Hierarchical Structures Based on Functionalized Magnetic Cores and Layered Double-Hydroxide Shells: Concept, Controlled Synthesis, and Applications

Mingfei Shao, Min Wei,* David G. Evans, and Xue Duan^[a]



4100 -



© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Abstract: The combination of magnetic particles and layered double hydroxide (LDHs) materials leads to the formation of hierarchical composites that can take full advantages of each component; this is an effective approach for achieving multifunctional materials with intriguing properties. This Concept article summarizes several important strategies for the fabrication of magnetic-core/LDH-shell hierarchical nanocomposites, including direct coprecipitation, layer-by-layer assembly, and in situ growth methods. The obtained nanocomposites exhibit excellent performance as multifunctional materials for promising applications in targeted drug delivery, efficient separation, and catalysis. The fabrication and application of magnetic-core/LDH-shell nanocomposite materials represent a new direction in the development of LDH-based multifunctional materials, which will contribute to the progress of chemistry and material science.

Keywords: Core-shell structures • layered double hydroxides • magnetic particles • magnetic properties • nanocomposites

Introduction

Recent advances in synthetic nanoscience and nanotechnology have enabled progress in the development of novel nanocomposites for integrating discrete components, interaction of the components, or formation of independent functionalities. Microspheres with magnetic core and functional shell architecture have attracted tremendous attention due to their unique morphology and properties associated with promising applications, such as targeted drug delivery,^[1] magnetic resonance imaging (MRI),^[2] separation, and sensors.^[3] The construction of the magnetic-core/shell structure is an interdisciplinary approach combining inorganic and organic synthesis. Several groups have employed a range of methods to modify or coat the surface of magnetic nanoparticles by insertion, attachment, or grafting, for the purpose of imparting a second functionality.^[4] The resulting nanoscale coatings can endow magnetic nanoparticles with interesting semiconducting, plasmonic, adsorptive, or magnetooptical properties. Despite all this progress, the shells are generally composed of small organic molecules or aggregated zero dimensional (0D) nanoparticles (such as metal particles^[5] or quantum dots^[6]), which to some extent limits their

 M. Shao, Prof. M. Wei, Prof. D. G. Evans, Prof. X. Duan State Key Laboratory of Chemical Resource Engineering Beijing University of Chemical Technology Beijing 100029 (P.R. China) Fax: (+86)10-6442-5385 E-mail: weimin@mail.buct.edu.cn applications as advanced multifunctional materials. Very little success has been achieved in constructing nanostructured shells with anisotropic building blocks, such as one-dimensional (1D) nanowires, nanotubes, and two-dimensional (2D) nanosheets. Therefore, a huge challenge still remains to achieve the effective design and synthesis of magneticcore/shell hierarchical materials with sophisticated structure and functionalities.

The combination of magnetic nanoparticles and two-dimensional layered shells offers a new area for developing nanohybrid materials with desired functionality. Layered double hydroxides (LDHs) are layered anionic clays generally expressed by the formula $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}]^{z+}[A]_{z/z}$ n^{n-1} yH₂O (M^{II} and M^{III} are divalent and trivalent metals, respectively; A^{n-} is the interlayer anion compensating for the positive charge of the brucite-like layers).^[7] Owing to the specific structure, tunable composition, and nanoscale size, LDH powdered materials have been widely used in the fields of catalysis,^[8] biology,^[9] magnetic,^[10] and optical materials.^[11] Recently, LDH microcrystals have been exfoliated into positively charged 2D monolayer sheets, which can be assembled alternately with various functional anions into ultrathin films by the layer-by-layer (LBL) technique.^[11,12] In addition, LDHs have been used as building blocks for the fabrication of well-defined 3D hierarchical nanocomposites (e.g., 3D macroporous LDHs,^[13] and core-shell and hollow spheres^[14]), which will definitely evoke considerable interest owing to their largely enhanced properties and potential applications. Hence, it is of interest to study the case of hierarchical nanocomposites with magnetic core and LDH shell structure, which are promising candidates for the integration of magnetism and LDH specific functionalities. Although some strategies have been developed to construct magneticcore/LDH-shell hierarchical structures with potential applications, the facile and cost-effective fabrication of these materials remains a major challenge.

In this Concept article, we will comprehensively summarize recent progress in the design and preparation of magnetic-core/LDH-shell hierarchical structures from direct coprecipitation, layer-by-layer assembly and in situ growth on the surface of magnetic particles. The typical properties and potential applications in the areas of targeted drug delivery, separation, and catalysis will also be introduced in the context. Current challenges and future strategies are discussed from the viewpoint of material design and practical application. It is anticipated that this Concept article will arouse more attention towards LDH-based 3D nanomaterials and encourage future work to push forward the advancement of this emerging area.

www.chemeurj.org

Synthesis of Magnetic-Core/LDH-Shell Hierarchical Nanocomposites

The preparation of magnetic-core/LDH-shell hierarchical composites is the first challenge to explore their fascinating properties and broad applications. Due to the same positively charged surface of magnetic nanoparticles and LDH materials, a direct adsorption route is not feasible. Therefore, surface modification of magnetic nanoparticles is a key step to render them accessible for LDHs shell. A number of studies have been devoted to manipulate the interactions between LDHs and magnetic nanoparticles by modifying magnetic nanoparticles with negatively charged species (e.g., oxhydryl- and carboxyl-group-based organic molecules, silica, or carbon). The negatively charged surface of magnetic nanoparticles exhibits strong adsorption ability for metal cations in solution, making them suitable supports for in situ growth of various kinds of LDHs. Moreover, since LDHs can be exfoliated into positively charged nanosheets for alternate deposition with functional anions by means of the layer-by-layer (LBL) technique, the assembly of LDHs

nanosheets and functional species on the surface of magnetic cores can lead to the formation of a series of LDH-based multifunctional core-shell nanocomposites. In this section, we aim to briefly summarize the different routes for the fabrication of magnetic-core/LDH-shell hierarchical materials by direct coprecipitation, the layer-by-layer technique, and an in situ growth method.

Coprecipitation: Coprecipitation is a traditional and commonly used method for the preparation of LDHs. When a substrate adsorbs a certain amount of cations in a mixed solution of two metal salts, precipitation will occur on the surface of the substrate, leading to the interface nucleation and crystal growth of LDHs. Furthermore, the particle–particle interaction of LDH nanoparticles also facilitates the adsorption of LDH nanocrystallites formed in solution onto the surface of introduced substrates. Zhang et al.^[15] fabricated magnetic-particle (MNP)-core/LDH-shell composites by mixing magnesium ferrite particles with an alkaline solution containing Mg^{2+} , Al^{3+} , and drug molecules (Figure 1 A). The drug diclofenac (DIC)–LDH is coated on the surface of



Figure 1. A) A schematic representation of the fabrication of magnetic drug-LDH nanohybrid (DIC=diclofenac). B) TEM image of the obtained magnetic drug-LDH nanohybrid.^[15a] C) The synthetic route of the Fe₃O₄@DFUR-LDH core-shell particles (DFUR=doxifluridine). D) SEM and E) TEM image of Fe₃O₄@DFUR-LDH.^[16] F) The synthetic strategy of the Fe₃O₄@MgAl-LDH@Au nanocomposite. G) SEM and H) TEM image of the Fe₃O₄@MgAl-LDH@Au.^[17] Copyright 2009 and 2011, Royal Society of Chemistry.

4102

magnesium ferrite core to produce a magnetic nanohybrid with particle size ranging from 90 to 150 nm (Figure 1B).^[15a] However, the DIC–LDH crystallites in the shell present a much smaller particle size compared with pristine DIC– LDH due to the prohibition effect of the magnetic core on the growth of LDH crystallites. In addition, some degree of phase separation between the LDH shell and the magnetic nanoparticles was observed by using the coprecipitation method,^[15b] resulting from an excess of LDH precursors. Therefore, both a suitable concentration of LDH precursors and sufficiently negative charge of magnetic core are necessary to ensure the effective combination of LDH shell and magnetic nanoparticles.

Magnetic particles functionalized with negatively charged groups can also be used as substrates for the growth of LDHs. For instance, the carbon-coated Fe₃O₄ microspheres with a large number of hydroxyl groups were effectively employed as a support to grow LDH nanoparticles (Figure 1 C).^[16] Typically, the carbon-coated Fe₃O₄@C microspheres were dispersed in a solution of NaOH in methanol and then ultrasonically agitated to form a uniform suspension; another solution of $Mg(NO_3)_2 \cdot 6H_2O$ and Al(NO₃)₃·9H₂O in methanol was added dropwise into the above suspension under vigorous stirring until the final pH reached to about 9.5. Hydrothermal treatment was subsequently carried out to obtain the resulting core-shell Fe₃O₄@C@LDH (Figure 1D and E). The particle size of LDH can be controlled by the temperature or the hydrothermal reaction duration. Apart from the chemical modification method, the negative charge of magnetic particles can also be obtained by tuning the pH value as well (Figure 1 F).^[17] First, the fully negatively charged Fe₃O₄ suspension was obtained by adjusting pH to about 10. Second, the hierarchical core-shell magnetic Fe₃O₄@MgAl-LDH was fabricated by interface nucleation and crystal growth of LDH with dropwise addition of salts and alkaline solutions. It is worth mentioning that the obtained Fe₃O₄@MgAl-LDH hierarchical microspheres are easy to further modify so as to give additional functionalities. In this work, Au nanoparticles were subsequently supported on the Fe₃O₄@MgAl-LDH microspheres by a deposition-precipitation method. In addition, the hollowed-magnetic-core/shell hierarchical submicrospheres Fe₃O₄@CuNiAl-LDH have been synthesized by the coprecipitation method.^[18] The core-shell composite presents honeycomb-like morphology with LDH nanoplatelets staggered perpendicularly on the hollow Fe₃O₄ surface.

The coprecipitation method gives rise to a facile and effective method for the combination of LDH materials with magnetic particles. However, magnetic-core/LDH-shell composites with a monodisperse, narrow particle size distribution as well as tunable morphology have not been successfully achieved by using this method, which restricts their further applications to some extent. Advanced methods with precise control of structure, size, and morphology are therefore needed.

CONCEPT

Layer-by-layer (LBL) assembly: Using exfoliated LDHs nanosheets as building blocks, the self-assembly of LDH nanosheets and functional species has been achieved. Sasaki et al.^[19] obtained LDH-based core–shell material with a polymer core and an LDH-nanosheet shell by the LBL self-assembly method. Li et al.^[20] demonstrated the coating of delaminated LDH nanosheets onto a magnetic core, such as Fe₃O₄. The synthesis scheme is shown in Figure 2A. Mag-



Figure 2. A) Synthesis of the magnetic-core/LDH-shell composite structure. SEM images of B) Fe₃O₄ core, C) Fe₃O₄ core coated with SiO₂ layer, D) Fe₃O₄@SiO₂ core/LDH-shell composite. E) TEM image of Fe₃O₄@SiO₂ core/LDH-shell composite.^[20]

netic Fe₃O₄ crystalline particles (ca. 400 nm) were coated with a layer of silica by a sol–gel process (Figure 2B and 2C). The Fe₃O₄@SiO₂ particles were dispersed alternately in a formamide suspension containing LDH nanosheets and Na₂CO₃ aqueous solution; a series of these operations for LDH nanosheets and carbonate were repeated *n* times to obtain multilayer nanoshells of $(CO_3^{2-}/LDH)_n$ coated on the

www.chemeurj.org

surface of $Fe_3O_4@SiO_2$ core. The resulting nanocomposite was finally heated at 480°C for 4 h, followed by dispersion in an aqueous solution to recover its original LDH structure. The SEM image (Figure 2D) shows that the Fe_3O_4 -core silica-shell beads maintain well-defined monodispersive spherical morphology after deposition of 20 layers of LDH shell. The thickness of LDH shell is estimated to be about 15 nm from Figure 2E.

The magnetic-core/LDH-shell nanocomposites obtained by the LBL self-assembly can inherit the intrinsic properties of both the magnetic particles and the LDHs. Furthermore, the obtained shell achieves nanometer scale and well-controlled chemical composition, which has potential applications in constructing advanced multifunctional materials. In most cases, however, only electrostatic force was adopted for the reassembly process and the nanocomposite structure is thus limited, which restricts further applications of the magnetic-particle LDH nanocomposites. Therefore, with the assistance of other type of driving forces, such as hydrophobic interaction and hydrogen bonding, the self-assembly method can be extended to a broad scope for obtaining advanced multifunctional magnetic-particle LDH nanocomposites.

In situ growth: Much effort has been focused on hierarchical LDHs materials with micro- and nano-functionalities with promising applications. Recently, our group reported a solgel process followed by in situ growth for the purpose of fabricating hierarchical LDH core–shell architectures.^[21] Firstly, to create negatively charged Fe_3O_4 microspheres

(Figure 3 A and 3E), a thin layer of silica was introduced by means of a sol-gel approach (Figure 3B and 3F). Secondly, a continuous and uniform AlOOH coating was deposited on the surface of Fe₃O₄@SiO₂ microspheres by the LBL method (Figure 3C and 3G). Finally, Fe₃O₄@SiO₂@AlOOH transformed into Fe₃O₄@SiO₂@LDH by an in situ growth technique in a solution containing the appropriate cations (Figure 3D and 3H). A series of hierarchical core-shell $Fe_3O_4@SiO_2@M^{II}Al-LDH$ (M = Ni, Co, Zn, Mg) microspheres have been prepared with fine control over the shell thickness and composition. EDX mapping analysis demonstrates that the iron is located in the center of the particle, while nickel is homogeneously distributed throughout the whole microsphere (Figure 3K and 3L). It is worth mentioning that the $Fe_3O_4@SiO_2@LDH$ core-shell microspheres cannot be obtained in the absence of the AlOOH layer, which confirms that the AlOOH coating plays a key role in providing the necessary aluminum source for the heterogeneous nucleation and growth of LDH nanocrystals. Moreover, the introduction of the SiO₂ layer facilitates the firm immobilization of AlOOH coating owing to the hydrogen-bonding interaction between them. LDH microspheres with tunable interior architecture were also synthesized by in situ growth approach.^[14] The obtained microspheres exhibit a three-dimensional architecture with core-

spheres exhibit a three-dimensional architecture with coreshell, yolk-shell, and hollow interior structures. It is expected that the synthesis approach for functional-core/LDHshell microspheres can be extended to other oxide or hydroxide materials with largely enhanced physiochemical property.

Applications

Targeted drug delivery: Drug–LDH hybrids have been synthesized and endowed with great potential as the basis of a controlled drug-delivery system, taking advantage of their biocompatibility, anion-exchange ability, and low cytotoxicity. Various pharmaceutically active compounds, such as ibuprofen, diclofenac, gemfibrozil, naproxen, tolfenamic acid, fenbufen, and so forth, have been readily intercalated into the LDH gallery through anion exchange or the coprecipitation route to produce the drug–LDH nanohybrids.^[22] The interlayer region of LDHs acts as a "container" for drug mol-



Figure 3. TEM and SEM images of A), E) Fe_3O_4 particles, B), F) $Fe_3O_4@SiO_2$, C), G) $Fe_3O_4@SiO_2@AlOOH$, D), H) $Fe_3O_4@SiO_2@NiAl-LDH$ microspheres. I) HR-TEM image of the NiAl-LDH shell and J)-L) EDX mapping results of a single $Fe_3O_4@SiO_2@NiAl-LDH$ microsphere, demonstrating the Fe_3O_4 -core/NiAl-LDH shell structure.^[21] Copyright 2012, American Chemical Society.

CONCEPT

ecules, and hence enhances its chemical and stereochemical stability. Moreover, the drug release is controlled by the strength of the host–guest interaction, LDH rigidity, and diffusion path length, which is of paramount importance to maintain pharmacologically active levels for long period. However, conventional drug–LDHs hybrids, particularly those involving poorly water-soluble anti-inflammatory drugs and anticancer agents in drug delivery systems, have been profoundly restricted due to lack of specific affinity toward the pathological sites.

Aiming to achieve drug targeting and enhance effective applications of the drug-LDHs in biomedicine, functional materials (e.g., magnetic nanoparticles) can be introduced to form a magnetic-targeted drug matrix. The obtained materials have the merits of both enhanced drug-loading capacity and significant magnetization strength. Recently, various novel magnetic-core/LDH-shell nanocomposites have been designed for simultaneous drug delivery.^[23,15,16] Intercalation of drug molecules into the LDH shell was successfully achieved by direct synthesis, ion exchange, and coprecipitation-calcination-reconstruction methods. For example, the Fe₃O₄@DFUR-LDH (DFUR: doxifluridine) nanocomposite shows both high magnetization strength $(17.4 \text{ emu g}^{-1})$ and drug-loading capacity (9.73 wt% for DFUR loading).^[16] The unique Fe₃O₄ core and DFUR-LDH shell structure of the Fe₃O₄@DFUR-LDH submicro particles not only allows targeting at a desired site with the aid of an external magnetic field (Figure 4A), but also exhibits an adjustable release behavior. The synthesis of the magnetic spinel core by calcin-



Figure 4. A) A schematic description of magnetic arthritis therapy with drug intercalated LDHs supported on a magnesium ferrite core.^[23a] Copyright 2009, American Chemical Society. B) A schematic drawing of DIC release from the core-shell nanocomposite with and without an external magnetic field.^[15a] Copyright 2009, Royal Society of Chemistry.

ing an iron-containing LDH precursor has been another attraction that affords stoichiometric magnesium ferrite.^[10a] MgFe₂O₄ is a soft magnetic material, and drug-loading in MgFe₂O₄-core/LDH-shell composites is an effective alternative to the conventional magnetic drug carriers. Recently, various magnesium ferrite-core/drug–LDH systems have been reported, such as MgFe₂O₄/5-aminosalicylic acid– LDH,^[23b] MgFe₂O₄/diclofenac (DIC)–LDH,^[15a] MgFe₂O₄/ ibuprofen (IBU)–LDH,^[15b] MgFe₂O₄/glucuronic acid (GLU)–LDH.^[23a] The potential use of these systems in magnetic-field-controlled drug delivery to the targeted organ is of great promise.

Zhang et al. investigated the in vitro release of drug in the MgFe₂O₄/DIC-LDH system with and without a magnetic field and proposed a microstructure-dependent release mechanism.^[15a] The results demonstrate that the release of DIC from the magnetic nanohybrid is controlled by particle microstructure, including the particle size and the aggregation extent of the nanocomposite (Figure 4B). In the absence of a magnetic field, the release of DIC molecules from the magnetic nanohybrids is mainly controlled by intraparticle diffusion between LDH layers (path I in Figure 4B) and interparticle diffusion among the DIC-LDH nanoparticles coated on the surface of magnetic cores (path II in Figure 4B). In the presence of a magnetic field, significant aggregation of the magnetic nanoparticles occurs, owing to the non-contact magnetic force. Consequently, besides the above two diffusion paths, the interparticle diffusion among the aggregated magnetic nanoparticles significantly affects the drug release property, due to the even longer diffusion path length and higher diffusion resistance, particularly for the DIC molecules entrapped deep in the interior of the aggregates (path III in Figure 4B). Taking into account the synergic effect, magnetic-particle/LDH nanocomposites are expected to be a promising targeted drug-delivery vector with high performance.

Adsorption and separation: Magnetic nanoparticles have several advantages for immobilization and separation of biomolecules, including easy and fast separation as well as a certain adsorption capacity. With the ongoing need for purified proteins in applications ranging from diagnostics to therapeutics, the development of efficient methods for the separation and purification of recombinant proteins is increasingly essential in proteomics. Our group reported a magnetic separation system for proteins, based on LDHcoated Fe₃O₄ core-shell composites (Fe₃O₄@SiO₂@NiAl-LDH).^[21] The Ni²⁺ in the NiAl-LDH shell provides docking sites for histidine (His) through coordination interactions and the composites exhibit excellent performance in the separation of a His-tagged protein, including high capacity and good recyclability. The protein separation efficiency of Fe₃O₄@SiO₂@NiAl-LDH microspheres was investigated by using His-tagged GFP (Figure 5A). The fluorescence emission intensity of the His-tagged GFP solution (curve a, Figure 5B) decreases to essentially zero after 20 min (curve b, Figure 5B), confirming that the microspheres efficiently

Chem. Eur. J. 2013, 19, 4100-4108

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

- 4105

A EUROPEAN JOURNAL



Figure 5. A) The photographs of His-tagged GFP separation process by the Fe₃O₄@SiO₂@NiAl-LDH microspheres with different time. B) Fluorescence spectra of the His-tagged GFP solution: a) the original solution, b) after reaction with the Fe₃O₄@SiO₂@NiAl-LDH microspheres for 20 min, c) the released His-tagged GFP solution. C) Fluorescence spectra of the GFP solution without His-tag: a) the original solution, b) after reaction with the Fe₃O₄@SiO₂@NiAl-LDH microspheres for 20 min. D) Magnetic separation and recycling of the Fe₃O₄@SiO₂@NiAl-LDH microspheres for His-tagged GFP. E) SDS-PAGE analyses of the cell lysate containing His-GFP (lane L) and proteins released from the reused Fe₃O₄@SiO₂@NiAl-LDH microspheres up to five times (lanes 1, 2, 3, 4, 5). Lane M is a molecular-weight marker.^[21] Copyright 2012, American Chemical Societv.

bind His-tagged GFP. Incubation of His-tagged GFP microspheres in a concentrated imidazole solution induces dissociation of the protein from the microspheres, resulting in a recovery of 90% of the initial fluorescence emission intensity (curve c, Figure 5B). As a control experiment, when GFP without a His tag reacted with Fe₃O₄@SiO₂@NiAl-LDH microspheres under identical conditions, a decrease of only 24% in the fluorescence emission intensity was observed for the supernatant (Figure 5C), indicating a weak interaction between GFP and microspheres. The recyclability test of the Fe₃O₄@SiO₂@NiAl-LDH microspheres demonstrates that the binding capacity of the microspheres to His-tagged GFP was about 232 μ g mg⁻¹ after five cycles, and the release percentage almost remained unchanged (Figure 5D). Sodium dodecyl sulfate/polyacrylamide gel electrophoresis (SDS-PAGE) analysis shows that the His-tagged GFP was efficiently separated from a cell lysate by the microspheres shown that decorating Fe₃O₄ nanoparticles on the surface of LDH enables a quick adsorption of organic dyes on the nanohybrid material and easy recycling by using external magnetic field.^[25] However, very little work on the adsorption and separation behavior of magnetic-core/LDH-shell composites has been reported, and further studies are still to be carried out.

Catalyst and support: The versatility in both chemical composition and structural morphology of LDH materials makes them attractive candidates as catalysts and supports. However, the catalytic activity of conventional LDHs particles generally suffers from aggregation and poor recyclability. A possible solution can be the development of hierarchical LDH materials with magnetic properties, not only ensuring high dispersion of catalysts, but also easy separation by simply applying an external magnetic field. Magnetic com-

4106 -

M. Wei et al.

(Figure 5E). Fe₃O₄@SiO₂@NiAl-LDH crospheres show good selectivity and recyclability for the separation of His-tagged proteins in the E. coli lysate.

The treatment of wastewater containing numerous inorganic (e.g., heavy metal cations or anions) and organic (e.g., dyes, oils) contaminants has aroused worldwide concern. Owing to the large surface area, positively charged surface, and extraordinary anion-exchange property, LDH materials have been demonstrated as low-cost adsorbents with high adsorption capacity for many pollutants in water (e.g., F⁻, Cr₂O₇²⁻, aromatic carboxylic acids, and phenols).^[24] Furthermore, calcination can lead to the transformation of LDHs to layered double oxides (LDOs), which possess enhanced adsorption capacity for anionic contaminants. However, the separation of LDH powdered materials from solution remains a serious problem, which limits their widespread application in environment protection. Further improvement in their performance can be expected if magnetic properties can be added to the colloidal LDHs; it is envisaged that this will enhance the separation and recycling behavior of the adsorbents. Recently, it was Α

10

8

2

0

EAST

в

0

SCIE INCE AND TH

2

ERSITY OF

4

6

 O_2

Figure 6. A) Mineralization of HCH as a function of irradiation time in

the presence of Fe₃O₄@SiO₂/W₇O₂₄⁶⁻-LDH nanocomposite. B) Photode-

Time (h)

[HCH] (mg L⁻¹)

posites with a core-shell structure allow the integration of multiple functionalities into a single-nanoparticle system, which possesses unique merits in catalysis. The magneticcore/LDH-shell composites as catalysts or supports would offer the following advantages: 1) the magnetic core guarantees easy separation of the catalysts from reaction systems, giving rise to significant economic and environmental benefits; 2) the LDH matrix would provide a confined and stable microenvironment for the active species to enhance their dispersion and stability.

Magnetic-core-functionalized/LDH-shell composites are expected to find important applications in catalysis. Li et al. prepared Fe₃O₄@MgAl–LDH through a LBL assembly method for loading W₇O₂₄^{6–} as the active species.^[20] The activity of the obtained Fe₃O₄@SiO₂-core/W₇O₂₄^{6–}–LDH shell structure catalyst was tested by the photodegradation of trace hexachlorocyclohexane (HCH) in aqueous solution (Figure 6A). A significant transformation of HCH to Cl[–] and CO₂ was observed upon irradiating the suspension containing the Fe₃O₄@SiO₂/W₇O₂₄^{6–}–LDH catalyst by UV light. In the reaction system, the concentration of the product Cl[–] increased along with the reaction time, suggesting that the degradation of aqueous HCH was based on photoexcited

Fe₃O₄/Carbonate-LDH

Fe₃O₄/W₇O₂₄-LDH

8

10

 $HCl + CO_{2}$

12

LET STE VA UNIVERSITY OF

CIFNEFILIND TECHNOLOGY

catalysis rather than direct photolysis. The lifetime test showed that the catalyst can be magnetically separated and reused for six times without any apparent decrease in its catalytic activity (Figure 6B).

Besides loading functional materials, the exploration of hierarchical architecture of magnetic-core/LDH-shell as support for active species is under progress. Zhang et al. reported a Fe₃O₄@MgAl-LDH@Au nanocatalyst, which consists of Au nanoparticles supported on oriented MgAl-LDH microcrystals grown on Fe₃O₄ nanospheres.^[17] This catalyst combines the excellent catalytic behavior of Au nanoparticles with the superparamagnetism of the Fe₃O₄ core. The catalytic oxidation of 1-phenylethanol over the Fe₃O₄@MgAl-LDH@Au nanocatalyst was evaluated. The yield of acetophenone is 99%, with a turnover frequency (TOF) of 66 h⁻¹. The high activity of the $Fe_3O_4@MgAl$ -LDH@Au is related to the honeycomb like morphology of the support Fe₃O₄@MgAl-LDH, which facilitates a high dispersion of Au nanoparticles. Five reaction cycles were carried out with easy magnetic separation, and no deactivation of the catalyst was observed (Figure 7).



Figure 7. Recycling results of the Fe₃O₄@MgAl-LDH@Au nanocatalyst towards the oxidation of 1-phenylethanol.^[17] Copyright 2011, Royal Society of Chemistry.

Conclusions and Perspectives

This Concept article summarizes recent developments in the fabrication of hierarchical magnetic-core/LDH-shell composites and their applications. Several synthesis approaches have been reported for the preparation of magnetic-core/ LDH-shell composites (including Fe₃O₄@SiO₂@M^{II}Al-LDH (M = Ni,Zn, Fe₃O₄@W₇O₂₄⁶⁻-LDH, Co, Mg), Fe₃O₄@MgAl-LDH@Au, Fe₃O₄@C@LDH, Fe₃O₄@drug-LDH, MgFe₂O₄@LDH), with different particle size (from nanometer to micrometer) and controllable core and shell structure. Many exciting research contributions are highlighted to illustrate the important applications of magneticcore/LDH-shell composites, which involve targeted drug delivery, adsorption/separation for biomaterials, and catalysis.

Despite all this progress, the synthesis of magnetic-core/ LDH-shell composites still presents significant conceptual challenges. The first one is the lack of economic highthroughput methods for synthesizing high-quality magnetic-



Chem. Eur. J. 2013, 19, 4100-4108

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

core/LDH-shell composites with controllable size, composition, and architecture. Secondly, to meet the requirements of practical applications, magnetic-core/LDH-shell composites with tunable components both in the core and shell are desirable. However, the modification of LDHs shell and the control over magnetic property of the core is another challenge. It thereby leaves a great deal of room for scientists to develop novel and facile methods to synthesis magneticcore/LDH-shell composites with more sophisticated and tunable structures for desired applications. In particular, for practical applications in biology, magnetic-core/LDH-shell composites with suitable size, shape, and enhanced properties (such as biocompatibility, luminescence, as well as intelligence) are needed to achieve the desired sensitivity and efficacy required for future medical diagnostics and therapeutics, as well as MRI optical multimodality imaging. Thirdly, the interaction between the magnetic core, the LDH shell, and the supported functional species is rather complicated; a deep insight into the precise structure modulation and host-guest interactions is still a great challenge. Therefore, inventive structural designs and effective strategies should be developed to fabricate hierarchical magnetic-core/LDHshell composites that can be potentially used in the areas such as separation, targeted drug delivery, catalysis, materials science, environmental science, and biology. Our future work will focus on the construction of these new types of materials.

Acknowledgements

This work was supported by the 973 Program (Grant No. 2011CBA00504) and the National Natural Science Foundation of China (NSFC). M.W. particularly appreciates the financial aid from the China National Funds for Distinguished Young Scientists of the NSFC.

- a) O. Veiseh, J. W. Gunn, M. Zhang, Adv. Drug Delivery Rev. 2010, 62, 284–304;
 b) N. Kohler, C. Sun, A. Fichtenholtz, J. Gunn, C. Fang, M. Q. Zhang, Small 2006, 2, 785–792;
 c) W. Zhao, J. Gu, L. Zhang, H. Chen, J. Shi, J. Am. Chem. Soc. 2005, 127, 8916–8917.
- [2] a) W. S. Seo, J. H. Lee, X. Sun, Y. Suzuki, D. Mann, Z. Liu, M. Terashima, P. C. Yang, M. V. McConnell, D. G. Nishimur, H. Dai, *Nat. Mater.* 2006, *5*, 971–976; b) J. Gao, G. Liang, J. S. Cheung, Y. Pan, Y. Kuang, F. Zhao, B. Zhang, X. Zhang, E. X. Wu, B. Xu, *J. Am. Chem. Soc.* 2008, *130*, 11828–11833; c) E. Taboada, R. Solanas, E. Rodríguez, R. Weissleder, A. Roig, *Adv. Funct. Mater.* 2009, *19*, 2319–2324; d) V. Salgueiriño-Maceira, M. A. Correa-Duarte, *Adv. Mater.* 2007, *19*, 4131–4144.
- [3] a) D. Wang, J. He, N. Rosenzweig, Z. Rosenzweig, *Nano Lett.* 2004, 4, 409–413; b) J. Peng, L. N. Feng, K. Zhang, J. J. Li, L. P. Jiang, J. J. Zhu, *Chem. Eur. J.* 2011, *17*, 10916–10923; c) I. S. Lee, N. Lee, J. Park, B. H. Kim, Y. W. Yi, T. Kim, T. K. Kim, I. H. Lee, S. R. Paik, T. Hyeon, *J. Am. Chem. Soc.* 2006, *128*, 10658–10659; d) L. Zhang, B. Liu, S. Dong, *J. Phys. Chem. B* 2007, *111*, 10448–10452.
- [4] a) H. Gu, R. Zheng, X. Zhang, B. Xu, J. Am. Chem. Soc. 2004, 126, 5664–5665; b) P. Yang, Q. Z. Xu, S. Y. Jin, Y. Zhao, Y. Lu, X. W. Xu, S. H. Yu, Chem. Eur. J. 2012, 18, 1154–1160; c) Y. B. Sun, X. B. Ding, Z. H. Zheng, X. Cheng, X. H. Hua, Y. X. Peng, Chem. Commun. 2006, 2765–2767; d) Y. T. Lim, M. Y. Cho, J. M. Lee, S. J. Chung, B. H. Chung, Biomaterials 2009, 30, 1197–1204; e) Y. H. Deng, D. W. Qi, C. H. Deng, X. M. Zhang, D. Y. Zhao, J. Am.

Chem. Soc. **2008**, *130*, 28–29; f) Y. Deng, C. Wang, X. Shen, W. Yang, L. Jin, H. Gao, S. Fu, *Chem. Eur. J.* **2005**, *11*, 6006–6013.

- [5] a) H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White, S. Sun, *Nano Lett.* **2005**, *5*, 379–382; b) X. Sun, S. Guo, Y. Liu, S. Sun, *Nano Lett.* **2012**, *12*, 4859–4863.
- [6] a) H. Kim, M. Achermann, L. P. Balet, J. A. Hollingsworth, V. I. Klimov, J. Am. Chem. Soc. 2005, 127, 544–546; b) Q. Ma, Y. Nakane, Y. Mori, M. Hasegawa, Y. Yoshioka, T. M. Watanabe, K. Gonda, N. Ohuchi, T. Jin, Biomaterials 2012, 33, 8486–8494.
- [7] A. M. Fogg, V. M. Green, H. G. Harvey, D. O'Hare, Adv. Mater. 1999, 11, 1466–1469.
- [8] a) B. Sels, D. D. Vos, M. Buntinx, F. Pierard, K. D. Mesmaeker, P. Jacobs, *Nature* **1999**, *400*, 855; b) J. S. Valente, H. Pfeiffer, E. Lima, J. Prince, J. Flores, *J. Catal.* **2011**, *279*, 196–204; c) Y. Zhao, S. Zhang, B. Li, H. Yan, S. He, L. Tian, W. Shi, J. Ma, M. Wei, D. G. Evans, X. Duan, *Chem. Eur. J.* **2011**, *17*, 13175–13181; d) J. L. Gunjakar, T. W. Kim, H. N. Kim, I. Y. Kim, S. J. Hwang, *J. Am. Chem. Soc.* **2011**, *133*, 14998.
- [9] Z. Gu, A. C. Thomas, Z. P. Xu, J. H. Campbell, G. Q. Lu, *Chem. Mater.* 2008, 20, 3715–3722.
- [10] a) F. Li, J. J. Liu, D. G. Evans, X. Duan, *Chem. Mater.* 2004, *16*, 1597–1602; b) M. F. Shao, M. Wei, D. G. Evans, X. Duan, *Chem. Commun.* 2011, *47*, 3171–3173.
- [11] a) J. Han, Y. Dou, M. Wei, D. G. Evans, X. Duan, Angew. Chem.
 2010, 122, 2217–2220; Angew. Chem. Int. Ed. 2010, 49, 2171–2174;
 b) D. Yan, J. Lu, J. Ma, S. Qin, M. Wei, D. G. Evans, X. Duan, Angew. Chem. 2011, 123, 7175–7178; Angew. Chem. Int. Ed. 2011, 50, 7037–7040; c) D. Yan, J. Lu, M. Wei, J. Han, J. Ma, F. Li, D. G. Evans, X. Duan, Angew. Chem. 2009, 121, 3119–3122; Angew. Chem. Int. Ed. 2009, 48, 3073–3076.
- [12] Z. P. Liu, R. Z. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, J. Am. Chem. Soc. 2006, 128, 4872–4880.
- [13] a) E. Géraud, V. Prévot, J. Ghanbaja, F. Leroux, *Chem. Mater.* 2006, *18*, 238–240; b) E. Géraud, S. Rafqah, M. Sarakha, C. Forano, V. Prévot, F. Leroux, *Chem. Mater.* 2008, *20*, 1116–1125.
- [14] a) P. Gunawan, R. Xu, *Chem. Mater.* 2009, 21, 781–783; b) M. Shao,
 F. Ning, Y. Zhao, J. Zhao, M. Wei, D. G. Evans, X. Duan, *Chem. Mater.* 2012, 24, 1192–1197.
- [15] a) H. Zhang, D. Pan, K. Zou, J. He, X. Duan, J. Mater. Chem. 2009, 19, 3069–3077; b) H. Zhang, D. Pan, X. Duan, J. Phys. Chem. C 2009, 113, 12140–12148.
- [16] D. Pan, H. Zhang, T. Fan, J. Chen, X. Duan, Chem. Commun. 2011, 47, 908–910.
- [17] F. Mi, X. Chen, Y. Ma, S. Yin, F. Yuan, H. Zhang, *Chem. Commun.* 2011, 47, 12804–12806.
- [18] X. Chen, F. Mi, H. Zhang, H. Zhang, Mater. Lett. 2012, 69, 48-51.
- [19] L. Li, R. Ma, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, *Chem. Commun.* 2006, 3125–3127.
- [20] L. Li, Y. Feng, Y. Li, W. Zhao, J. Shi, Angew. Chem. 2009, 121, 6002–6006; Angew. Chem. Int. Ed. 2009, 48, 5888–5892.
- [21] M. Shao, F. Ning, J. Zhao, M. Wei, D. G. Evans, X. Duan, J. Am. Chem. Soc. 2012, 134, 1071–1077.
- [22] a) A. I. Khan, L. Lei, A. J. Norquist, D. O'Hare, *Chem. Commun.* 2001, 2342–2343; b) M. Del Arco, E. Cebadera, S. Gutierrez, C. Marten, M. J. Montero, V. Rives, J. Rocha, M. A. Sevilla, *J. Pharm. Sci.* 2004, *93*, 1649–1658; c) M. Wei, M. Pu, J. Guo, J. Han, F. Li, J. He, D. G. Evans, X. Duan, *Chem. Mater.* 2008, *20*, 5169–5180.
- [23] a) A. N. Ay, B. Zumreoglu-Karan, A. Temel, V. Rives, *Inorg. Chem.* **2009**, 48, 8871–8877; b) H. Zhang, K. Zou, H. Sun, X. Duan, J. Solid State Chem. **2005**, 178, 3485–3493.
- [24] a) Y. Zhao, S. He, M. Wei, D. G. Evans, X. Duan, *Chem. Commun.* 2010, 46, 3031–3033; b) L. Yang, Z. Shahrivari, P. K. T. Liu, M. Sahimi, T. T. Tsotsis, *Ind. Eng. Chem. Res.* 2005, 44, 6804–6815.
- [25] C. Chen, P. Gunawan, R. Xu, J. Mater. Chem. 2011, 21, 1218-1225.

Published online: February 19, 2013

4108 -