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The coating of cadmium compounds with copper compounds

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Fine particles of cadmium carbonate ($CdCO_3$) were prepared by heating aqueous solutions containing dissolved urea and cadmium sulfate at 85°C for 1 h. Effect of the composition of the reactant mixture on the morphology of the precipitated particles was investigated. It was found that the cadmium sulfate content of the reactant mixture significantly affected the shape and size of the precipitated particles. At certain range of reactant mixture composition, cauliflower-shaped uniform particles were obtained. The later particles were coated with basic copper carbonate ($Cu_2(OH)_2CO_3$) by heating aqueous dispersions, containing $CdCO_3$ particles, copper (II) nitrate, and urea at 85°C for various periods of time with constant stirring. The coating process was found sensitive to the experimental conditions and in most of the trials; mixtures of the coated and coating precursor particles were obtained. As such, extensive optimizations were carried out and conditions were established for the production of uniformly coated particles.

On calcination at 700°C for 1 h, the $CdCO_3$ particles converted into CdO, whereas the coated particles ($CdCO_{3(\text{core})}$/ $Cu_2(OH)_2CO_{3(\text{coating})}$ transformed into $CdO_{(\text{core})}/CuO_{(\text{coating})}$) without sintering. In the coated particles, the core and coating materials stayed mutually inert during the calcination reaction and independently converted into their respective oxides.

All the calcined and uncalcined products were characterized by various physical and chemical methods.

1. Introduction

Research in science and technology of producing fine particles of uniform shapes, sizes, and chemical compositions for advanced applications is the focus of attention of various research groups in different parts of the world [1–7]. It has been reported [8–11] that by varying the synthesis conditions batches of uniform particles having the same chemical composition but different morphologies can be produced. Since the particle morphology significantly affects the properties of the powders of the given chemical composition; therefore, there is scope in this area in order to tailor particles with different novel morphologies.

Another area of interest to the material scientists and engineers is the synthesis of coated particles because of their numerous applications in various fields of science and technology [12–16]. Especially, coating becomes essential when a precipitation process fails to generate particles of the desired morphology from a given homogeneous reactant mixture. In such cases, precipitation is carried out in the presence of the dispersed core particles of the desired shape and size under controlled experimental conditions [17–23].

To-date, we have produced a number of uniformly coated particles of various morphological features and chemical compositions [2, 19–23]. The present work is the continuation of our research in this area.

This work describes the preparation of cadmium carbonate particles in nearly cauliflower shape and their coating with basic copper carbonate. In the absence of the core particles, basic copper carbonate precipitates in the form of small (~0.4 μm) spherical particles. On calcination at the elevated temperatures, the bare and coated cadmium carbonate particles convert into cadmium oxide and copper oxide$_{(\text{coating})}$/cadmium oxide$_{(\text{core})}$, respectively.

It is essential to mention that copper compounds were produced in different particle morphologies, ranging from needles to spheres [23–26]. However, powders, comprised of particles, having copper compounds on cauliflower shaped cores, have never been reported before.

2. Experimental procedures

2.1. Material

Reagent grade cadmium (II) sulfate (Merk), copper (II) nitrate (Merk), and urea (Merk) were employed as the

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starting materials and were used as received. Doubly distilled water was used for making stock and other chemical solutions. Stock solutions were never used longer than 4 days. Pyrex glass vessels were employed for storing stock solutions, as well as performing experiments. All the glass vessels were washed with diluted nitric acid (1:1 volume ratio), rinsed thoroughly with doubly distilled water, and then dried in a drying oven before use.

2.2. Preparation of core particles

For this purpose, the precursor reactant mixtures were prepared by mixing equal volumes of aqueous solutions of urea (0.8 mol dm^{-3}) and cadmium sulfate (0.02–0.08 mol dm^{-3}) at room temperature. 500 cm^3 of each reactant mixture were transferred to a 600 cm^3 reactor (double-walled Pyrex glass vessel), pre-heated at 85°C by means of hot circulating water. Temperature control accuracy of the reactor was ±1°C. The reactor was closed up at the top with a stopper, having an outlet, which allowed the gas to go out when the internal pressure in the reactor was higher than the atmospheric pressure. The reacting solution was then heated for 1 h. At the end of this treatment, temperature of the reactor was brought down to room temperature (25°C) by switching from hot to cold circulating water. The precipitated solid, produced in the reacting mixture, was separated from the mother liquor by vacuum filtration through 0.2 μm pore size membrane filter, and washed several times with doubly distilled water. The cleaned wet solids were then stored in a desiccator for drying.

2.3. Preparation of coated particles

In this case, a dry powder of the core particles (0.1–0.5 g) was dispersed ultrasonically in 500 cm^3 aqueous solution, containing 0.007–0.02 mol dm^{-3} copper (II) nitrate and 0.2–1.0 mol dm^{-3} urea. These dispersions were first allowed to stay for about 6 h at room temperature, and then heated at 70–85°C for various periods of time (20–120 min) in a double-walled Pyrex glass vessel with constant stirring. At the end of the heat treatment, the content of the reactor was cooled down to room temperature in the same manner, as described in B. The dispersed solid was separated from the liquid, washed with distilled water and stored in desiccator for drying.

2.4. Calcination

The as-prepared core and coated particles were calcined at 700°C in air for1 h at the heating rate of 5°C min^{-1} in a tube furnace, equipped with a programmable controller.

2.5. Characterization

Morphology of the particles was examined by scanning electron microscopy (SEM; Jeol, JSM-6300). For this purpose, the powder sample was mounted on a standard stub, on which a thin conducting layer of gold was deposited in a gold sputter before microscopic study.

The coated particles were analyzed for qualitative estimation of their metal content by energy-dispersive X-ray analysis system, coupled with the same SEM. Moreover, wet chemical methods were used for the quantitative determination of the metal, carbonate, and base content of these particles, as described in our earlier paper [2].

Crystallinity of the particles was checked by X-ray diffractometry (XRD, Siemens D500), using Cu K_α radiations. The power of the machine was adjusted to 40 kV and 20 mA during the analysis. Continuous scanning was performed on all the samples in the 2θ range from 5 to 80°.

Thermogravimetric analyses were performed on the desired powder samples in the flow of nitrogen at the heating rate of 10°C min^{-1} by using Perkin Elmer 7, TGA system.

3. Results and discussion

3.1. Core particles

Aqueous solutions, containing cadmium sulfate and urea (described in Section 2.2) changed into dispersions of the precipitated particles, when the former solutions were heated at 85°C for 1 h. The heating process initiated the decomposition of the dissolved urea, which caused a steady increase in pH, as well as liberating carbonate ions in the ambient solution [21, 23]. Both these changes in the reactant mixtures triggered out the precipitation of the dissolved cadmium ions in the form of insoluble cadmium compound. Scanning electron microscopy revealed that particle morphology of the precipitated solids was dependent upon the composition of the precursor reactant mixture. For example, the particles shown in Figs 1A and 2 were obtained when aqueous solutions, containing 0.4 mol dm^{-3} urea, and 0.03 and 0.05 mol dm^{-3} respectively of $CdSO_4$, were heated at 85°C for 1 h. It is evident from these figures that the particles shown in Fig. 1A are cauliflower shaped and those in Fig. 2 are mixture of small (~1 μm) and large (~9.0 μm) spheroids. It is worth mentioning that only large spheroids (~9.0 μm) were obtained [2] when a solution containing 0.4 mol dm^{-3} urea and 0.04 mol dm^{-3} $CdSO_4$ was heated at 85°C for one hour.

In order to account for the above observations, it is believed that the precursor primary particles, initially appeared in the aging mixture, aggregated together originally in a cauli-flower morphology (e.g., SEM, Fig. 1A). Further growth of these particles did not proceed due to the insufficient amount of the cadmium species in the reactant mixture and thus settled out as such. However, they grew into spheroids (~9.0 μm) [2] when the reactant solution contained a relatively large amount (0.04 mol dm^{-3}) of the cadmium sulfate. Moreover, the appearance of a mixture of small and large particles in Fig. 2 suggests that at the cadmium sulfate concentration >0.04 mol dm^{-3}, large spheroids could not grew any further and thus the excess amount of the dissolved cadmium species incepted a secondary nucleation which ended with the observed mixture (Fig. 2).

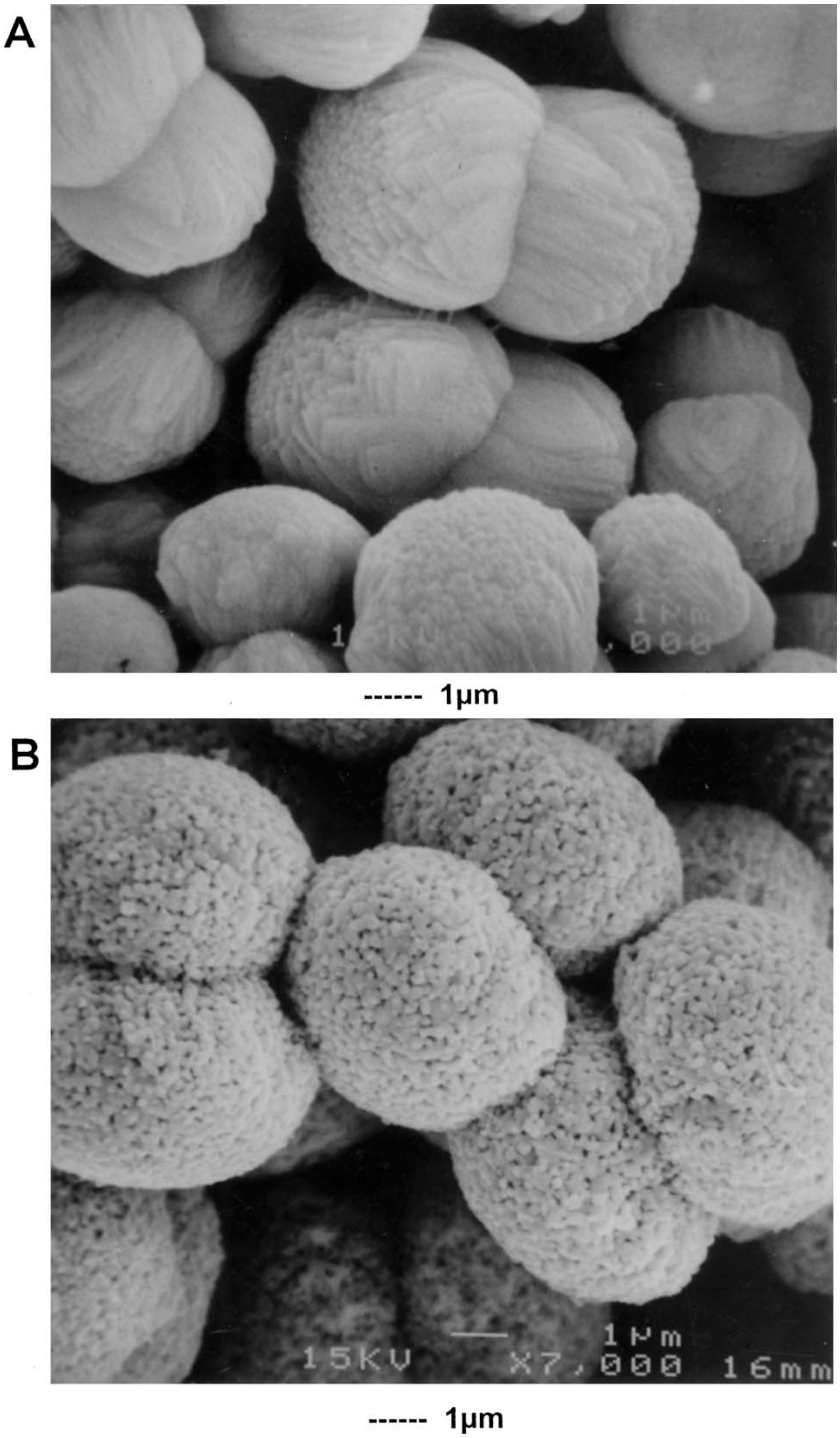

Figure 1 Scanning electron micrographs (SEM) of the particles obtained, when (A) aqueous solution, 0.03 mol dm^{-3} in $CdSO_4$ and 0.4 mol dm^{-3} in urea was heated for 1 h at 85°C; (B) the particles shown in A were calcined at 700°C for 1 h at the heating rate of 5°C min^{-1}.

X-ray diffractometry (XRD) analysis indicated that the products shown in Figs 1A and 2 were crystalline and composed of $CdCO_3$. The latter composition was also confirmed by the chemical methods. It is mentioned that only the particles shown in Fig. 1A were selected for further study in this work.

Fig. 3A shows the XRD pattern, corresponding to the particles shown in Fig. 1A. It was interesting to note that the XRD pattern, depicted in Fig. 3A, matched very well with the XRD pattern of the spheroids of $CdCO_3$, reported earlier [2]. This showed that in both the cases, the primary particles had the same crystal structure, and the spheroids [2] carried merely more building units (primary particles) compared to the particles, show in Fig. 1A.

Thermogravimetric analysis (Fig. 4B) showed that on heating in the temperature range of 30 to 700°C, the $CdCO_3$ particles (Fig. 1A) lost a significant amount

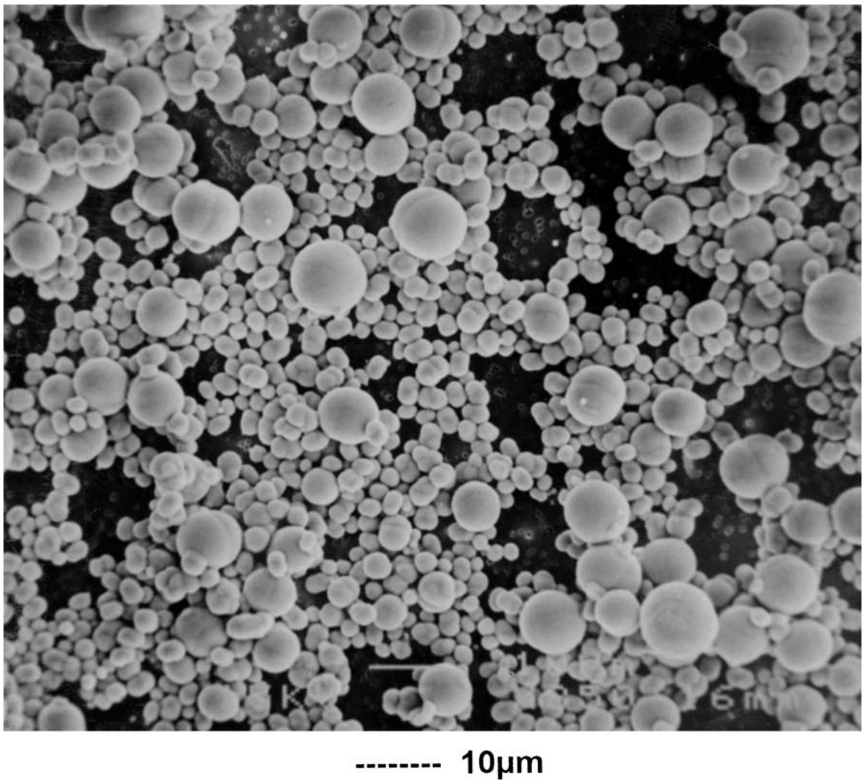

Figure 2 Scanning electron micrograph (SEM) of the particles obtained, when an aqueous solutions, containing 0.05 mol dm^{-3} $CdSO_4$ and 0.4 mol dm^{-3} urea was aged for 1 h at 85°C.

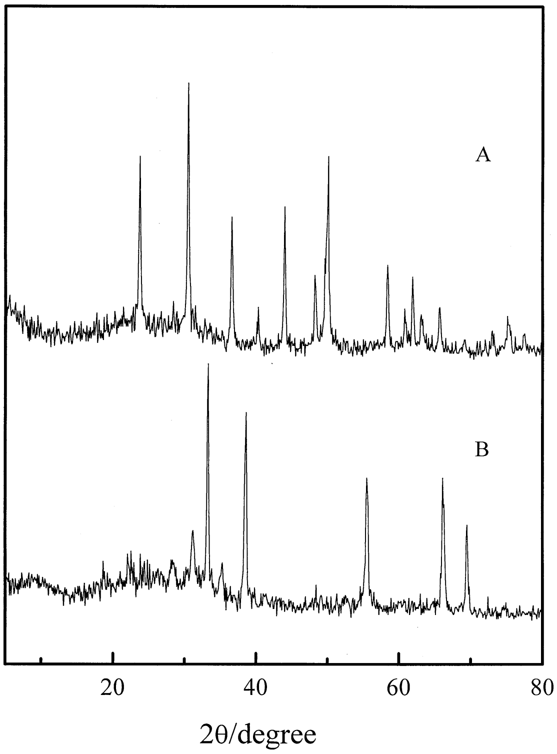

Figure 3 X-ray diffraction (XRD) patterns of the particles shown Fig. 1A (A); and Fig. 1B (B). Symbols: a, $CdCO_3$; b, CdO.

of material. The maximum weight loss (∼26.1 wt%) occurred around 350°C, after which temperature the weight loss was relatively negligible.

In a separate experiment, a known amount of the particles shown in Fig. 1A were calcined at 700°C for 1 h in a tube furnace, as explained in Section 2.4. Weight measurement of the calcined particles (SEM, Fig. 1B) showed a material loss of about 26.3%, which agreed very well with the weight loss, registered in the TGA experiment. It is believed that the calcinations reaction took place according to the reaction 1, since the indicated theoretical weight loss agreed well with the practical weight losses, observed in the TGA and calcination experiments.

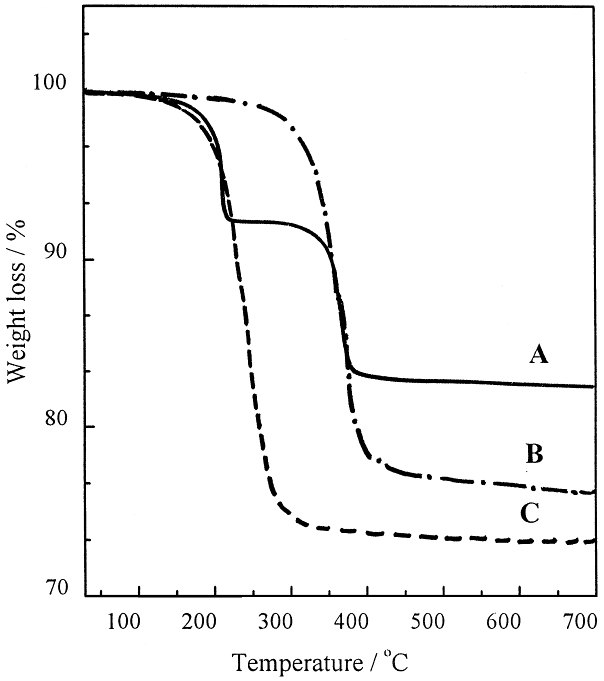

Figure 4 Thermogravimetric analysis (TGA) curves for the particles shown in Fig. 5A (A); Fig. 1A (B); and Fig. 6 (C).

$$CdCO_3 \xrightarrow[700°C]{25.3\,\text{wt\%}} CdO + CO_2 \qquad (1)$$

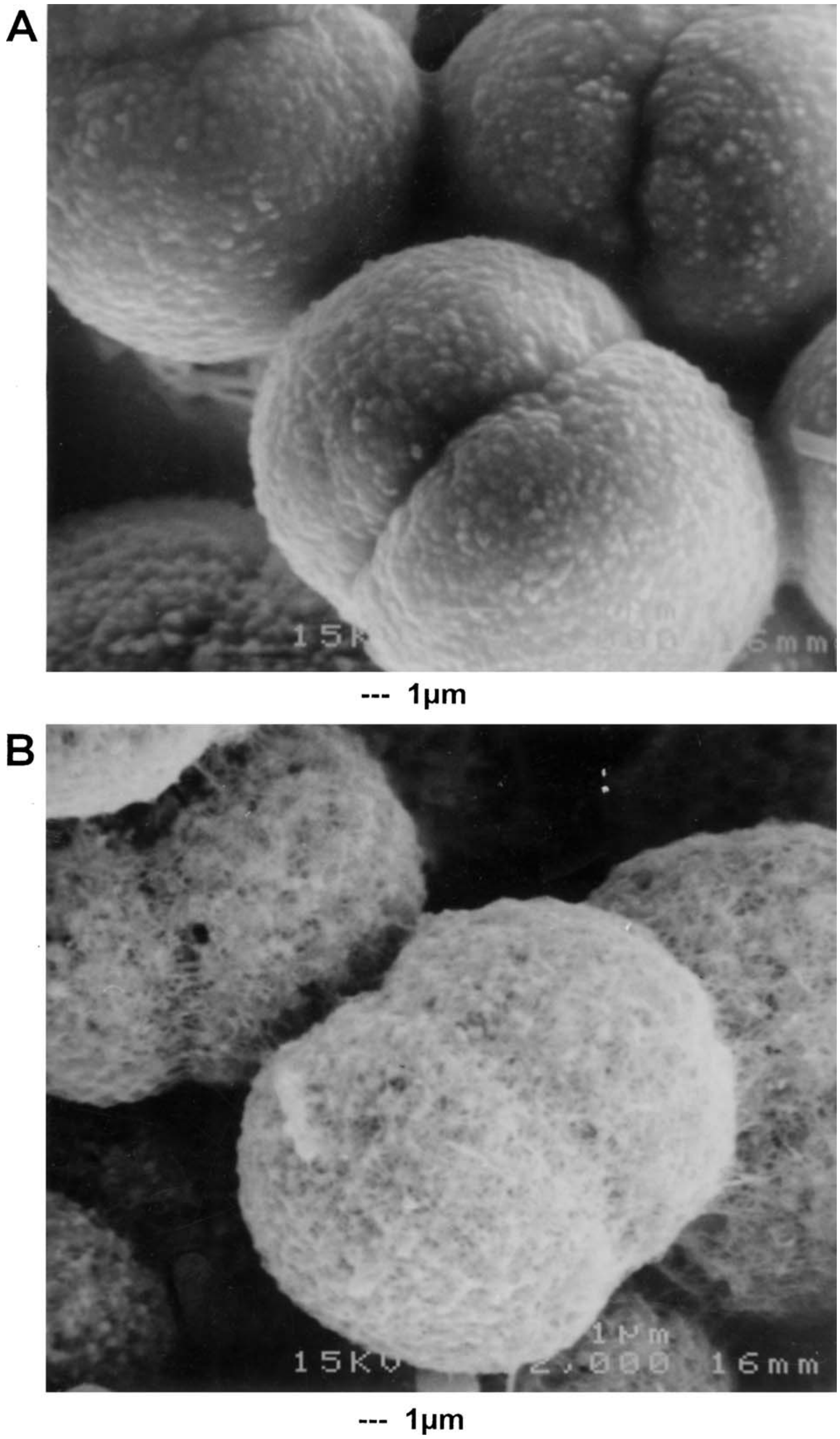

Figure 5 Scanning electron micrographs (SEM) of the coated particles obtained, when (A) an aqueous dispersion containing 0.4 g dm^{-3} $CdCO_3$ cores, shown in Fig. 1A, 0.009 mol dm^{-3} $Cu(NO_3)_2$, and 0.4 mol dm^{-3} urea was aged for 30 min at 85°C; (B) particles shown in A were calcined at 700°C for 1 h at the rate of 5°C min^{-1}.

The little difference between the theoretical and practical weight loss might be due to the traces of sulfate, trapped in the precipitated solid during synthesis. X-ray diffraction analysis (Fig. 3B) showed that the calcined solid was composed of CdO.

Inspection of SEM (Fig. 1B) of the calcined particles demonstrated that calcination had little effect on the particle shape. However, it did affect the surface features of the particles. As is evident from this figure, each particle is made-up of nearly uniform spherical subunits, each nearly of 0.3 μm diameter. This property of the calcined particles supported the idea that a well-grown precipitated particle comes into existence by the aggregation of the small subunits, i.e., primary particles. Moreover, it also indicated that these subunits were also present in the precursor $CdCO_3$ particles (SEM, Fig. 1A) but were most probably bridged by the material, which was lost during calcination. The binding

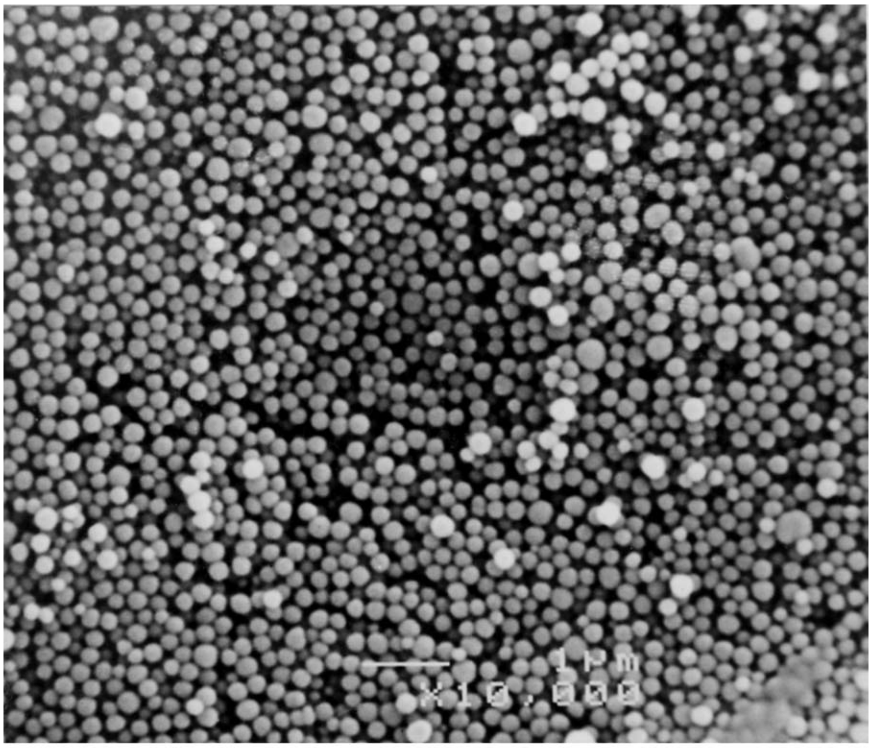

Figure 6 Scanning electron micrograph (SEM) of the particles produced, when an aqueous solution, containing 0.009 mol dm^{-3} Cu(NO$_3$)$_2$ and 0.4 mol dm^{-3} urea was aged for 30 min at 85°C.

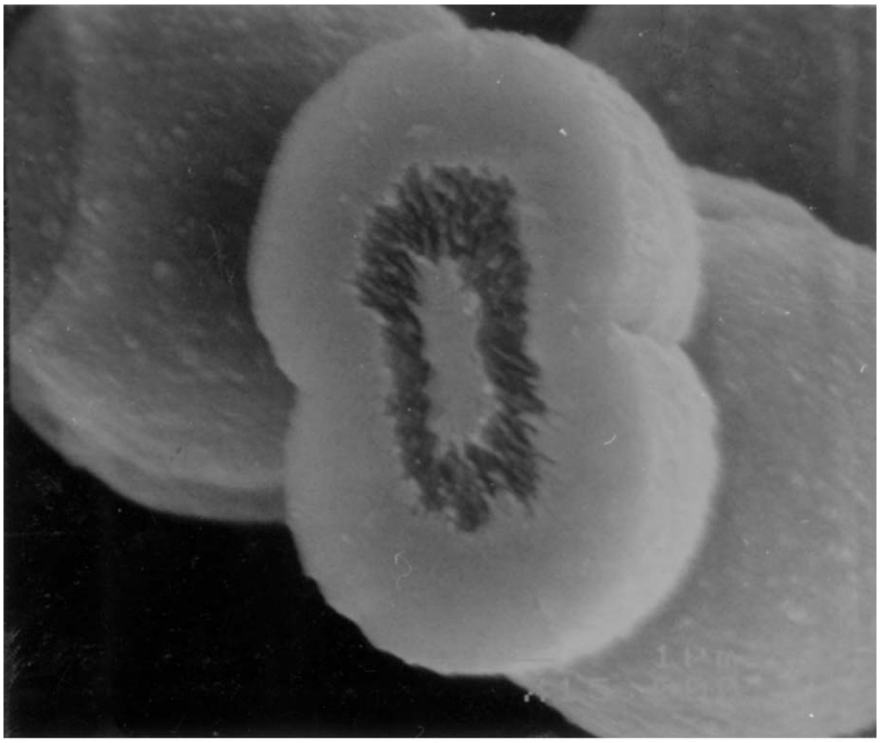

Figure 7 Scanning electron micrograph (SEM) of the accidentally broken particle, found in the sample of the magnetically stirred dispersion of the coated particles, displayed in Fig. 5A.

force between these subunits was strong enough both in the calcined and uncalcined products to be uncharged by sonication or magnetic stirring of these products in aqueous dispersions, since neither of these treatments affected the morphology of these particles.

3.2. Coated particles

The particles shown in Fig. 1A were selected as cores for coating with copper compound. Dispersions of the former particles in aqueous solutions, containing copper nitrate and urea, when heated at 85°C for 1 h, produced coated particles. In the first instance, coating was evident from the change in color, and later from the gain in weight of the dispersed core particles. Scanning electron microscopic analysis of the obtained solids demonstrated that the coating process was very much sensitive to the experimental conditions, since in most of the experiments, mixtures of the coated and coating precursor particles were obtained. As such, extensive optimization of the experimental conditions was carried out in order to obtain uniformly coated particles. The optimization trials lead to the conclusions that uniform coating was possible under very limited experimental conditions.

The picture shown in Fig. 5A is of the typical coated particles sample, obtained under the described conditions. In this case, the dispersed cores acquired ∼29% increase in weight. The grainy appearance of the coating layer showed that coating initially took place by the coagulation of the coating precursor particles of the copper compound, formed in the same medium, with the dispersed core particles. The former then cohered by partial lateral growth and produced a sort of continuous grainy shells on the core particles. The formation of the coating precursor particles in the coating mixture was substantiated by the fact that a dispersion of the greenish particles (Fig. 6) of the copper compound was obtained, when the latter reactant mixture was heated under similar conditions in the absence of the core particles. Yield of the coating precursor particles (Fig. 6) corresponded well to the increase in weight of the cores during the coating experiment. The latter observation showed that the presence of core particles had negligible effect on the precipitation process of the coating material.

Shells of the coated particles, shown in Fig. 5A, were hard enough to be broken down by magnetic stirring in an aqueous dispersion. In contrast, copper compound shells on titania cores were fragile enough and broken down, when their dispersion was subjected to magnetic stirring in our earlier study [23]. It is worth mentioning that in the latter case, coating apparently took place by surface precipitation process. These observations lead to the conclusion that nature of the core/coating material as well as the mode of coating affects the strength of the coating layer on the coated particles.

It was interesting to find an accidentally broken particle (SEM, Fig. 7) in the solid, recovered from the magnetically stirred dispersion of the coated particles (Fig. 5A). As can be seen, this particle is hollow from inside, having apparently ellipsoidal solid material in the center, which is attached with the particle wall by means of tiny strings, more populated in the center region. As such, it appears that the central strings kept the particle wall in place during the particles growth, which resulted a notch in the center of the full-grown particles. No further explanation could be offered at present regarding the particles hollow nature and the build up of their internal as well as external morphology. This interesting aspect of the study is further being investigated in our laboratories.

The coated particles, shown in Fig. 5A, were analyzed by energy-dispersive X-ray technique (Fig. 8), which gave qualitative indication of the Cu and Cd in these particles. Quantitative chemical analysis showed the molar ratio "[Cu]/[Cd]" to be 0.4 in the coated particles.

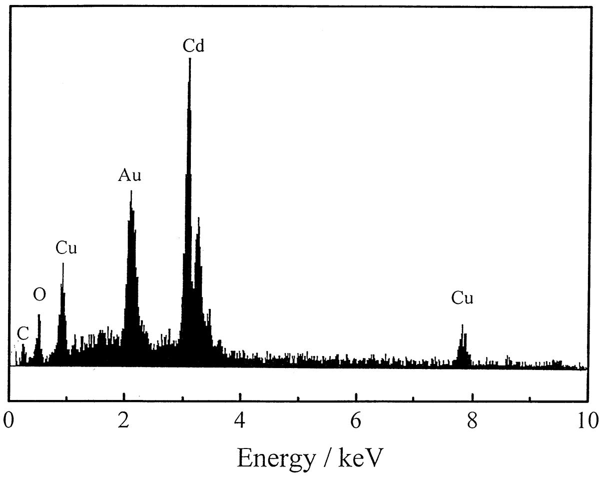

Figure 8 Energy-dispersive X-ray analysis (EDX) pattern of the particles shown in Fig. 5A.

XRD analysis (Fig. 9A) of the coated particles (Fig. 5A) indicated amorphous nature of the coating layer, since their XRD pattern was identical to that (XRD, Fig. 3A) of the core particles (SEM, Fig. 1A). The amorphous nature of the coating material demonstrated that cores did not affect the properties of the coating material, since the coating precursor particles (Fig. 6) obtained in the absence of the cores under similar conditions were also amorphous. Moreover, wet chemical analysis demonstrated that the coating

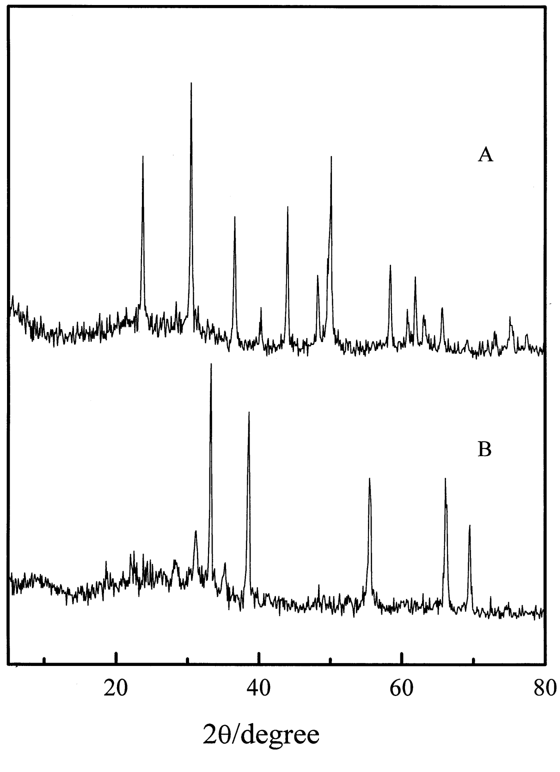

Figure 9 X-ray diffraction (XRD) patterns of the coated particles, displayed in Fig. 5A (A); and Fig. 5B (B). Symbols: a, $CdCO_3$; b, CdO; c, CuO.

material and coating precursor particles have the same chemical compositions, i.e., $Cu_2(OH)_2CO_3$.

Thermogravimetric analysis (Fig. 4A) of the coated particles (Fig. 5A) gave prominent weight loss regions at ∼200 and 350°C, which were due to the loss of material from the coating and core materials, respectively. Similarly, the TGA experiments (Fig. 4B and C), performed independently with the $CdCO_3$ cores (Fig. 1A) and $Cu_2(OH)_2CO_3$ coating precursors (Fig. 6) also showed weight losses respectively at ∼200 and 350°C. The latter observation demonstrated the fact that in the coated solids, core and coating materials had no influence on one another's weight loss reactions.

When calcined at 700°C, the core ($CdCO_3$) and coating ($Cu_2(OH)_2CO_3$) of the coated particles (Fig. 5A) respectively transformed into CdO and CuO without any chemical interaction (XRD, Fig. 9B). The latter behavior agreed with some of our coated systems, reported elsewhere [19, 21, 23]. SEM of the calcined coated particles is shown in Fig. 5B. Inspection of the figure revealed that coating got damaged during the calcination process, while the cores retained their morphological features to a significant extent. The damaging of the shell material of the coated particles was further supported by the fact that the coating precursors (Fig. 6) were damaged and sintered together when calcined under similar experimental conditions.

4. Conclusions

Aqueous solutions, containing dissolved cadmium sulfate and urea, converted into dispersions of precipitated particles, when heated at 85°C for 1 h. The precipitated solids turned out to be crystalline $CdCO_3$. Experiments revealed that cadmium sulfate content of the starting solution significantly affected the particle morphology. A domain of the reactant solution composition was explored in which the precipitated particles ($CdCO_3$) acquired cauliflower shape. These particles were then coated with amorphous layer of copper compound ($Cu_2(OH)_2CO_3$) by homogeneous precipitation process. In the absence of the core ($CdCO_3$) particles, the same reactant mixture produced small spherical particles of $Cu_2(OH)_2CO_3$, when treated under similar conditions.

On calcination at 700°C the core ($CdCO_3$), and coated ($CdCO_{3(\mathrm{core})}/Cu_2(OH)_2CO_{3(\mathrm{coating})}$) particles transformed into CdO, and $CdO_{(\mathrm{core})}/CuO_{(\mathrm{coating})}$ systems, respectively. It was noted that in the coated particles, core and coating materials stayed mutually inert, and transformed independently to their respective oxides during the calcination process.

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