J Mater Sci (2007) 42:7750–7756
DOI 10.1007/s10853-007-1636-4

The coating of cadmium compounds with nickel compounds

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Received: 8 December 2005 / Accepted: 20 February 2007 / Published online: 3 June 2007

Abstract Micrometer-sized particles of cadmium carbonate (cores) were prepared by homogeneous precipitation from aqueous solution containing urea in the presence of cadmium sulfate. These particles were then homogeneously coated with a layer of nickel hydroxy carbonate by heating their dispersion in aqueous solution, containing nickel sulfate and urea, at 85 °C for 70 min with constant agitation. The same solution mixture produced spheroids of nickel hydroxy carbonate (coating precursors), when heated under similar conditions in the absence of the cadmium carbonate particles. The existence of the coated layer on the cores and its composition was confirmed by various physical methods. The as-prepared carbonated solids (cores, coating precursors, and coated particles) were converted into their oxide forms by calcination at 700 °C. The cores became porous, whereas the coating precursors and coating layer disintegrated into smaller particles during the calcination process.

Introduction

Materials in powder form are used in many applications, such as dentistry [1], ceramics [2], gas sensors [3], catalysts [4], adsorbents [5], lubricants [6], pigments [7], chemical mechanical polishing [8], controlled release drugs, [9], etc. On most of the occasions, these materials are produced by mechanical means. However, the powders produced by mechanical methods are usually composed of irregular shaped particles with broad size distribution. The latter properties reduce the reproducibility in performance of these materials in the finished products. Alternatively, colloid chemists have explored various wet chemical methods [10–17] for the synthesis of powder materials, comprised of particles with uniform characteristics. Among these methods, urea based homogeneous precipitation method [16, 17] proved to be a versatile method for producing bare and coated particles. It is worth mentioning here that Matijević and his co-workers [18–22] did pioneering work in this area and produced a number of novel systems of uniform fine particles by the urea based homogeneous precipitation technique. Following their approach, we also produced a number of inorganic powders, as reported elsewhere [23–30]. These powders were comprised of bare as well as coated systems of uniform fine particles of various chemical compositions and novel morphological features.

In this study, our target was the synthesis of such uniformly coated particles, composed of shells of nickel compound around the cadmium carbonate particles, which could be employed as precursor material for obtaining externally composite system of $NiO_{coating}/CdO_{core}$ by the calcination process at the elevated temperatures. We believe that our targeted products would be the first of their kind to be reported, both in respect of chemical composition, and morphological features, and thus would behave differently in applications. For example, nickel oxide and cadmium oxide posses the semiconducting properties and gas sensing properties [31–34] and thus the composite oxide system ($NiO_{coating}/CdO_{core}$) could very well be utilized in the preparation of hybrid electrical gas sensor, possibly of novel performance. It is added that the possibility of producing the composite oxides system

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[$CdO_{coating}$/NiO_{core}] is under investigation and would be reported in the subsequent publications.

In this study we report the synthesis of cadmium carbonate particles and their coating with basic nickel carbonate by means of urea based homogeneous precipitation method. In the absence of the core particles, the optimized coating mixture generates spheroids of crystalline nickel hydroxy carbonate precipitates, designate as coating precursors. On calcination at the elevated temperatures, the core, coated, and coating precursor particles convert into CdO, $NiO_{(coating)}$/$CdO_{(core)}$, and NiO, respectively.

Experimental procedures

Material

Cadmium sulfate, nickel sulfate, and urea were taken as the starting materials in this study. All these chemicals were obtained from Merck and used in the as-received form without further purification. Thoroughly cleaned Pyrex glass vessels were used for the preparation of aqueous solutions of the described chemicals, needed in this study. Doubly distilled water was used for making all the stock and working solutions. In order to get rid of any dust contaminant, all the solutions were filtered through 0.1 μm pore size membrane filter before use.

Synthesis of coated particles

The synthesis of coated particles was carried out in two steps. In the first step, core particles of cadmium carbonate were obtained by homogeneous precipitation [30]. For this purpose, 200 cm^3 aqueous solution of cadmium sulfate (0.06 mol dm^{-3}) was mixed with equal volume of aqueous solution of urea (0.8 mol dm^{-3}) at room temperature in an open 500 cm^3 beaker. This mixture was then aged at 85 °C in a pre heated 600 cm^3 double walled Pyrex glass reactor for 1 h. Hot water was kept circulating through the double walled jacket of the reactor from the constant temperature bath for keeping temperature of the reactor at 85 °C during the aging period. Following this treatment, white precipitates appeared in the reactant mixture. The resulting suspension was immediately cooled down to room temperature in the same reactor by changing the line of hot circulating water to tape water. Finally, the suspension was transferred to open beaker and the solid contents were isolated from the liquid by filtration through 0.1 μm pore size membrane filter. These solids were cleaned of undesired ions by washing with copious amount of the doubly distilled water. The washed solids were dried in air at laboratory temperature for several hours, and then stored in stoppered bottles.

In the second step, the coating mixture was prepared by ultrasonically dispersing the known amounts (0.2–0.8 g) of the dry core ($CdCO_3$) particles in 500 cm^3 aqueous solution mixtures, 0.4 mol dm^{-3} in urea and 0.01–0.08 mol dm^{-3} in nickel sulfate. After constant agitation for 1–7 h at room temperature in a double walled Pyrex glass reactor (described above), each dispersion was aged in the same vessel for 20–160 min at 85 °C, while keeping the agitation on. Following the predetermined aging period, temperature of the reaction mixtures was brought to room temperature. The solids in the coating mixture were separated from the liquid, washed, and then dried in the same manner, as used during the preparation process of the core particles.

In some cases, the above-mentioned coating mixtures were treated under similar conditions in the absence of the dispersed core particles, which produced dispersions of the greenish precipitated particles (coating precursors). These particles were recovered from their mother liquor, and handled like the core and coated particles.

It is added here that similar experimental strategy was also adopted in our earlier studies [25–28] as well as by other researchers [21] for obtaining different types of coated particles.

Calcination

Selected batches of the core, coated and coating precursor particles were calcined in a tube furnace at 700 °C for 1 h. Ramp rate of the furnace was kept at 10 °C min^{-1}. At the end of the calcination process, the furnace was turned off and the calcined samples were allowed to stay inside the furnace till it acquired the room temperature.

Characterization

The morphological characteristics of the particles (as-prepared and calcined) were investigated by scanning electron microscope (SEM; JEOL, JSM-6300). The standard procedures were adopted in making samples for observation in the SEM. To mention briefly, very small amount of the desired powder was sputtered with thin layer of gold after mounting it on a standard stub with the help of a silver paint before microscopic study. The power of the SEM was kept at 15 keV during examination of all the test powder samples.

The qualitative atomic composition of the coated particles with respect to metal content was confirmed through the use of X-ray energy-dispersive microanalysis (EDX, Noran Voyager X-ray microanalysis system), attached with the same SEM. Moreover, the coated particles were also analyzed for the quantitative determination of the metals by the chemical methods, described in our earlier paper [28].

X-ray diffractometry was employed for ascertaining the crystallinity and composition of the as-prepared and coated particles before and after the calcinations process. The XRD patterns for these solids were obtained with Siemens D500, X-ray diffractometer, with CuK_α radiations. The detector of the machine was moved stepwise ($\Delta 2\theta = 0.05°$) between 5° and 80°.

Parts of the powder samples, analyzed with SEM, EDX, and XRD analysis, were also subjected to thermal analysis. These analyses were performed with Perkin–Elmer 7, TGA machine. The machine operating conditions were kept uniform during analysis of all the test samples. The latter were heated at the rate of 10 °C min^{-1} in dynamic air atmosphere.

Results and discussion

Core particles of cadmium compound

Figure 1a shows scanning electron micrograph of the cadmium carbonate particles, prepared by homogeneous precipitation method [30] under the conditions, mentioned in the legend of the same figure. Composition of these particles was confirmed by X-ray diffractometric measurements (XRD, Fig. 2a). The former were white in color and on calcination at 700 °C, they converted into brown powder of cadmium oxide (XRD, Fig. 2b) with the generation of uniform pores in the body of the particles. The formation of pores in the calcined particles (SEM, Fig. 1b) was obviously due to the thermally induced loss of material in the form of CO_2 according to the reaction 1.

$$CdCO_3 \xrightarrow[\text{Wt. loss}]{25.52\ \text{wt.\%}} CdO + CO_2 \qquad (1)$$

Similar results were also obtained in our earlier study [30]. It may also be added here that the generation of pores in such a uniform manner points to the size uniformity of the primary particles ($CdCO_3$), which on aggregation produced the full-grown core particles.

It appears that the weight loss of 25.52% in the total solids (reaction 1) was at the primary particles' level, which caused the observed porosity in the calcined solids (CdO particles).

Coated particles

The core particles of cadmium carbonate were uniformly coated with shells of nickel compound by the homogeneous precipitation method. For this purpose, dispersions of the core particles in aqueous solutions, containing urea and nickel sulfate were heated at 85 °C for various periods of time. It was observed that the coating process was very much sensitive to the applied experimental conditions. Uniformly coated particles were obtained only when the coating mixtures, containing 0.3–0.6 g dm^{-3} of cores, 0.02–0.0348 mol dm^{-3} $NiSO_4$, and 0.25–0.45 mol dm^{-3} urea, were heated at 85 °C for 130 min with constant agitation. These particles carried variable amounts of the coating material, depending upon the composition of the coating mixture, described above. For example, at constant amount of urea (0.4 mol dm^{-3}) and cores (0.5 g dm^{-3}) in the coating mixture, the amount of coating material on the dispersed cores increased (Fig. 3) with the increase in concentration of $NiSO_4$ in the same mixture within the above mentioned concentration domain. Increasing the concentration on $NiSO_4$ beyond the indicated limit, mixture of coated and coating precursor particles was obtained.

Figure 4a shows typical example of the coated particles, obtained under the experimental conditions, given in the legend of this figure. These particles got light green coloration due to the intrinsic color of the shell material (nickel compound). Similarly, the light green particles (coating precursors) shown in Fig. 5a were produced, when the coating mixture described in the legend of Fig. 4a was treated under similar conditions in the absence of the core particles. Inspection of these figures reveals that surface features of the shell material in the coated particles (Fig. 4a) and those of the coating precursors (Fig. 5a) were identical.

Similarly, XRD analysis showed that the coated particles (Fig. 4a) were composed of cadmium carbonate, and nickel hydroxy carbonate (XRD, Fig. 6a). Obviously, those were core and coating materials, respectively. Similarly, the coating precursors (Fig. 5a) turned out to be nickel hydroxy carbonate (XRD, Fig. 7a). These observations pointed to the fact that in the absence of core particles, the described reactant mixture generated spheroids of nickel hydroxy carbonate, while in the presence of dispersed core particles; it produced shells of the same compound around the latter particles. Identical composition of the shell and coating precursors materials showed that the presence of cores had negligible effect on the precipitation mechanism of the nickel compound under the described conditions. Moreover, the shell-core association appeared to be physical in nature, since the XRD analysis (Fig. 6a) of the coated particles gave no indication of any sort of intermediate compound formation possibly at the shell/core interface during the synthesis.

The composite nature of the coated particles was also authenticated by EDX analysis (Fig. 8), which showed that these particles contained nickel and cadmium. Obviously, those were the metals, present in the coating and core materials respectively.

Similarly, wet chemical analysis revealed that the coated particles shown in Fig. 4a were composed of 13.6% nickel and 46.2% cadmium. A close agreement was found between the calculated composition (14% Ni, and 46.9% Cd),

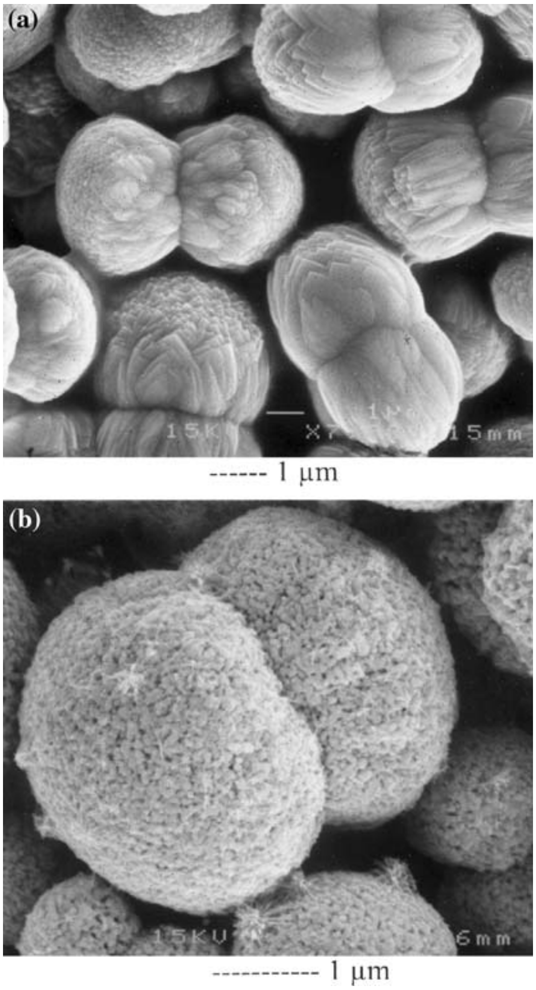

Fig. 1 Scanning electron micrographs (SEM) of the $CdCO_3$ particles produced in a solution mixture, containing 0.03 mol dm^{-3} $CdSO_4$ and 0.4 mol dm^{-3} urea by heating it 85 °C for 60 min (**a**), and CdO particles obtained from the $CdCO_3$ particles in A on calcination at 700 °C (**b**)

estimated from the amounts of the shell ($NiCO_3 \cdot Ni(OH)_2 \cdot H_2O$; ~28 wt.%) and core ($CdCO_3$; ~72 wt.%) materials in the given amount of the coated particles.

The coated particles, shown in Fig. 4a, were also subjected to thermogravimetric analysis (TGA). It was observed (Fig. 9a) that these particles suffered 9% weight loss at 340 and 19% weight loss at 390 °C. Following the amounts of the shell (~28 wt.%) and core materials (~72 wt.%) in the coated particles, we believed that the two weight losses at 340, and 390 °C were due to the thermal decomposition (phase transition) of the shell and core materials, according to reactions 2, and 1, respectively.

$$\mathrm{NiCO_3 \cdot Ni(OH)_2 \cdot H_2O} \xrightarrow[\text{Wt. loss}]{34.87\,\text{wt.\%}} \mathrm{2NiO + CO_2 + H_2O} \qquad (2)$$

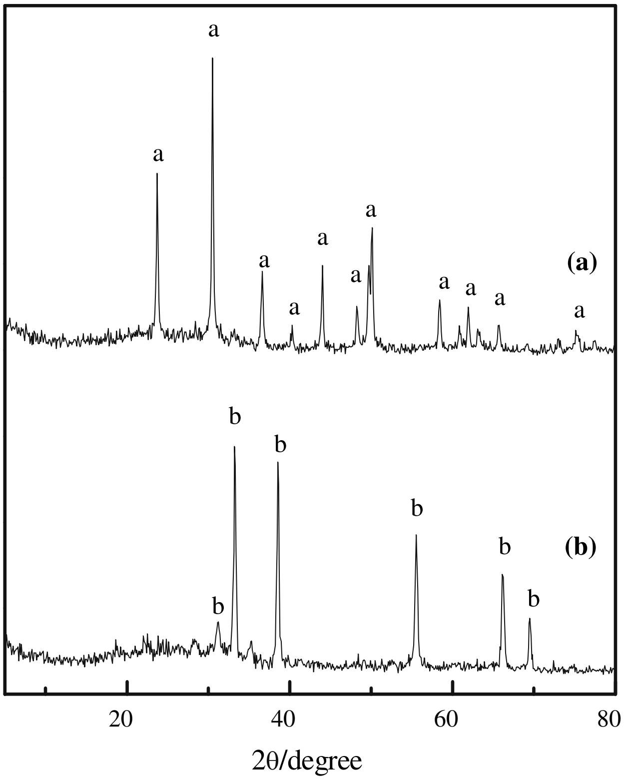

Fig. 2 XRD traces of the solids, displayed Fig. 1a (**a**), and Fig. 1b (**b**). Symbols: a, $CdCO_3$; b, CdO

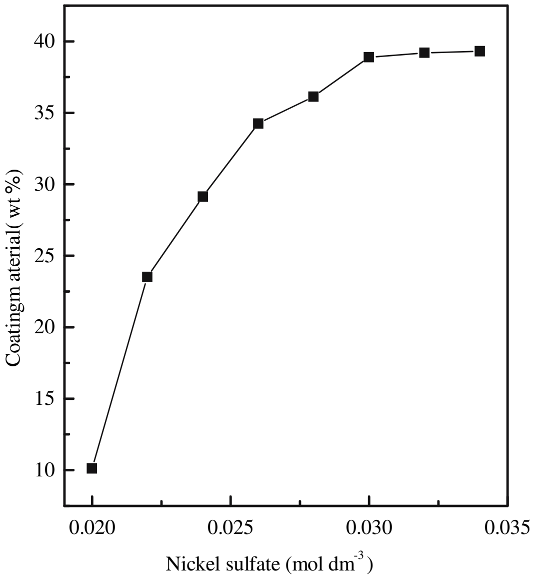

Fig. 3 Variation in the amount of the coating material, deposited on the dispersed cores, when the coating mixtures containing 0.4 mol dm^{-3} urea, 0.5 g dm^{-3} cores ($CdCO_3$), and 0.020–0.034 mol dm^{-3} nickel sulfate, were heated at 85 °C for 130 min with constant agitation

In order to confirm this idea, TGA experiments were performed separately with the core and coating precursors under the same conditions, as employed for the coated

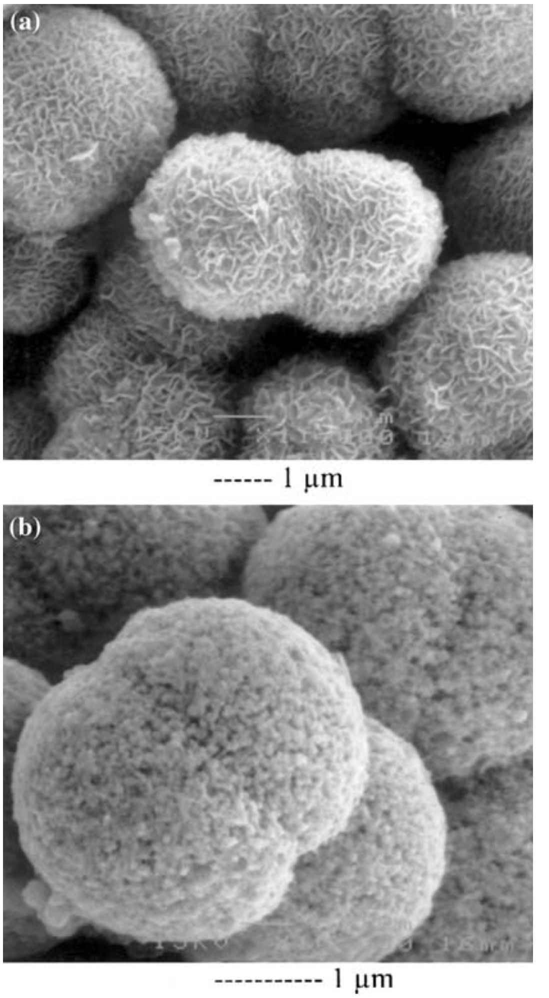

Fig. 4 Scanning electron micrographs (SEM) of the coated particles obtained by heating at 85 °C, aqueous dispersion, containing 0.5 g dm^{-3} $CdCO_3$ particles, 0.03 mol dm^{-3} in $NiSO_4$, and 0.4 mol dm^{-3} urea for 130 min with constant agitation (**a**); calcination of the particles shown in A at 700 °C for 1 h produced the particles in displayed in B

particles. The TGA traces for these materials have been included in Fig. 9 at b (for cores), and at c (for coating precursors). The latter traces clearly revealed that the coating precursors and cores lost significant weights between 340–370 °C, and 380–420 °C, respectively. The weight loses registered in the TGA traces (b and c in Fig. 9) agreed with the calculated weight loses indicated in reactions 1, and 2, respectively. It is added that the close agreement between (i) the phase transition temperature of nickel hydroxy carbonate in the coating precursors and shells of the coated particles, and (ii) cadmium carbonate in the bare cores and coated cores, supported the fact that the shell/core association was purely physical in nature, and both the materials stayed mutually inert during the heating process in the TGA experiments.

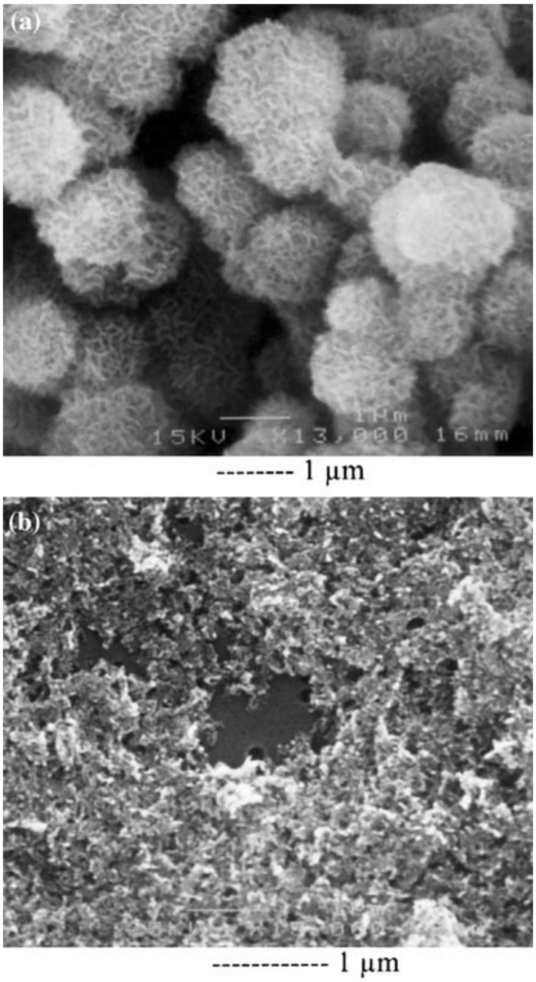

Fig. 5 Scanning electron micrographs (SEM) of the $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$ particles obtained by aging aqueous solution, 0.03 mol dm^{-3} in $NiSO_4$, and 0.4 mol dm^{-3} in urea at 85 °C for 130 min (**a**), and NiO particles, obtained from the particles in A on calcination at 700 °C for 1 h (**b**)

Following the information, gathered from the above thermal study of the coated particles, the latter were calcined at 700 °C in the static air atmosphere. The calcined coated particles, which acquired black color with brown tint (originated from the calcined cores), are shown in Fig. 4b. As is clear from this figure that the shell material lost its original morphological features and transformed possibly into densely packed smaller particles, adhered with the cores surfaces. It was interesting to note that the coating precursors also lost their morphological features and disintegrated into black colored smaller particles (SEM, Fig. 5b), when calcined under similar conditions. These observations pointed to the fact that nickel hydroxy carbonate was fragile enough to sustain its original morphology in the shell as well as in the coating precursors under the described calcination conditions.

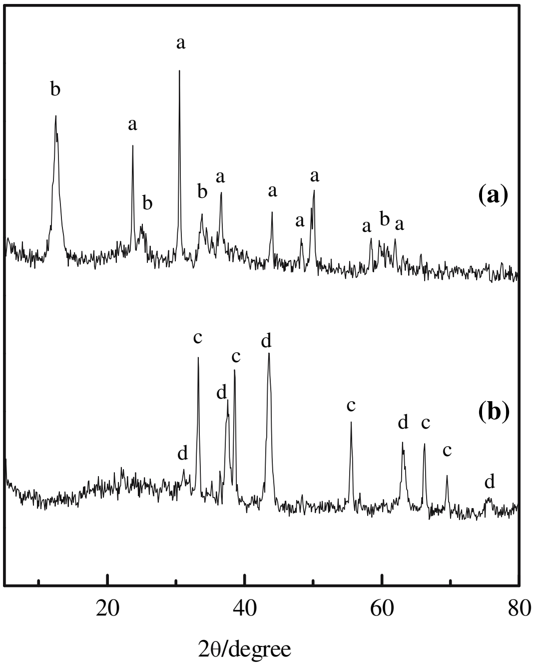

Fig. 6 X-ray diffraction (XRD) patterns of the coated particles, shown in Fig. 4a (**a**); and in Fig. 4b (**b**). Symbols: a, $CdCO_3$; b, $NiCO_3.Ni(OH)_2{\cdot}H_2O$; c, CdO; d, NiO

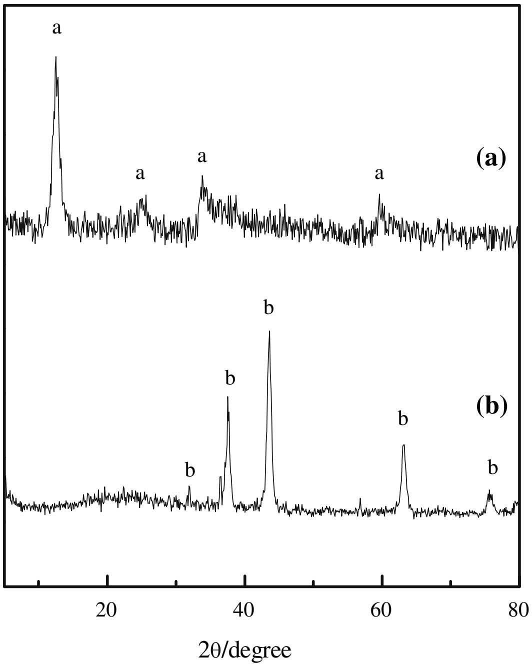

Fig. 7 X-ray diffraction (XRD) patterns of the particles, shown in Fig. 5a (**a**); and in Fig. 5b (**b**). Symbols: a, $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$; b, NiO

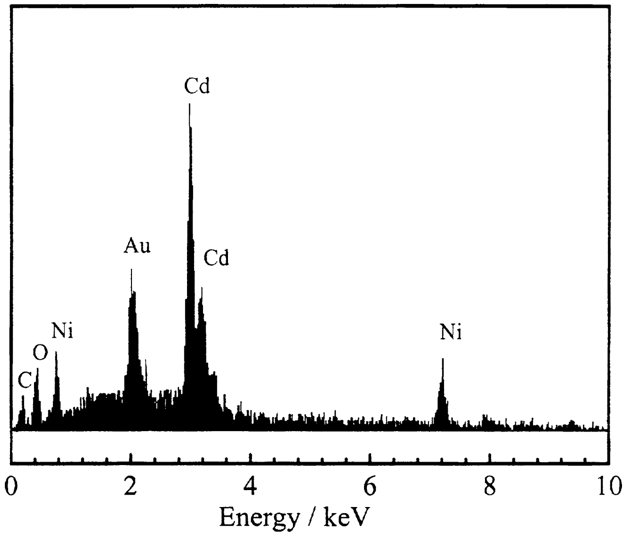

Fig. 8 Energy-dispersive X-ray analysis (EDX) pattern of the coated particles shown in Fig. 4a

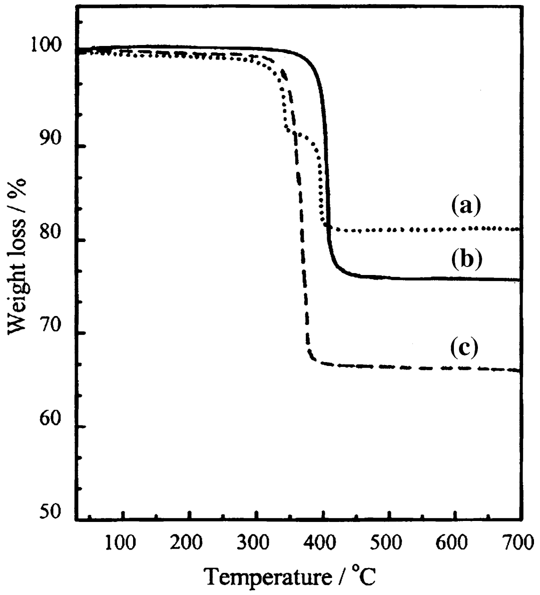

Fig. 9 Thermogravimetric analysis (TGA) curves for the particles displayed in Fig. 4a (**a**); Fig. 1a (**b**); and Fig. 5a (**c**)

XRD analysis (Figs. 6b, and 7b) revealed that the solids shown in Figs. 4b, and 5b, were composed of CdO/NiO, and NiO, respectively. It means that in both cases the carbonated solids completely converted into their respective oxides. Furthermore, the absence of the diffracted peaks in the XRD pattern (Fig. 6b) of the calcined coated particles, other than those of the CdO and NiO designated peaks, showed the absence of any sort of the thermally generated product at the core/shell interface. Similar behavior was shown by our previously reported coated particles, i.e., $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O_{(shell)}/MnCO_{3(core)}$ [26], and $2CoCO_3{\cdot}Co(OH)_2{\cdot}H_2O_{(shell)}/CdCO_{3(core)}$ [27] during calcination process at the elevated temperature. In contrast, calcination resulted the formation of the composite solid phase at the core/shell interface in the coated particles, composed of $CoCO_{3(shell)}/NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O_{(core)}$ [28], $TiO_{2(shell)}/ZnO_{(core)}$ [35], and $Y(OH)CO_{3(shell)}/SiO_{2(core)}$ [36]. This indicated that composition of the core and coating material play a vital role in the initiation of the solid-state reaction between the core and coating material at the elevated temperatures.

Conclusions

1. Heating of the aqueous, (a) solution of urea and cadmium sulfate produced $CdCO_3$ particles, and (b) dispersion of $CdCO_3$ particles in urea and nickel nitrate solution generated coated particles, composed of $CdCO_{3(core)}/NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O_{(coating)}$. The same coating mixture produced spheroids of $NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$ (coating precursors), when heated under similar conditions in the absence of the dispersed cores ($CdCO_3$).
2. On calcination at 700 °C, the core ($CdCO_3$), coating precursors ($NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O$), and coated ($CdCO_{3/[core]}/NiCO_3{\cdot}Ni(OH)_2{\cdot}H_2O_{[coating]}$) particles converted into CdO, NiO, and $CdO_{[core]}/NiO_{[coating]}$, particles, respectively.
3. Calcination resulted in, (a) porosity in the core particles due to the loss of thermally decomposable carbonate rich material, (b) disintegration of the coating precursors into smaller fragments, and shells on the coated particles into densely packed small particles. The observed behavior in (b) and (c) pointed to the fragile nature of this material under the applied heat treatment.

Acknowledgements The authors are grateful to Dr. Egon Matijević, Victor K. LaMer Professor of Colloid and Surface Science, Center for Advanced Materials Processing, Clarkson University, Potsdam, New York 13699, USA, for providing all sorts of facilities for the characterization of the powder samples.

References

1. Fleming GJ, Farooq AA, Barralet JE (2003) Biomaterials 24:4173
2. Takemura D, Aihara S, Hamano K, Kise M, Nishimura T, Urushibata H, Yoshiyasu H (2005) J Power Sources 146:779
3. Shimizur Y, Jono A, Hyodo T, Egashira M (2005) Senso Actuator B108:56
4. Li X, Liu H, Cheng LF, Tong HJ (2003) Environ Sci Technol 37:3989
5. Rongcheng W, Jiuhui Q, Yongsheng C (2005) Water Res 39:630
6. Rapoport L, Leshchinsky V, Lvovsky M, Lapsker I, Volovik YU, Feldman Y, Popovitz-Biro R, Tenne R (2003) Wear 255:794
7. Le H-P (1980) J Imag Sci Technol 42:49
8. Jin SY, Woo PS, Hoon KN, Goo CE, Sun LW (2005) Microelectron Engg 77:358
9. Jennifer F, Jie F, Justin H (2004) J Contrl Rel 96:411
10. Košak A, Makovec D, Žnidaršič A, Drofenik M (2004) J Europ Ceram Soc 24:959
11. Clifford YT, Bor-Yuan H, Hsien-Yi C (2004) Coll Surf A 237:105
12. Rosenband V, Gany A (2004) J Mater Process Technol 153/154:1058
13. Hee SK, Jong RS, Yun C, Kyeong YJ, Seung BP (2005) J Alloys Comp 398:40
14. Ritva L, Johan S, Göran S (1995) Coll Surf A 99:79
15. Isao M, Yu I, Masato T (2005) Mater Res Bull 40:1202
16. Boschini F, Robertz B, Rulmont A, Cloots R (2003) J Europ Ceram Soc 23:3035
17. Ocaña M., Morales MP, Serna CJ (1999) J Coll Interf Sci 212:317
18. Matijević E (2002) Encyclopedia of surface and colloid science. Marcel Dekker, NY, p 4322
19. Wang L, Sondi I, Matijević E (1999) J Coll Interf Sci 218:545
20. Krathohvil S, Matijević E (1991) J Mater Res 6:766
21. Aiken B, Hsu WP, Matijević E (1988) J Am Ceram Soc 71:845
22. Her YS, Matijević E, Wilcox WR, Bailey OG, Fischman GS (1992) J Mater Sci Lett 11:1629
23. Haq I, Matijević E (1993) Coll Surf A 81:153
24. Durand-Kiklikian L, Haq I, Matijević E (1994) Coll Surf A 92:7267
25. Haq I, Matijević E (1997) J Coll Interf Sci 192:104
26. Haq I, Matijević E, Akhtar K (1997) Am Chem Soc Chem Mater 9:2665
27. Haq I, Akhtar K (2000) J Mater Sci 35:2565, DOI: 10.1023/A:1004762928982
28. Haq I, Akhtar K (2000) Adv Powder Technol 11:175
29. Haq I, Fraser I, Matijević E (2003) Coll Polym Sci 281:542
30. Haq I, Akhtar K (2004) J Mater Sci 39:3357, DOI: 10.1023/B:JMSC.0000026936.62696.1b
31. Xingqin L, Zhengliang X, Yafei L, Yusheng S (1998) Sens Actuators B 52:270
32. Chol JS, Kang YH, Kim KH (2001) J Phys Chem 81:2208
33. Soon-Dan C, Bong-Ki M (2001) Sens Actuator B 77:330
34. Liu J, Huang X, Ye C, Liu W, Jiao Z, Chao W, Zhou Z, Yu Z (2003) Sensors 3:110
35. Ocana M, Hsu WP, Matijević E (1991) Langmiur 7:2911
36. Giesche H, Matijević E (1994) J Mater Res 9:436