

A new strategy for finely controlling the metal (oxide) coating on colloidal particles with tunable catalytic properties†

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In this contribution, we present an efficient, versatile and green strategy for finely controlling the metal (oxide) coating on core particles through *in situ* reaction of precursors in CO₂ expanded ethanol without using any precipitants. It not only avoids the formation of free metal (oxide) and/or naked cores, but also permits individual dispersion of all the resultant particles without aggregation. With this method, the composition, thickness, uniformity, and structure of the metal (oxide) shell could be precisely controlled. A wide variety of unreported high-quality core-shell particles with a shell consisting of highly dispersed metal (oxide) nanocrystals or nanoalloys, such as C@Ni, CoO/C, C@Ni&Co and C@Ni&Pd particles have been fabricated, and the properties of the resultant particles were precisely tailored, such as the promising catalytic performance obtained over Ni/C and C@Ni particles in the hydrogenation of nitrobenzene. The present coating strategy is more simple and precisely controllable compared to the conventional deposition method and it is suitable for most precursors and even for multi-component materials, enabling the fabrication of nanostructured materials more easily and precisely.

1. Introduction

The preparation of core-shell structured micro- and nanoparticles has been attracting great interest because they often behave distinctly different from bulk materials and exhibit improved properties over single-component counterparts.¹ Up to now, most of them are fabricated by coating pre-synthesized core particles with a layer of desired materials.² To date, metals and metal oxides are the most fascinating shell materials due to their intriguing structural, electronic and magnetic properties. In this way, it not only expands the applications of metals (oxides) in the areas of catalysis,³ optics,⁴ lithium batteries,⁵ environmental science⁶ and biotechnology,⁷ but also gives rise to a wide variety of multifunctional particles with more excellent performance.⁸ For example, catalyst seeds encapsulated by metal (oxides), such as Pt@CoO,⁹ Au@ZrO₂,¹⁰ and Pd@Au,¹¹ show higher stability, activity, and/or selectivity than naked cores owing to the local effect and synergistic interactions between cores and metal (oxides) shell.

However, a common difficulty that has been puzzling researchers in such template-based methods is how to coat metals (oxides) on particles quantitatively and uniformly without particle aggregation and avoiding the generation of free metals (oxides).¹² Generally, the traditional coating strategy is started by dispersing particles (functionalized or not) into the solution of precursors (soluble metal salt¹³ or nanoscale building blocks^{2a,14}), the precursors then adsorb on to particles, and then the residual solution is decanted^{13a} or directly dried.¹⁵ Alternatively, it could also be precipitated by precipitants^{13b} or treated by hydrothermal methods,¹⁶ or hydrolyzed if metal alkoxides were used.¹⁷ With these procedures, either primary precursors, or generated intermediates such as metal hydroxide or metal (oxide) (crystalline or not), were coated on particles before post-treatment to form the crystalline metal (oxide) shell. Unfortunately, there are several intrinsic disadvantages in the above approaches. For example, difficulty in achieving an accurate coating because a certain amount of precursor always remains in the abandoned solution^{13a} and/or precipitation of the free shell materials and/or naked cores; the agglomeration of final particles,¹⁸ which results from the coalescence of core particles during the precipitation or hydrolyzation. Except for the effects of incompatibility between the core surface and the solid intermediates,¹² most defects were largely determined by the intrinsic properties of the liquid solvent (for instance: high viscosity, the existence of surface tension and low diffusivity as compared with gases). These properties strongly limit the ability of solvent to disperse precursors and core particles uniformly and transfer generated solid intermediates to the surface of cores as soon as possible. Furthermore,

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additional precipitants and/or surfactants,¹⁹ or a long reaction time or multi-step coating procedures were required in some cases, such as several days of hydrolyzation^{17a} or layer-by-layer adsorption.^{14a} Moreover, different precursor often required different treatments, in which optimized synthetic conditions need continual exploring and testing.^{16b,17b,20} Thus, another well-known challenge is to design a universal, clean and effective method that is suitable for most precursors.

Herein, we present an efficient, versatile, and green strategy for finely coating the metals (oxides) on core particles (*e.g.*, carbon colloids and silica gel) through *in situ* reaction of precursors in scCO₂-expanded ethanol without using any precipitants. With this new strategy, the common difficulties that exist in traditional deposition methods were completely overcome. A wide variety of unreported high-quality core-shell particles with a shell consisting of highly dispersed metal (oxides) nanocrystals or nanoalloys have been fabricated easily, and the composition, thickness, uniformity, and structure of the metal (oxides) shell could be finely controlled allowing the properties of the resultant particles were precisely tailored.

2. Experimental

Materials

The chemical reagent of Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, glucose, and C₂H₅OH were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd, and PdCl₂ was purchased from Aldrich. The core particles of carbon colloids and silica gel were synthesized by the hydrothermal method²¹ and Stöber process,²² respectively. A typical procedure for the synthesis of carbon colloids is as follows: 3.75 g glucose was dissolved in 30 ml deionized water under rapid stirring to form a clear solution, which was transferred into a 50 mL Teflon-sealed autoclave and maintained at 180 °C for 5 h. Cooling down to room temperature and centrifugation of the black colloidal solution gave rise to about 60 mg carbon colloids. A larger amount spheres could be obtained by prolonging the reaction time.

Coating procedures

The as-prepared core particles (50 mg) were well dispersed in ethanol solution of hydrous metal salt (10 ml) in a glass bottle under ultrasonic treatment. The dense colloidal solution was then transferred into an autoclave (50 ml), which subsequently was placed into an oil bath at a 150 °C and then pumped CO₂ to form a homogeneous expanded fluid under rapid stirring (12.0 MPa). And then the reactor was heated to the reaction temperature of 200 °C, at which the pressure went up to ~22.0 MPa. 2 h later, the autoclave was cooled down to room temperature, and then CO₂ was released slowly. After centrifugation, the core-shell structured particles were collected and the ethanol was recycled. The same procedures were also used for the multi-component coatings.

Post-treatment for metal (oxides) shell

The as-prepared sample were calcined in the tube furnace with or without N₂ atmospheres according to the requirement.

The calcination was carried out at 500 °C for 30 min with a heating rate of 3 °C min⁻¹.

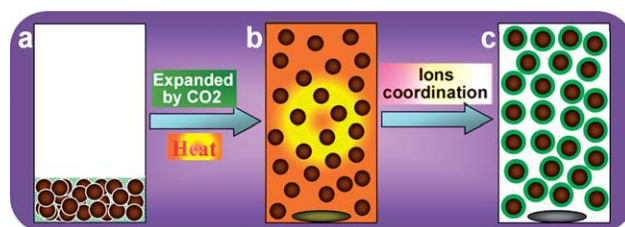
Characterization

Crystallographic information was investigated by XRD patterns, which were measured on a Bruker D8 GADDS diffractometer using Co K α radiation (1.79 Å). The morphology of the core-shell structured particles were characterized by field emission scanning electron microscopy (FESEM), which was taken on a XL30 ESEM microscope operated with a beam energy of 20 kV. The core-shell structures were characterized by transmission electron microscopy (TEM) images using a JEOL-2100F microscope operated at 200 kV. The chemical composition of the shell were measured by inductively coupled plasma atomic emission spectrometer (ICP-AES) (Thermo Scientific iCAP 6000 Series) and energy dispersion X-ray analysis (EDXA), respectively. The catalytic reaction in supercritical CO₂ were carried out by the procedures described in previous work.²³

3. Results and discussion

Coating in CO₂ expanded fluid

Scheme 1 illustrates the coating process according to the investigation of the actual situation in a viewable autoclave (Fig. S1, ESI†). A primary colloidal solution of precursors was firstly expanded by CO₂ to form a homogeneous fluid (Scheme 1a, b) in which the colloidal particles have more space and easily disperse in the solution before and during coating, thereby allowing the preservation of good dispersity of the particles even after deposition. Subsequently increasing the temperature, the soluble precursors could convert into a solid compound and then adsorb/deposit on the core particles uniformly. The physicochemical properties of such a specific fluid could facilitate the nucleation/transfer/deposition of such solid compounds, therefore minimizing the formation of free solid and/or naked cores and thus leading to a perfect coating (Scheme 1c). FESEM and TEM images (Fig. 1) show the solid compounds (or metal salts) were always perfectly coated on the core particles without the formation of any independent solid compound or naked cores. Furthermore, another highlight of the obtained composite particles is that they have a good individual dispersity in large-scale (Fig. S2, ESI†), which is being strongly demanded in materials science but has not been fully satisfied.¹²



Scheme 1 Schematic drawing of the coating process. (a) Dense carbon colloidal ethanol solution of precursors within an autoclave. (b) Introduction of CO₂ to form an expanded fluid. (c) Coordination of dissociated ions and/or molecules to form a solid compound and then deposited uniformly on the surface of the core particles.

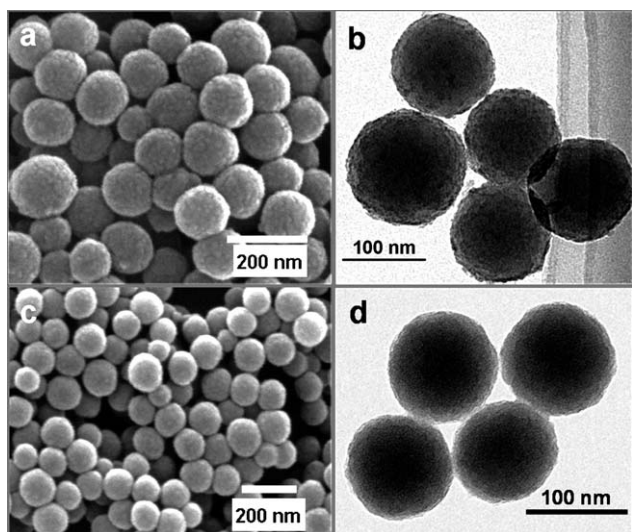


Fig. 1 FESEM and TEM images of core-shell structured C@metal-salt particles. (a, b) C@Ni-salt (0.02 M Ni²⁺). (c, d) C@Co-salt (0.01 M Co²⁺).

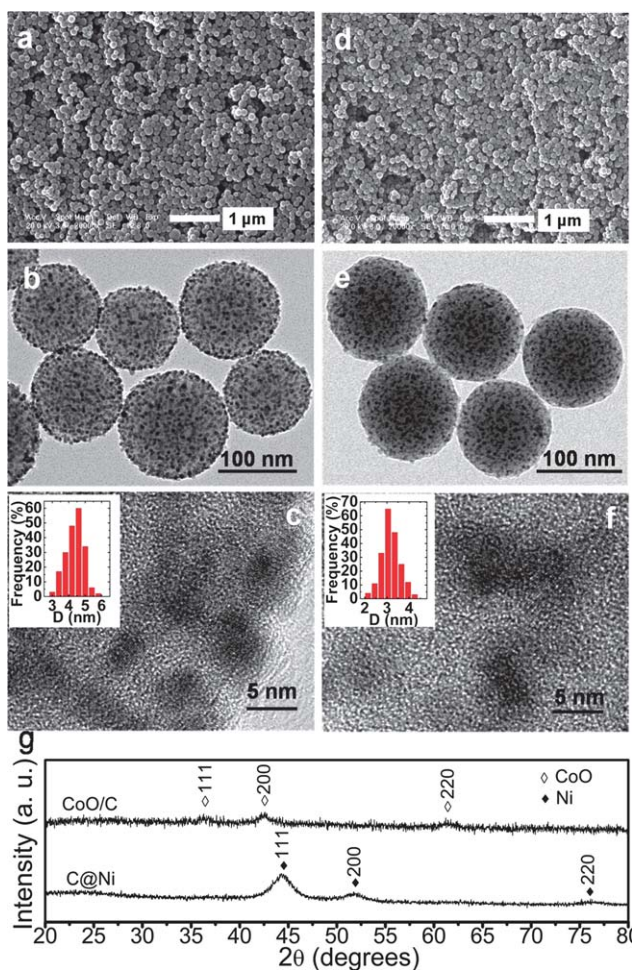


Fig. 2 FESEM, TEM and HRTEM images of (a–c) C@Ni particles and (d–f) CoO/C particles. (g), XRD patterns of composite particles.

Core-shell particles with a shell consisting of metal (oxide) nanocrystals

With this versatile strategy, a perfect coating layer on core particles was finely controlled with precise loading from the soluble precursors, directly giving rise to a series of perfect and unique core-shell structured particles, such as C@metal-salt, which could have potential applications in diverse areas. More importantly, the unique shell of each particle could experience a wide range of transformations of compositions, phases and structures while maintaining their perfect coating and individual dispersion. Therefore, they provide a great way for finely controlling the metal (oxide) shell and the preparation of a wide variety of high-quality particles. For example, perfect core-shell structured C@Ni and supported CoO/C particles were produced by calcination of intermediates under an inert atmosphere. FESEM images show these particles preserved a good individual dispersion in a large area without any aggregation, and each particle has an extra uniform coating as confirmed by TEM images (Fig. 2). The formation of the perfect shell consisting of highly dispersed nanocrystal was derived from the uniform layer of the metal salt, which is difficult to obtain through other deposition methods. The highly dispersed nanocrystals as the building blocks of the shell have a narrow size distribution with a particle size of less than 5 nm (Fig. 2c, f, inset), which should endow the resultant particles with a series of unique properties. Although such carbon colloids have been widely used as sacrificial templates to prepare hollow particles,^{13,24} this is the first time metal (oxide) shell coating on carbon cores has been controlled without burning the cores.

To investigate the versatility of the present coating strategy, core particles with different diameters, surface curvature and

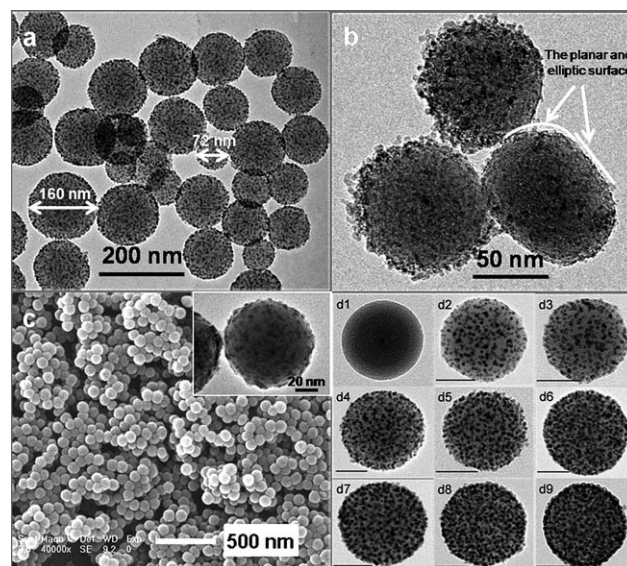


Fig. 3 TEM and FESEM images of core-shell structured particles fabricated with different core particles or concentration of precursors. (a) C@Ni (0.02 M). (b) SiO₂@NiO (0.02 M). (c) SiO₂@Fe₂O₃ (0.015 M). (d1–d9) Ni/C and C@Ni particles with different loading of nickel nanocrystals fabricated through varying the concentration of precursors from (d1) 0 M (pure carbon colloid), (d2) 0.01 M, (d3) 0.015 M, (d4) 0.02 M, (d5) 0.025 M, (d6) 0.03 M, (d7) 0.035 M, (d8) 0.04 M to (d9) 0.05 M. The scale bar is 50 nm.

surface properties were examined. Promisingly, a uniform nanocrystal shell was perfectly coated on the surface of carbon colloids, even when the diameter of cores varied from 72 to 160 nm in one system (Fig. 3a). Furthermore, perfect and well-dispersed $\text{SiO}_2@\text{NiO}$ and $\text{SiO}_2@\text{Fe}_2\text{O}_3$ core-shell particles were also successfully fabricated when common silica gel was used as a core particle (Fig. 3b, c). Fig. 3b shows that the nanocrystals could deposit not only on the spherical surface, but also on the planar and elliptic surfaces. Fig. 3c confirms that other components such as ferric oxide nanocrystals could be regularly assembled on each SiO_2 nanoparticles with a good dispersion of the resultant $\text{SiO}_2@\text{Fe}_2\text{O}_3$ nanoparticles. As an effective method, the shell could also be controlled precisely just by varying the concentration of precursor, for instance from the dispersed nickel nanocrystals to the nickel nanocrystal layer (Fig. 3d1–d9). Obviously, a uniform layer that is composed of metal (oxide) nanocrystals coated on the core particles could be precisely controlled based on our strategy, thereby enabling the fabrication of the multifunctional core-shell particles more commonly and easily.

Core-shell particles with a shell consisting of metal (oxide) nanoalloys

Although a wide variety of core-shell particles have been fabricated during the past few decades, the investigation of assembling more than one kind of metal (oxide) into a single shell is very limited and also is difficult because the deposition of solid

shells from different precursors often requires different synthetic conditions that are hard to control simultaneously in one system, let alone finely controlling the shell coating. However, the intriguing properties of the resultant materials strongly encourages researchers to pursue a perfect and convenient method to assemble multi-components into a single shell.²⁵ Promisingly, our present coating strategy could meet these requirements very well. Based on the same procedures, many kinds of new core-shell particles with a uniform layer of multi-component shell were successfully fabricated. For example, core-shell structured $\text{C}@\text{Ni}\&\text{Co}$ particles with tunable mole ratio of nickel to cobalt, as well as the $\text{C}@\text{Ni}\&\text{Pd}$ particles, were prepared in large quantities with preserving a good individual dispersion (Fig. 4). TEM micrographs (Fig. 4b, d) and XRD patterns (Fig. 4e) show that a uniform layer of metal nanoalloys were formed on the core particles. The uniform composition of nanoalloys resulted from the simultaneous coordination of the different metallic ions with anions. For instance, Ni^{2+} and Co^{2+} could coordinate with one anion (*e.g.*, NO_3^-) simultaneously to form a structure of $(-\text{Ni}-\text{ONOO}-\text{Co}-)$, which gives rise to an extra uniform mixture of chemical compounds after releasing of the NO_x and O_2 . The molar ratio of compositions was well in accordance with the primary values of precursors, as confirmed by the ICP-AES results (2.03 : 1 for Ni : Co, 19.75 : 1 for Ni : Pd) and EDXA spectra (1.97 : 1 for Ni : Co, 19 : 1 for Ni : Pd) (Fig. S3, ESI[†]), strongly indicating that the compositions of the shell could be precisely controlled through varying the concentration and kind of precursors. Undoubtedly, the present strategy was a flexible and easy-controlled method for finely coating the multi-component shell on the particles while preserving a good individual dispersion of all the resultant particles. It is noteworthy that this is the first time that highly dispersed nanoalloys on colloidal particles in the form of a shell have been assembled, and the obtained materials are expected to have applications in the areas of catalysis, magnetics and electrics, *etc.*, due to the unique properties of the nanoalloys.²⁶

The unique features of the present strategy

Materials science strongly demands an efficient, versatile and green method for coating metals (oxides) on colloidal particles uniformly and precisely.¹² Our present strategy was proved to meet these requirements very well, with the common difficulties existing in traditional deposition method completely overcome, and a wide variety of perfect and novel core-shell structured particles with tunable composition, thickness, uniformity and nanostructures were fabricated successfully. Preliminary results reveal that the coating process has several advantages: (i) suitable for most precursors and core particles, even with different diameters, surface properties and variable surface curvature; (ii) the thickness and composition of the shell could be precisely controlled by varying the concentration and kind of precursor (including multi-component system), because all the precursors could be deposited onto the core particles completely without any independent metal-salt formed or residual metallic ions remaining in solution; (iii) it is a green process without using any harmful precipitants and the solvent could be recycled after simple phase (gas-liquid-solid) separation avoiding waste solution treatment.

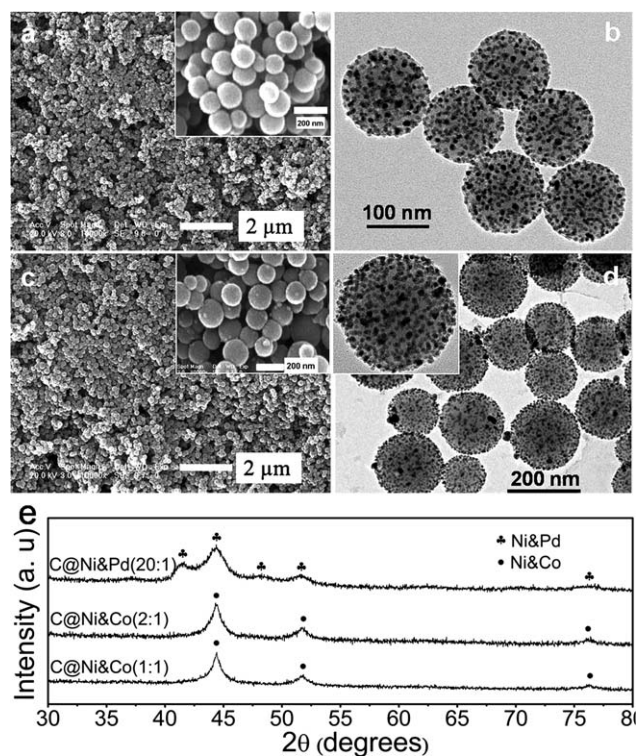


Fig. 4 FESEM and TEM images of particles with a shell consisting of nanoalloys. (a, b) $\text{C}@\text{Ni}\&\text{Co}$ particles (0.01 M Ni^{2+} :0.005 M Co^{2+}). (c, d) $\text{C}@\text{Ni}\&\text{Pd}$ particles (0.02 M Ni^{2+} :0.001 M Pd^{2+}). (e) XRD patterns of corresponding particles.

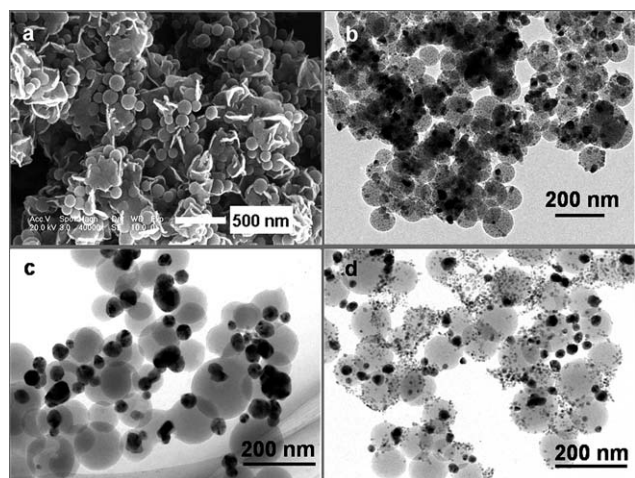
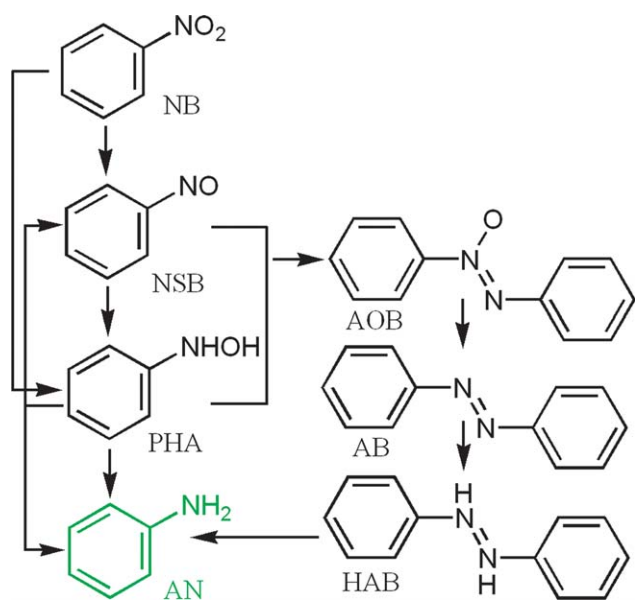


Fig. 5 (a) FESEM images of C/Ni-salt (0.02 M Ni²⁺). (b–d) TEM images of composite particles. (b) C/CoO (0.01 M Co²⁺). (c) C/Ni&Pd (0.02 M Ni²⁺; 0.001 M Pd²⁺). (d) C/Ni&Pd (0.005 M Ni²⁺; 0.00025 M Pd²⁺), 40 ml ethanol were used instead of CO₂ expansion.

All the advantages are based on employing the inexpensive and environmentally friendly solvent of CO₂. The use of CO₂ not only optimizes the physicochemical properties of the solution,²⁷ but also offers some chemical groups, such as CO₃²⁻ and HCO₃⁻, to facilitate the deposition completely and more uniformly through the coordination of metallic cations with these anions. If the preparation was performed in pure ethanol without the expansion with CO₂, large amounts of independent metal salts were formed, and resulted in a poor dispersity and an agglomeration of the final particles (Fig. 5a–c). Moreover, simply increasing the volume of solution through increasing the amount of ethanol instead of CO₂ expansion also gave rise to a poor coating (Fig. 5d). Therefore, the presence of CO₂ is not providing a simple physical expansion only, but also building an efficient system with improved performance for materials synthesis and chemical reactions.



Scheme 2 The possible reaction pathways of the hydrogenation of NB.

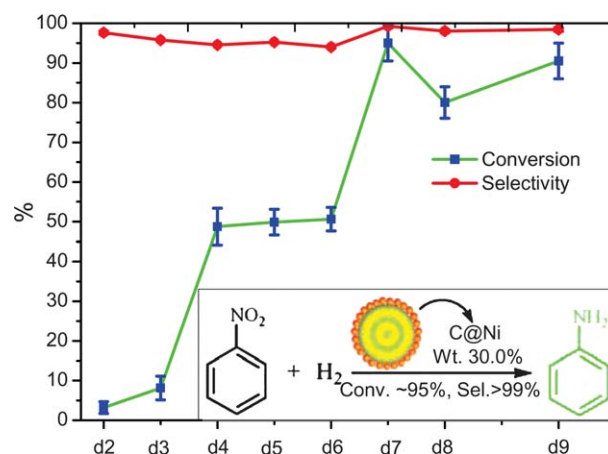


Fig. 6 The catalytic performances of Ni/C and C@Ni nanoparticles in the hydrogenation of NB. Labels d1–d9 represent the particles in Fig. 3, with different loading of Ni nanocrystals.

The catalytic properties of the resultant particles

Compared with the traditional deposition method, our proposed strategy was more accurate and effective for designing and fabricating nanostructured materials with tailored properties. For example, the catalytic activities of Ni/C and C@Ni particles were finely tuned and checked in the hydrogenation of nitrobenzene (NB). It is well known that hydrogenation of NB is a significant reaction because the product of aniline is an important intermediate for preparation of polyurethanes, dyes, pharmaceuticals, explosives, and agricultural products.²⁸ However, nitrosobenzene (NSB), *N*-phenylhydroxylamine (PHA), azoxybenzene (AOB), azobenzene (AB), and hydrazobenzene (HAB), which are poisonous, are always formed along with the desired AN product (Scheme 2).²⁹ Therefore, successfully avoiding the formation and accumulation of these undesired intermediates together with a higher activity on non-noble catalyst are being strongly pursued for the green production of AN. Surprisingly, the reproducible results (Fig. 6) show that a suitable loading of nickel nanocrystals (wt. 30%) on carbon colloids gives a high conversion of 95%, which was almost one times higher than that of Ni/Al₂O₃ under the same conditions.^{23a} And a high selectivity of >99.9% was achieved without any intermediates accumulated in the hydrogenation.

4. Conclusions

In summary, we report an efficient, versatile, and green strategy for finely controlling of the metal (oxide) coating on colloidal particles, successfully avoiding the formation of free metal (oxide) and/or naked cores and also preserving a good individual dispersion of all the resultant particles. With the present *in situ* deposition of precursors in CO₂-expanded fluid, not only the common difficulties of traditional deposition methods were overcome, but also the composition, thickness, uniformity, and structure of the metal (oxide) shell could be precisely controlled. It is a promising way for preparing high-quality nanostructured materials with tailored properties. The present strategy could be widely used in materials science, such as in shell coating and doping, because it is not only suitable for metal salts if only the

metallic ions have the ability of coordination, but also for multicomponent systems. The more precisely and easily it is to fabricate nanostructured materials, the more extensive applications could be explored.

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References

- (a) X. G. Peng, M. C. Schlamp, A. V. Kadavanich and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1997, **119**, 7019; (b) F. Caruso, *Adv. Mater.*, 2001, **13**, 11; (c) X. W. Lou, J. S. Chen, P. Chen and L. A. Archer, *Chem. Mater.*, 2009, **21**, 2868; (d) S. H. Joo, J. Y. Park, C. K. Tsung, Y. Yamada, P. D. Yang and G. A. Somorjai, *Nat. Mater.*, 2008, **8**, 126; (e) J. Ye, C. J. Wang, P. Su, H. Wu, Y. D. Zhou, K. Yao, J. Yang and Z. R. Gou, *J. Mater. Chem.*, 2010, **20**, 9025.
- (a) F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111; (b) S. R. Guo, J. Y. Gong, P. Jiang, M. Wu, Y. Lu and S. H. Yu, *Adv. Funct. Mater.*, 2008, **18**, 872; (c) Y. H. Deng, C. H. Deng, D. W. Qi, C. Liu, J. Liu, X. M. Zhang and D. Y. Zhao, *Adv. Mater.*, 2009, **21**, 1377; (d) H. Zhang, D. K. Pan, K. Zou, J. He and X. Duan, *J. Mater. Chem.*, 2009, **19**, 3069; (e) H. W. Liang, S. Liu and S. H. Yu, *Adv. Mater.*, 2010, **22**, 3925.
- M. V. Barmatova, I. D. Ivanchikova, O. A. Kholdeeva, A. N. Shmakov, V. I. Zaikovskii and M. S. Mel'gunov, *J. Mater. Chem.*, 2009, **19**, 7332.
- L. M. LizMarzan, M. Giersig and P. Mulvaney, *Langmuir*, 1996, **12**, 4329.
- Z. X. Chen, Y. L. Cao, J. F. Qian, X. P. Ai and H. X. Yang, *J. Mater. Chem.*, 2010, **20**, 7266.
- Y. Deng, D. Qi, C. Deng, X. Zhang and D. Zhao, *J. Am. Chem. Soc.*, 2008, **130**, 28.
- J. Kim, H. S. Kim, N. Lee, T. Kim, H. Kim, T. Yu, I. C. Song, W. K. Moon and T. Hyeon, *Angew. Chem., Int. Ed.*, 2008, **47**, 8438.
- M. M. Ye, Q. Zhang, Y. X. Hu, J. P. Ge, Z. D. Lu, L. He, Z. L. Chen and Y. D. Yin, *Chem.–Eur. J.*, 2010, **16**, 6243.
- Y. D. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai and A. P. Alivisatos, *Science*, 2004, **304**, 711.
- P. M. Arnal, M. Comotti and F. Schuth, *Angew. Chem., Int. Ed.*, 2006, **45**, 8224.
- J. M. Yan, X. B. Zhang, T. Akita, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5326.
- X. W. Lou, L. A. Archer and Z. C. Yang, *Adv. Mater.*, 2008, **20**, 3987.
- (a) X. M. Sun, J. F. Liu and Y. D. Li, *Chem.–Eur. J.*, 2006, **12**, 2039–2047; (b) H. S. Qian, G. F. Lin, Y. X. Zhang, P. Gunawan and R. Xu, *Nanotechnology*, 2007, **18**, 355602.
- (a) F. Caruso, M. Spasova, A. Sussha, M. Giersig and R. A. Caruso, *Chem. Mater.*, 2001, **13**, 109; (b) J. Liu, Y. H. Deng, C. Liu, Z. K. Sun and D. Y. Zhao, *J. Colloid Interface Sci.*, 2009, **333**, 329.
- Y. D. Xia and R. Mokaya, *J. Mater. Chem.*, 2005, **15**, 3126–3131.
- (a) X. W. Lou, C. L. Yuan and L. A. Archer, *Small*, 2007, **3**, 261; (b) X. W. Lou and L. A. Archer, *Adv. Mater.*, 2008, **20**, 1853.
- (a) P. M. Arnal, C. Weidenthaler and F. Schuth, *Chem. Mater.*, 2006, **18**, 2733; (b) Y. Li, J. S. Wu, D. W. Qi, X. Q. Xu, C. H. Deng, P. Y. Yang and X. M. Zhang, *Chem. Commun.*, 2008, 564.
- S. H. Lim, N. Phonthammachai, S. S. Pramana and T. J. White, *Langmuir*, 2008, **24**, 6226.
- C. H. Kuo, T. E. Hua and M. H. Huang, *J. Am. Chem. Soc.*, 2009, **131**, 17871.
- (a) F. Caruso, X. Y. Shi, R. A. Caruso and A. Sussha, *Adv. Mater.*, 2001, **13**, 740; (b) C. L. Fang, K. Qian, J. H. Zhu, S. B. Wang, X. X. Lv and S. H. Yu, *Nanotechnology*, 2008, **19**, 125601.
- X. M. Sun and Y. D. Li, *Angew. Chem., Int. Ed.*, 2004, **43**, 597.
- W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
- (a) X. C. Meng, H. Y. Cheng, Y. Akiyama, Y. F. Hao, W. B. Qiao, Y. C. Yu, F. Y. Zhao, S. Fujita and M. Arai, *J. Catal.*, 2009, **264**, 1–10; (b) X. C. Meng, H. Y. Cheng, S. Fujita, Y. F. Hao, Y. J. Shang, Y. C. Yu, S. X. Cai, F. Y. Zhao and M. Arai, *J. Catal.*, 2010, **269**, 131–139.
- A. G. Dong, N. Ren, Y. Tang, Y. J. Wang, Y. H. Zhang, W. M. Hua and Z. Gao, *J. Am. Chem. Soc.*, 2003, **125**, 4976.
- (a) Y. L. Min, Y. Wan and S. H. Yu, *Solid State Sci.*, 2009, **11**, 96; (b) D. Jian, P. X. Gao, W. J. Cai, B. S. Allimi, S. P. Alpay, Y. Ding, Z. L. Wang and C. Brooks, *J. Mater. Chem.*, 2009, **19**, 970; (c) J. Zhang, X. H. Liu, S. H. Wu, M. J. Xu, X. Z. Guo and S. R. Wang, *J. Mater. Chem.*, 2010, **20**, 6453.
- R. Ferrando, J. Jellinek and R. L. Johnston, *Chem. Rev.*, 2008, **108**, 845.
- (a) M. C. McLeod, M. Anand, C. L. Kitchens and C. B. Roberts, *Nano Lett.*, 2005, **5**, 461; (b) Z. Y. Sun, H. Y. Zhang, G. M. An, G. Y. Yang and Z. M. Liu, *J. Mater. Chem.*, 2010, **20**, 1947; (c) Z. Y. Sun, X. R. Zhang, B. X. Han, Y. Y. Wu, G. M. An, Z. M. Liu, S. D. Miao and Z. J. Miao, *Carbon*, 2007, **45**, 2589.
- A. S. Travis, in Z. Rappoport (Ed.), *The Chemistry of Anilines*, John Wiley and Sons, 2007, p. 715.
- (a) F. Cardenas-Lizana, S. Gomez-Quero and M. A. Keane, *Appl. Catal., A*, 2008, **334**, 199; (b) P. Baumeister, H. U. Blaser and M. Studer, *Catal. Lett.*, 1997, **49**, 219.