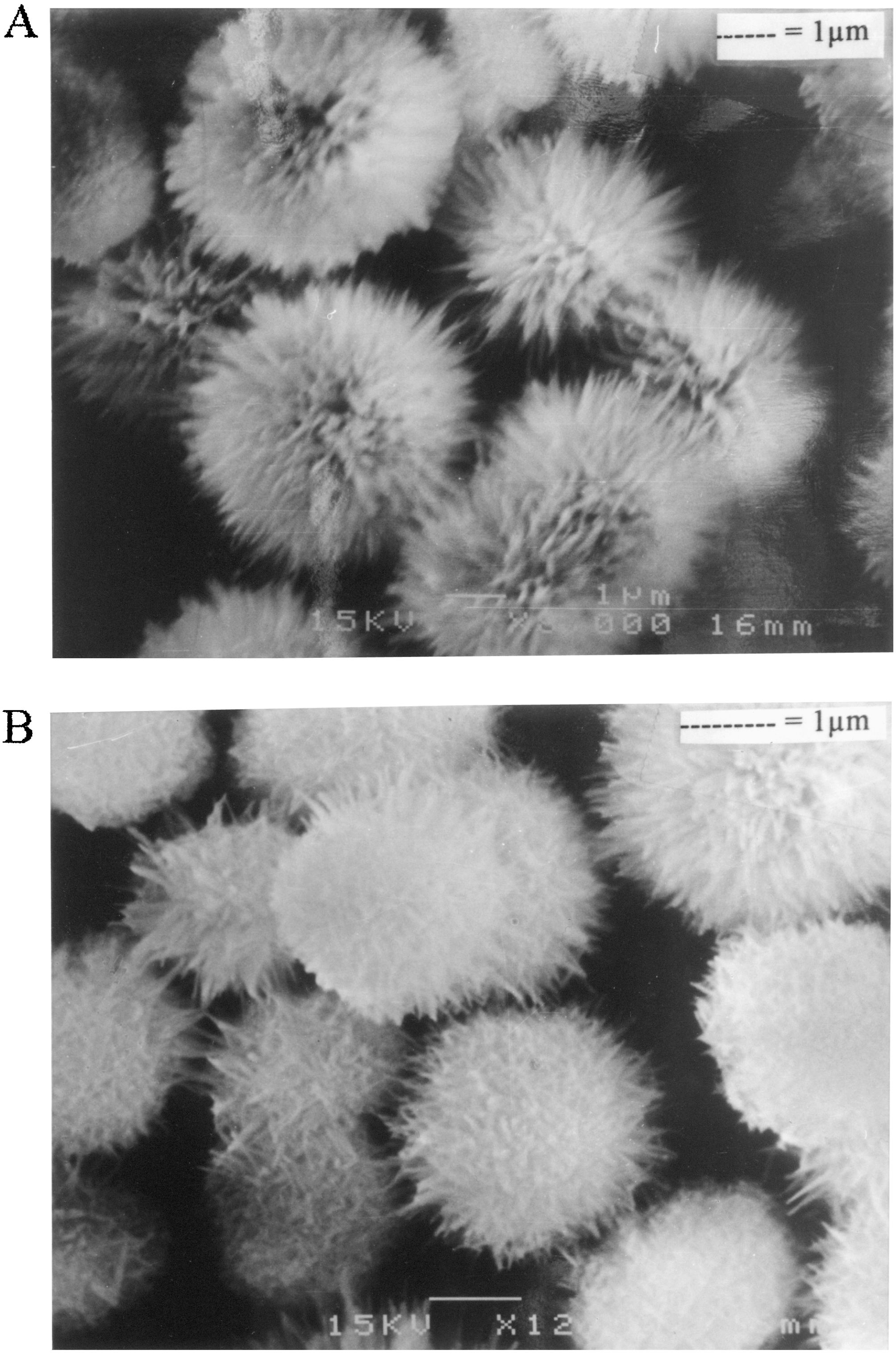

Figure 7 Scanning electron micrographs (SEM) of the particles obtained when (A) the coating solution of the particles, shown in Fig. 4A, was heated in the absence of cores under the conditions mentioned in the same figure; (B) particles shown in A were calcined at 700 °C.

The indicated theoretical weight loss [Equation 2] agreed well with the experimental loss of 31.8% which supported the correctness of the given composition of this compound.

Moreover, it is worth mentioning that precipitation of $2CoCO_3 \cdot Co(OH)_2 \cdot H_2O$ as coating in the presence of cores and uniform particles in the absence of cores demonstrated the fact that the presence of cores

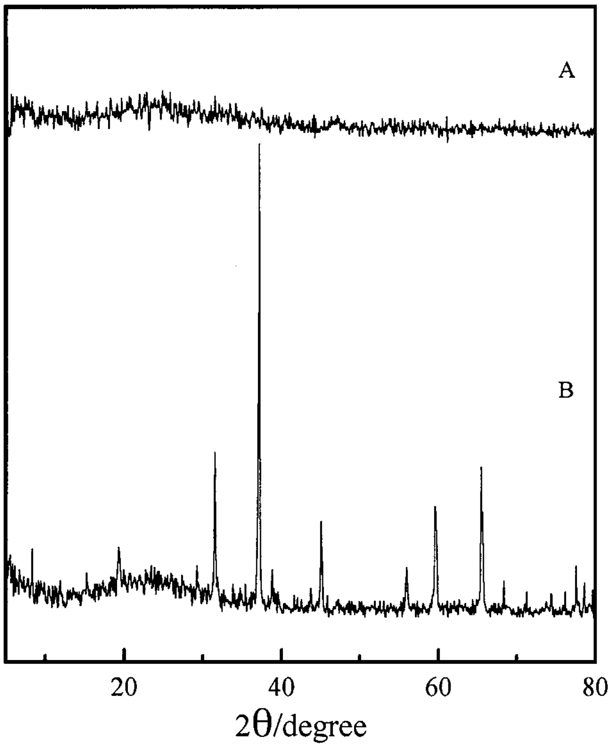

Figure 8 X-ray diffraction (XRD) patterns of the particles shown in Fig. 7A (A), and Fig. 7B (B).

did not affect the precipitation process of the cobalt compound.

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