Iron Triad (Fe, Co, Ni) Nanomaterials: Structural Design, Functionalization and Their Applications

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Iron Triad (Fe, Co, Ni) Nanomaterials: Structural Design, Functionalization and Their Applications

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The structure and the composition are two key factors that influence the physical, chemical, and other properties of the materials. Correspondingly, structural design and functionalization with inorganic or organic materials provide efficient routes to enhance some properties. Herein, the iron triad nanomaterials with a wide range of applications in energy, environment and other fields were chosen as target materials. The paper reviews various approaches for designing three typical structures (hollow and porous, ultrathin two-dimensional, and complex three-dimensional structures) of iron triad nanomaterials with high specific surface area as well as their feasible functionalization for special purpose. Furthermore, some amazing work in recent years are introduced and discussed especially in the energy field including the energy transfer, conversion and storage, and the environmental field including the adsorption and degradation of heavy metal irons and organic pollutants. This review aims at developing potential application of the nanomaterials by structural adjustment and functionalization to overcome their intrinsic shortcoming and enhance their performances.

Key learning points

(1) Structural design on three typical structures with high specific surface area.
(2) Feasible functionalization to enhance structural stability, conductivity and adsorption.
(3) Recent intriguing work about structural design and functionalization.

1. Introduction

Nanomaterials have been studied for decades, and remarkable development for them might be the controllable chemical synthesis with adjustable nanostructures. At the very beginning, only simple irregular nanoparticles (NPs, all abbreviations see ESI) could be prepared in chemical solutions. Then, through understanding mechanisms on nanocrystals (NCs) growth and getting more advanced scientific equipment and instruments, researchers developed gradually different synthetic strategies, by which various nanostructures such as regular polyhedrons, hollow particles, one-dimensional (1D) structures, and even complex three-dimensional (3D) spatial structures have been fabricated. These studies continue to thrive as many efforts have been made to develop advanced nanomaterials by structural design and functionalization in pursuit of applications.

Iron triads (Fe, Co, Ni) are a class of materials covering metals(0), oxides, sulfides, hydroxides and their composites, those are potentially advantageous for lithium-ion batteries (LIBs), electrochemical capacitors (ECs), adsorbents, and nanocatalysts in the fields of energy and environment. For example, oxides of iron, nickel and cobalt, and mixed oxides thereof, are studying choices for electrode materials in (LIBs), while hydroxides of nickel and cobalt usually possess high specific capacitances, being favourable for high energy density storage in ECs.[1] Besides, magnetic nanomaterials among iron triad series can be used as adsorbents for heavy metal ions, which can be easily re-collected by magnetic separation after adsorption.[2] Sometimes, they can also serve as catalysts for pollution degradation.[3] That is, iron triad nanomaterials are chosen as they can provide vivid examples for nano-structural design and functionalization with hot applications in the fields of energy and environment, not mention their low cost, low toxicity, and flexible synthesis.

Iron triad materials in conventional form such as bulk or aggregated NPs have no competitive advantage in the electrochemical, adsorbing and catalytic performances, as their low specific surface area (SSA) would lead to poor contact between the active materials and the electrolyte/pollutants. Thus, the fundamental prerequisite for structural design is to ensure high SSA. Additionally, functionalization is also an efficient route to enhance the properties. However, different performance needs different functionalization. For instance, high-quality active materials for electrodes prefer to be improved in conductivity and structural stability, while adsorbents and nanocatalysts prefer more adsorbing sites.

Here, we choose three kinds of typical nanostructures of iron triad with high SSA, i.e., hollow and porous structures, ultrathin two-dimensional (2D) structures, and complex 3D structures. We will summarize the intriguing synthetic methods based on recent progress, provide dominant strategies for functionalization on nanostructures, and give classical applied examples of iron triad nanomaterials in electrode materials, adsorbents, and catalysts. The much enhancement of the properties by structural fabrication and functionalization based on iron triads would also drive the development of other alternative nanomaterials.

2. Nano-structural design for high SSA

It's a simple way to increase the SSA of the materials by decreasing their sizes. But small NPs tend to aggregate to lower their surface energy, which will definitely lower the SSA and even influence the related properties. Instead, three typical nanostructures with high SSA attract much attention, covering hollow and porous structures, ultrathin 2D structures, and complex 3D structures. All these structural design strategies refer to reported interesting work in recent years.

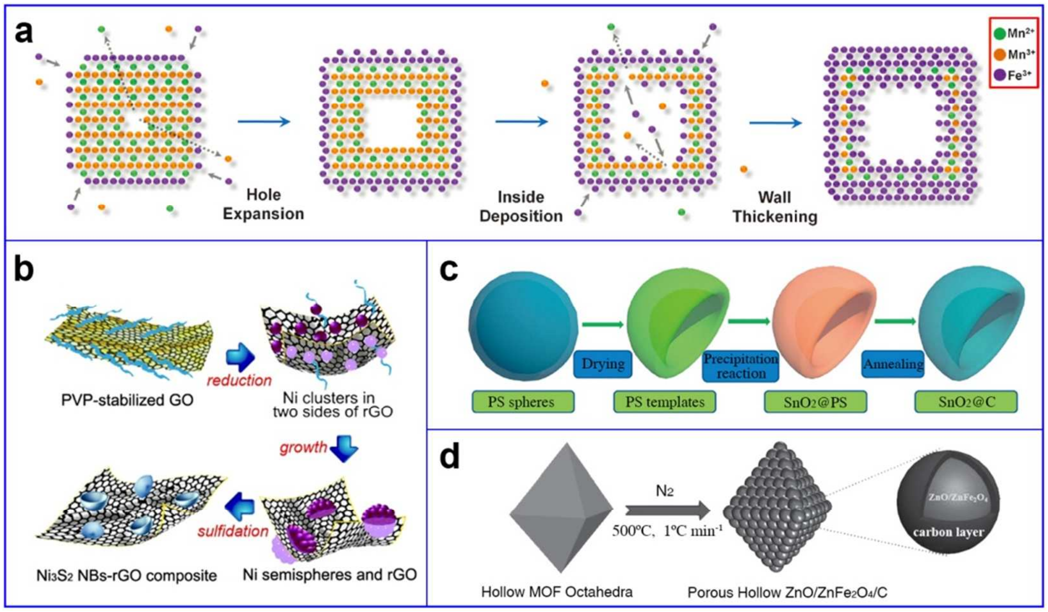

Fig. 1 (a) Schematic illustration of galvanic replacement reaction of Mn_3O_4 and Fe_2O_3, showing the localized dissolution of Mn_3O_4 and the surface precipitation of γ-Fe_2O_3 (ref.4, copyright 2013 American Association for the Advancement of Science), (b) Ni_3S_2 nanobowls wrapped by rGO sheets synthesized by Kirkendall effect (ref.6, copyright 2014 Elsevier), (c) Schematic illustration of the formation procedure of bowl-like SnO_2@C hollow particles (ref.7, copyright 2014 Wiley-VCH), (d) Schematic illustration for the preparation process of porous hollow

$ZnO/ZnFe_2O_4/C$ octahedra (ref.8, copyright 2014 Wiley-VCH).

2.1 Hollow and porous structures

It is highly desirable to develop generalized and efficient methods to synthesize hollow or porous structures as their improved physical and chemical properties with larger SSA and void space in comparison with their solid nanoscale counterparts. Four typical methods will be introduced in detail.

The first one is the galvanic replacement reaction for hollow metal oxides, reported by Oh et al. in Science in 2013.[4] The method is usually used to fabricate hollow nanostructures of noble metals with controllable compositions (detailed mechanism see ESI). When manganese oxide (Mn_3O_4) NCs reacted with iron(II) perchlorate, hollow box-shaped NCs of $Mn_3O_4/\gamma\text{-}Fe_2O_3$ were produced. These nanoboxes ultimately transformed into hollow cage-like $\gamma\text{-}Fe_2O_3$ via the localized dissolution of Mn_3O_4 and the surface precipitation of $\gamma\text{-}Fe_2O_3$, as Figure 1a shown. The generality of this approach was demonstrated with other metal pairs, including Co_3O_4/SnO_2 and Mn_3O_4/SnO_2.[4] Besides, adding extra chemical agents for further reaction, a series of hollow metal hydroxides could be obtained.[5]

The second one is the nanoscale Kirkendall effect, a well-known method, firstly reported by Alivisatos' group in Science in 2004 (details see ESI). It is mainly used to prepare hollow or core-shell nanostructures of metal oxides and sulfides. By introducing soft substrates of graphene, peculiar hollow particles, nano-bowls were fabricated using Kirkendall effect.[6] As shown in Figure 1b, the existence of polyvinylpyrrolidone (PVP)-stabilized graphene oxide (GO) sheets made nickel clusters aggregate and form semispheres instead of spheres. Thus, the Ni solid semisphere templates turned into nickel sulfide nanobowls by sulfidation with Kirkendall effect.[6]

Obviously, the final hollow samples based on galvanic replacement or Kirkendall effect are limited in structure (determined by the original template) and components. As a good compensation, template-sacrificial method is proposed. The target structure depends on the nanostructure of the template. That is, we can synthesize different hollow structures by choosing different templates. For example, Liang et al. used bowl-like polystyrene (PS) spheres (made from PS hollow spheres after drying in air naturally) as substrates and synthesized bowl-like $SnO_2@C$ particles with SSA of ~103.8 m^2g^{-1} (process illustrated in Figure 1c).[7] Recently, inspired by their diverse configurations, metal-organic frameworks (MOFs) have also been used as sacrificial templates to fabricate porous structures. Zou et al. prepared porous $ZnO/ZnFe_2O_4/C$ octahedra with hollow interiors (SSA of ~140 m^2g^{-1}) using MOFs as both the precursor and the self-sacrificing template as shown in Figure 1d.[8] The templates can be removed by annealing or suitable chemical agents, which won't react with the target materials.

Additionally, heat decomposition provides an efficient simple route to fabricate porous structure. Usually, unstable nanostructured precursors such as $Co(CO_3)_{0.5}(OH)0.11H_2O$ nanobelt arrays were heated, decomposed, and turned into metal oxides with mesoporous structure.[9]

2.2 Ultrathin 2D nanostructures

As for 2D nanostructures, $Ni(OH)_2$, $Co(OH)_2$ and their composites layered double hydroxides (LDHs) are our familiar materials. LDHs are a class of ionic lamellar compounds composed of positively charged brucite-like layers with metal cations occupying the centers of edge-sharing octahedra and hydroxide ions connecting to vertexes. Thus, the nature of the layered structure of hydroxides provides feasible routes to make ultrathin iron triad nanosheets.

We could directly produce ultrathin sheets by controlling the growth of metal hydroxide and preventing thin layers from stacking. For example, Zhu et al. synthesized $\alpha\text{-}Ni(OH)_2$ sheets (~ 2 nm in thickness) via microwave-assisted liquid-phase growth under low-temperature atmospheric conditions. After heat treatment, the corresponding NiO ultrathin nanosheets were also obtained.[10] The process was simply illustrated in Figure 2a. It was believed the rapid microwave heating could facilitate a super saturation of reactant species, lead to the instantaneous formation of ultrafine nanocrystals, and then self-assemble spontaneously by intrinsic driving force of lamellar structure with 2D anisotropic growth. More thin sheets with only five-atom thickness could be obtained under a very slow liquid-phase growth rate.[1] The detail about the seeds attachment and growth was shown in Figure 2b.

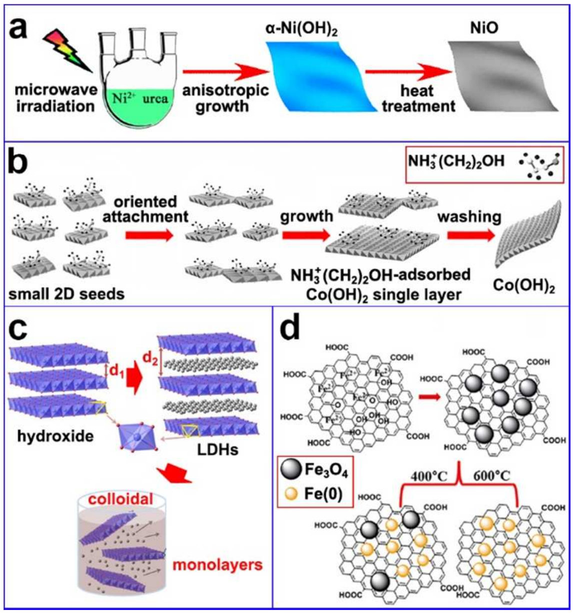

Fig. 2 (a) Schematic formation of $Ni(OH)_2$ and NiO nanosheets of ~2 nm in thickness (ref.10, copyright 2014 American Association for the Advancement of Science), (b) Schematic of the 2D oriented attachment for the formation of the five-atom-thickness $Co(OH)_2$ ultrathin layer (ref.1, copyright 2014 Wiley-VCH), (c) Schematic of the exfoliated LDH monolayers dispersed in a colloidal solution by inter-layer anions and water molecules (ref.11, copyright 2014 Nature Publishing group), (d) Illustration of synthesis of the rGO–Fe(0)–Fe_3O_4 and the rGO–Fe(0) sheets (Reproduced from Ref. 2 with permission from The Royal Society of Chemistry).

Considering the layered structure of the hydroxides, the liquid-exfoliation method can peel 2D sheets into ultrathin 2D sheets. As shown in Figure 2c, metal hydroxides and oxyhydroxides are composed of edge-sharing octahedral MO_6 layers. The anions and solvation molecules within interlayer which could enlarge the inter-layer distance (from d_1 to d_2) can be used for exfoliation. A typical exfoliation process includes adding Br^-, exchanging Br^- with NO_3^-, redispersing in degassed formamide, and obtaining monolayers.[11]

As is known, graphene constructed by sp^2 carbon atoms arranged in hexagonal rings, can be used as templates to produce ultrathin 2D composite sheets. As represented in Figure 2d, the Fe_3O_4 NPs were intercalated in reduced graphene oxide (rGO) layers and subsequently converted to Fe(0) by thermal annealing at different temperatures in a H_2/Ar atmosphere, forming the rGO–Fe(0)–Fe_3O_4 and the rGO–Fe(0) sheets.[2]

2.3 Complex 3D nanostructures

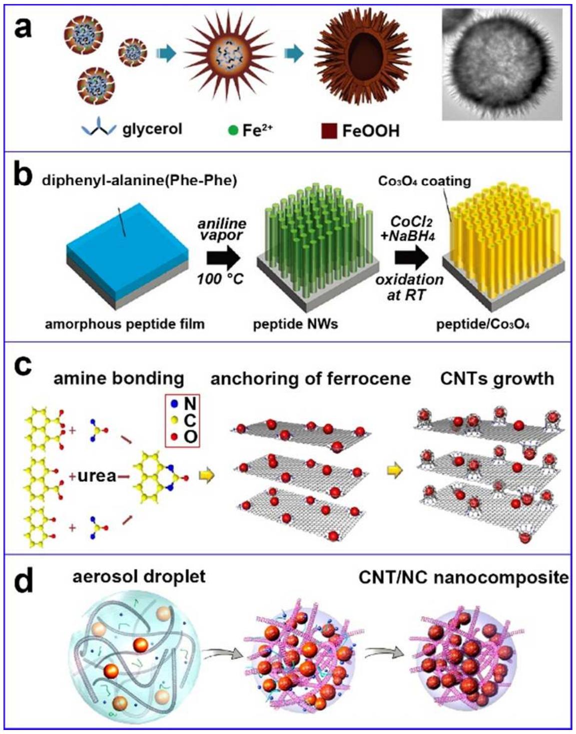

Fig. 3 (a) Morphological evolution process and TEM image of the urchin-like hierarchical α-FeOOH sphere (ref.12, copyright 2012 Wiley-VCH), (b) Illustrative scheme for the synthesis of peptide/Co_3O_4 hybrid nanowire array. (ref.14, copyright 2010 American Chemical Society), (c) Schematic diagram of growth of CNTs on graphene sheets functionalized by amino (ref.15, copyright 2013 American Chemical Society), (d) Schematic fabrication of 3D CNT/NC nanocomposites through an aerosol spray drying process followed by thermal annealing. (ref.16, copyright 2014 American Chemical Society).

Complex 3D nanostructures have emerged as transformative constructions due to their high SSA, special spatial stability, and more reacting cavities, which can be fabricated by many routes. Some hierarchical 3D structures can be obtained through one-pot solution method. As shown in Figure 3a, the hollow structure was formed using glycerol/water (oil/water) particles as soft templates in a quasi-micro-emulsion system. The urchin-like hollow structure was then prepared through further epitaxial growth of 1D FeOOH from the initial shell and the removal of inner glycerol.[12] Besides, we can use 2D sheets to roll into 3D tubes or cones. For example, $Co(OH)_2$ thin nanosheets turned into 3D nanocones by rolling, while their interlayer spacing could be adjustable by intercalating different anions (dodecylsulfate, benzoate, and nitrate).[13]

At present, researchers like to build 3D structures with the aid of hard templates such as carbon cloth, nickel foam, fluorine doped tin oxide (FTO) glass, metal, and even organic substrate. One example for the formation of peptide/Co_3O_4 hybrid nanowire (NW) array was illustrated in Figure 3b. Peptide NWs were prepared by treating amorphous diphenylalanine film with aniline vapor at an elevated temperature. They were used as templates and hybridized with Co_3O_4 NCs through the reduction of cobalt ions in a $NaBH_4$ aqueous solution.[14] Undoubtedly, one amazing idea of constructing 3D structure is to combine 2D sheets with 1D structures, such as combining graphene and carbon nanotubes (CNTs). Vadahanambi et al. synthesized 3D structure with CNTs vertically standing on graphene sheets and iron oxide NPs decorated on both the graphene and the CNTs (Figure 3c).[15] The key point was to add ferrocene (one kind of catalyst for the formation of CNTs) into the fresh amino-functionalized graphene under microwave irradiation to produce iron oxide and CNTs.[15]

The simplest method to fabricate 3D structure is to mix existing 0D, 1D, or 2D structures together. As shown in Figure 3d, the aerosol droplets composed of Fe_3O_4 NCs and 1D CNTs were condensed into solidified 3D nanocomposite after annealing.[16]

3. Hybridization and surface functionalization

The structure and the composition are two key factors that influence the physical or chemical properties of the nanomaterials. The above structural design provides an important route for improving the properties. Functionalization of nanomaterials is also an effective way to make up for the intrinsic defects of materials by introducing extra organic or inorganic components. For instance, we can coat metal oxides nanomaterials with amorphous carbon layer to improve their conductivity and structural stability. Also we can introduce Ag to form Ni@Ag core-shell structure to replace nickel NPs for a better conductivity. Sometimes, we need to cap the inorganic NPs with DNA or other organic molecules for biomaterials, adsorbents and other applications. Herein, we group roughly these newly formed inorganic hybrid nanomaterials as one kind of functionalization, and surface functionalization by organic molecules as another kind.

3.1 Inorganic hybrid nanomaterials

Carbon coating is a simple, low-cost, and high-efficiency modifying approach to improve conductivity, keep nanostructure stable, and prevent some components from oxidation. The selectable carbon source includes glucose, dopamine, aniline, and other small organic molecules. Usually, a thin carbon-rich polymer layer forms on the surface of the nanomaterials by polymerization of carbon source, which will generate a carbon layer later in a protective atmosphere after annealing.[17] As carbon materials can be doped with boron, nitrogen and other heteroatoms, we can achieve N-, or B-doped carbon coating by choosing some boron source (B_2H_6, $NaBC_{24}H_{20}$, etc.) and nitrogen source (NH_3, pyridine, urea, etc.). Because the doping could break the electroneutrality, create many active sites, and enhance the electrical properties of carbon-based materials.[18]

To keep some voids between the inorganic nanomaterial and the surface carbon layer, a temporary interlayer such as a silica layer could be introduced. As shown in Figure 4a, the Fe_2O_3 NPs were firstly coated by a silica layer through the hydrolysis of tetraethoxysilane (TEOS). Then the α-Fe_2O_3@SiO_2 NPs were coated by the polymerized dopamine, which were converted to FeO_x@SiO_2@C after annealing at 700 °C for 5 h under Ar. Finally, FeO_x@C yolk-shell NPs were obtained after washing with NaOH for 12 h to remove the silica layer. By adjusting the thickness of the silica layer, the void space can be optimized for improved electrochemical performance.[19]

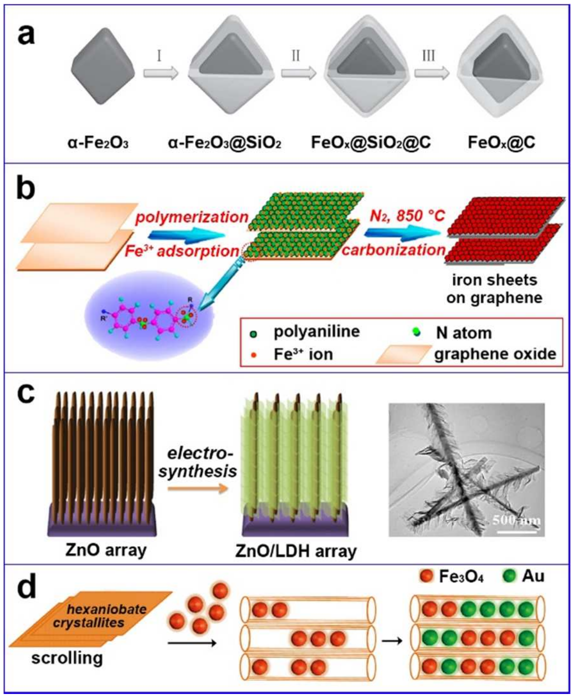

Fig. 4 (a) Illustration of the synthesis of FeO_x@C yolk–shell structures (ref.19, copyright 2014 Wiley-VCH), (b) Schematic illustration of the formation of iron nanocomposite with fish scale-like iron nanosheets supported on graphene (ref.20, copyright 2013 American Chemical Society), (c) Schematic illustration of the fabrication of ZnO@LDH core-shell nanowire array and TEM image of the sample (ref.22, copyright 2014 Wiley-VCH), (d) Au NP in situ growth in preformed hexaniobate nanoscrolls partially filled with Fe_3O_4 NPs. (ref.25, copyright 2014 Wiley-VCH).

Besides carbon coating, carbon-based hybrid material can be prepared using carbon materials (graphene, CNTs, carbon cloth, etc.) as substrates. A facile strategy was reported to prepare fish scale-like Fe sheets supported on graphene with high SSA of ~218 m^2g^{-1} (Figure 4b). Firstly, 2D fish scale-like polyaniline (PANI) on graphene oxide (GO) was prepared by in situ polymerization. After the carbonization, scale-like pyrolytic carbon nanosheets formed on GO sheets. Meanwhile, Fe^{3+} cations were adsorbed onto PANI/GO composite by electrostatic interaction with nitrogen and oxygen-containing functional groups on PANI and GO. The adsorbed Fe^{3+} ions and GO were then reduced to metallic iron and graphene by pyrolytic carbon from PANI. Obviously, PANI served both as the reducing agent and the template.[20]

Other heterogenous materials (noble metal, semiconductor, etc.) can also been used to form hybrid nanocomposites.[21] Using prepared nanostructures as cores, they can be coated uniformly by further electrochemical deposition or hydrothermal (solvothermal) growth. As shown in Figure 4c, the ZnO@CoNi-LDH nanoarray was synthesized by using ZnO NWs grown on FTO substrate as template and coating LDH nanoflakes through an electro-synthetic route.[22] One-pot mixing could also be useful to synthesize hybrid nanomaterials. Unlike multiple steps for core-shell structures, various metal ions should be mixed in the solvent prior to chemical reaction to make sure the compositional uniformity.[23]

Both the galvanic replacement and the nanoscale Kirkendall effect described above for hollow structures can also be applied for hybrid inorganic nanocomposites by controlling the reaction process. For example, hollow chains of nickel sulfide were prepared by total sulfidation, while Ni@Ni_3S_2 peapod-like structure was achieved by partial sulfidation.[24] As is known, 2D sheets could roll into 1D hollow tubes. If some heterogenous NPs are embedded in the tubes, some fantastic peapod-like hybrid nanocomposite would be produced. For example, Adireddy et al. synthesized partially filled hexaniobate nanoscrolls with Fe_3O_4 and Au NPs, forming bifunctional peapod-like structures as illustrated in Figure 4d.[25]

3.2 Surface functionalization by organic molecules

In recent years, we are familiar with iron oxides NPs modified by polymers as their biological application. Although the polymer coating is very sensitive to temperature and easily loses its stability at high temperature, study on polymer coating with small organic molecules plays a great role in the fields of energy and environmental protection. For energy materials, coating or mixing conducting polymer such as polypyrrole (PPy) is an efficient way to enhance conductivity and flexibility of nanomaterials, and a feasible way to produce carbon layers by annealing. For nano-adsorbents on heavy metal ions or organic pollutants, the organic coating will make the adsorbents disperse stably in solution as it creates steric repulsion to balance the attractive forces such as magnetic and van der Waals forces. Furthermore, the linked long-chain molecules will provide more active sites for adsorption.

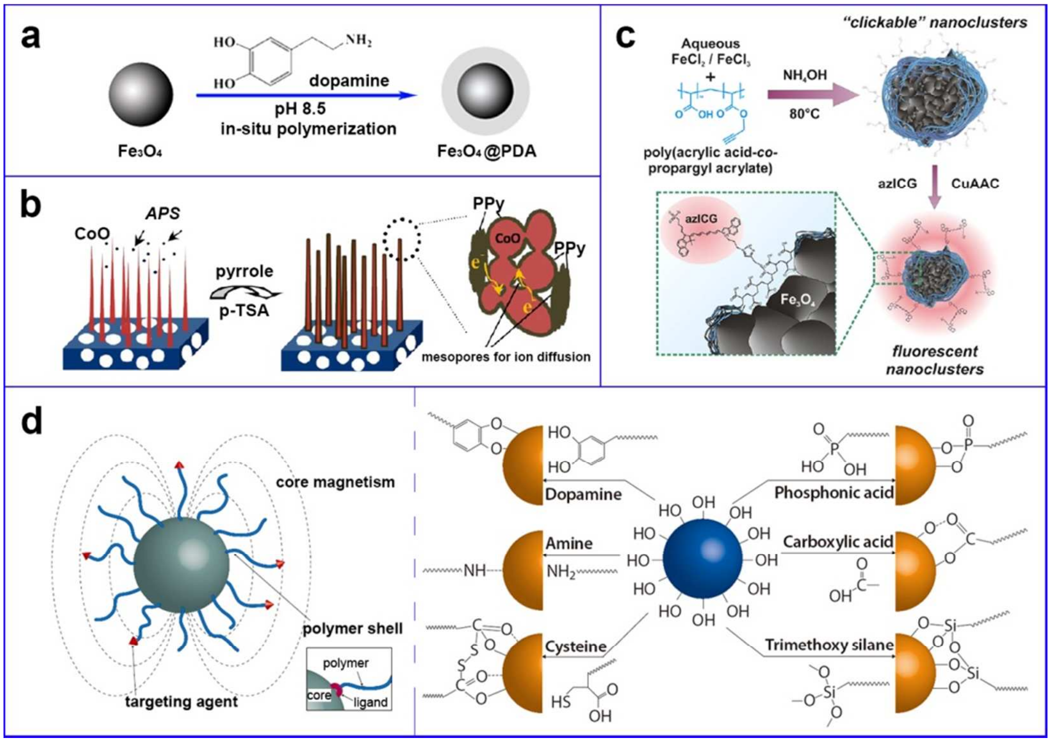

Fig. 5 (a) Schematic illustration of the preparation of Fe_3O_4@PDA nanocrystals. (ref.26, copyright 2014 American Chemical Society), (b) Representative synthesis of well-aligned CoO nanowire array grown on 3D nickel foam with PPy firmly anchored to each nanowire surface (ref.27, copyright 2013 American Chemical Society), (c) Schematic of the production of polymer-stabilized nanoclusters by chemisorption of poly(acrylic acidco-propargyl acrylate) to Fe_3O_4 NPs and functionalized with an azide-modified indocyanine green derivative (azICG) attached by copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction (ref.28, copyright 2013 American Chemical Society), (d) Functional polymers are grafted onto an inorganic core of iron oxide through an anchoring group; Groups that can be used to anchor polymers on iron oxide particle surfaces (ref.29, copyright 2010 Nature Publishing Group).

Referring to chemical functionalization, self-polymerization is a commonly used method.[26] In Figure 5a, the Fe_3O_4@polydopamine (PDA) core-shell nanocomposite was achieved through an in-situ self-polymerization of dopamine.[26] The thickness of polymer layers can be adjusted by solution conditions, such as pH. The self-polymerization method can also be used to fabricate outer layers for 3D structures. As illustrated in Figure 5b, CoO nanowire array grown on nickel foam was coated with PPy through self-polymerization of pyrrole monomers. PPy was immobilized onto the nanowire array based on a simple chemical polymerization by using ammonium persulphate (APS) as the oxidant and *p*-toluenesulfonic acid (*p*-TSA) as the doping agent.[27]

Most nanomaterials synthesized by solution method have chemical residual on their surfaces such as hydroxyl, carboxyl, or other functional groups, which can link other organic molecules to make chemisorption feasible. As shown in Figure 5c, Fe_3O_4 NPs were stabilized by poly(acrylic acidco-propargyl acrylate) through mixing them together and stirring for a time. Further graft was carried out by organic reaction to form fluorescent nanoclusters.[28] As for chemisorption, hydroxyl groups on the surface of iron oxide NPs play important role in chemical functionalization, which serve as binders to immobilize organic molecules such as dopamine, amine, cysteine, phosphonic acid, carboxylic acid, and trimethoxy silane as shown in Figure 5d.[29] The obtained ligands by these organic molecules could be further used to anchor polymers.

Most inorganic nanomaterials are synthesized by adding some surfactants or organic reagents. And the residual organic molecules adhering on the surface are hard to be washed away. Although inorganic NPs stabilized by surface functionalization of organic molecules have a better dispersion in solutions, sometimes they cause poor electronic conductivity. To remove these unpopular molecules, ligand exchange is an easy way, which can be used to replace long alkyl-chains by short ones to eliminate the disadvantages. For example, the capping oleylamine molecules can be removed by stirring the NPs in n-butylamine for several days.[30]

4. Applications in energy and environment

Recent intriguing work about iron triad nanomaterials in the fields of energy and environment, reminds the above summarized approaches for structural design and functionalization, and explains basically the relationship between the structures and their properties.

4.1 Electrode materials in energy

This part introduces iron triad nanomaterials with application focusing on electrode materials in lithium-ion batteries and supercapacitors. It will emphasize the importance of structural design and functionalization in improving the electrochemical properties. The enhanced electrochemical performances require iron triad electrode materials to have better electrical conductivity, higher SSA, and improved structural stability, which would be the criterion of designing optimal structures and functionalization.

4.1.1 Lithium-ion batteries

The transitional metal oxides and sulfides can deliver reversible capacities between 500 and 1000 $mAhg^{-1}$, as their reaction mechanism includes both lithium ions insertion/extraction and the cyclic redox process. Take low-cost and non-toxicity hematite (Fe_2O_3) for example. It yields a total theoretical capacity of 1007 $mAhg^{-1}$ by the formation of Fe^0 from Fe^{3+}, much higher than traditional anode material of graphite (~372 $mAhg^{-1}$).

All metal oxides (Fe_2O_3, Fe_3O_4, Co_3O_4, CoO, etc.) and sulfides (NiS, CoS, FeS_2, etc.) can be used as anode active materials. Allowing for increasing charging/discharging rates in LIBs, nanostructures with high SSA will benefit the transfer of Li-ion flux through the liquid electrolyte/nanosized electrode material interface. Additionally, some nanostructures with shorter path lengths for electronic and ionic transport would also improve the charging/discharging rate by eliminating the disadvantage of oxides and sulfides of poor conductivity. That's why the porous, hollow, ordered mesoporous and other hierarchical nanostructures were used in LIBs.[31] Besides, the electrode materials suffer badly from irreversible expanded volume and easily pulverized structures during lithiation and delithiation processes. Experiments have confirmed the unstable structural arrangement after the first lithiation is unfavorable for electronic transport.[32] That is, better electrode materials prefer more stable nanostructures.

To meet high SSA, short electronic-transfer path, and stable structure, 1D nanostructures with small diameter have their advantage, because they couldn't aggregate or curl easily like 0D NPs or 2D sheets.[33] Hollow, porous, hierarchical and other 3D structures are also good choices. Meanwhile, some carbon materials such as CNTs or graphene can be mixed to improve the electrical conductivity of the nanomaterials. For example, we designed bowl-like Ni_3S_2 NPs wrapped by rGO sheets (Fig. 6a), showing enhanced cycle stability with specific capacity of 443 $mAhg^{-1}$ after 500 cycles, while Ni_3S_2 hollow chains faded dramatically to 147 $mAhg^{-1}$ after 100 cycles.[6] The wrapped graphene improves the conductivity and also acts as a mechanical buffer for the volume expansion of Ni_3S_2 during cycling. More importantly, a bowl-like hollow structure excludes the unnecessary void space in conventional hollow particles, thus allows packing more active materials per volume.

The tap density of LIBs can be increased.[7] There is another example using carbon material to form hybrid nanocomposite. Fe_3O_4 NPs ~5-7 nm in size were decorated on CNTs and formed a sheath layer, which showed a reversible capacity over 800 $mAhg^{-1}$.[34] As shown in Fig. 6b, a little volume expansion could be observed without any structural destruction by comparing the TEM images before and after cycles. Obviously, the poor intrinsic electrical conductivity of metal sulfides or oxides and their structural stability both can be improved by introducing CNTs or graphene.

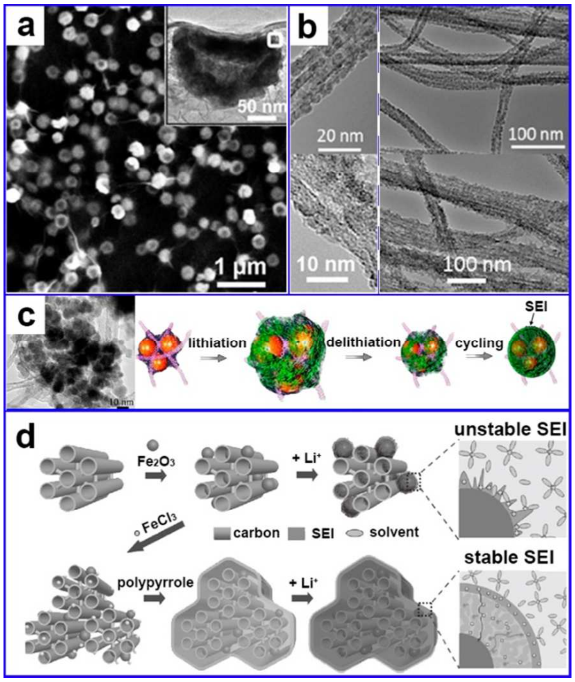

Fig. 6 (a) Ni_3S_2 bowl-like structures wrapped by rGO sheets with TEM image of one particle inserted (ref.6, copyright 2014 Elsevier), (b) TEM images of Fe_3O_4 sheath/CNTs at high and low magnification before (above) and post cycles of LIBs (below). (ref.34, copyright 2013 American Chemical Society), (c) TEM image showing interweaved networks of CNT/Fe_3O_4 nanocomposites, and schematic of volume expansion and SEI formation during cycling (ref.16, copyright 2014 American Chemical Society), (d) Illustration of the nanoengineering principles of PPy-coated Fe_2O_3@C multifunctional composites and scheme of enhanced cycle performance (ref.35, copyright 2013 Wiley-VCH).

Among various hybrid nanomaterials, 3D architectures assembled by 0D and 1Dstructures (Fig. 6c), are becoming popular as this kind of structures can shorten the ion and electron transfer routes, bear volume changes, and decrease compositional segregation.[16] The PPy-functionalized Fe_2O_3@C nanocomposite as illustrated in Figure 6d shows stable cycle performance. Because the PPy coating bridged the Fe_2O_3 NPs and the tubular mesoporous carbon together into a larger unit, which prevented the aggregation of NPs and maintained the structural integrity of active materials, in addition to effectively enhancing the electronic conductivity and keeping the stability of as-formed solid electrolyte interface (SEI) films.[35]

4.1.2 Supercapacitors

As one kind of supercapacitors, pseudocapacitors provide high specific capacitance using fast reversible multi-electron redox reaction on the surface of the electrode materials ($Ni(OH)_2$, $Co(OH)_2$, NiO, Co_3O_4, CoO, etc). As the charge storage only occurs on the surface or near the surface, ultrathin 2D freestanding nanosheets arouse great attention as electrode materials in supercapacitors (Fig. 7a).[10] When the sheets are too thin, they tend to curl and form other structures such as tubes or cones (Fig. 7b).[36] To prevent further curling or aggregation and keep their contact with electrolyte, surface stabilizers or assisted substrates can be introduced.[23,36,37] Carbon cloth and nickel foam are two kinds of typical substrates, as they have rough surfaces, high stability, structural flexibility, and good conductivity.[23,37] Considering smooth electrolyte flow and faster reaction kinetics, porous structures are beneficial to electrochemical performance (Fig. 7c).[37]

As the poor conductivity of the oxides and hydroxides, these electrode materials show limited electrochemical stability at high current density. To increase the electron transfer, other components (CNTs, graphene, conductive polymers or metal compounds) can be introduced to form hybrid nanocomposites.[27] Nickel-cobalt LDH nanosheets and nickel-cobalt-aluminum layered hydroxides (LHs) have been prepared as efficient electrode materials. Besides, 2D ultrathin sheets can also improve the poor electrical conductivity. For example, the all-solid-state asymmetric supercapacitor made by the β-$Co(OH)_2$ single-layer sheets (only five atoms in layer thickness) achieved a high cell voltage of 1.8 V and an exceptional energy density of 98.9 Whkg^{-1} at an ultrahigh power density of 17981 Whkg^{-1}. Also, this integrated nanodevice exhibited excellent cyclability with 93.2% capacitance retention after 10000 cycles.[1]

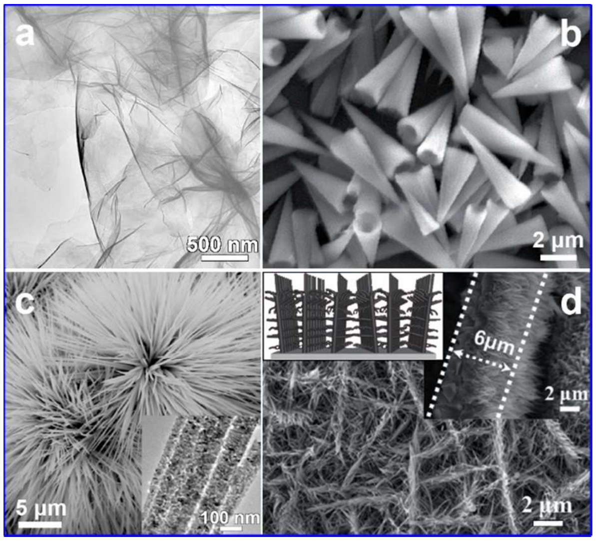

Fig. 7 (a) α-$Ni(OH)_2$ ultrathin nanosheets (ref.10, copyright 2014 Nature Publishing), (b) $Co(OH)_2$ nanocones formed by curling sheets (ref.36, copyright 2014 Wiley-VCH), (c) Co_3O_4 nanowires with brush-like morphology grown on carbon fiber paper. TEM image of porous nanowires inserted (ref.37, copyright 2012 American Chemical Society). (d) Network-like 3D structure of nickel and cobalt compounds arrays with structural illustration inserted (ref.17, copyright 2014 Wiley-VCH).

Some scientists mixed two or three strategies about structural design and functionalization mentioned above to improve the electrochemical properties. They formed multi-component electrode materials with complex 3D structures, such as nanohybrids of NiAl LDHs/MWNTs/Ni foam and carbon-coated $CoNi_3O_4$ nanoarrays with network-like structure on a stainless steel substrate (Fig. 7d).[17,38]

4.1.3 Other applications in energy

The oxides (NiO, Fe_2O_3, etc) of iron triad have been studied as photoelectrode materials in dye-sensitized solar cells (DSSCs), one kind of photovoltaic devices. More interestingly, the sulfides (NiS, CoS, etc) have been verified as prospective Pt-free counter electrodes (CEs), as they have high catalytic activities towards the redox couple of I^{3-}/I^- in DSSCs.[39] Yu et al. grew 3D nickel sulfide and cobalt sulfide hierarchical nanospheres on F-doped SnO_2 substrates as CEs for DSSCs, showing power conversion efficiencies of 6.81% and 6.59%, respectively, approaching an efficiency of 6.85% based on the sputtering Pt CE.[39]

Besides, iron pyrite (FeS_2) is an ideal abundant photovoltaic material that can substitute for silicon, which may accelerate the development of flexible cells and wearable devices. As FeS_2 is thermodynamically unstable, its functionalization becomes important. The researchers used trioctylphosphine oxide (TOPO) in the reaction system to modify the product and synthesized pyrite film with over-one-year air stability. It indicated the TOPO passivated both iron and sulfur atoms on the surface of FeS_2 naocrystals.[40]

The iron triad materials can also be used as electrocatalysts in fuel cells and metal-air batteries. The metal oxides NPs (Co_3O_4, Fe_2O_3, NiO, etc) supported on carbon materials could replace traditional expensive Pt catalysts for oxygen reduction reaction (ORR) in alkaline media. The component and the size of the NPs are the key factors for battery properties. Sun et al. synthesized a series of sub-10 nm NPs loaded on commercial carbon, among which $Mn_xFe_{3-x}O_4$ NPs showed comparable efficiency as commercial Pt catalyst.[41]

Obviously, the prepared oxide or sulfide nanopowder would be spin-coated on substrates in the form of 2D film to assemble devices. To eliminate the influence of particle dispersity, organic binder, and some operating techniques, we can grow directly the nanomaterials on suitable substrates for a better conductivity. Even we can design optimal structures providing high SSA and special exposed crystal planes. For example, Zhao et al. developed flexible mesoporous iron oxide nanopyramid arrays with a high SSA of ~175 m^2 g^{-1} on flexible Ti foil. The integration of plasmonic gold with 3D nanopyramids remarkably improves the performance of photoelectrochemical conversion.[42]

4.2. Adsorbents and nanocatalysts in environment

The iron triad adsorbents and nanocatalysts in environment concentrate on structures with high SSA and the adsorption sites, which can be enhanced by surface functionalization. The detailed examples would further talk about the importance of structural fabrication and functionalization.

4.2.1 Adsorption and degradation of harmful inorganic ions

Researchers have used iron group nanomaterials (Fe_2O_3, Fe_3O_4, FeOOH, etc) to remove toxic ions from waste water, in view of their environmental benignity, natural abundance, and low cost. Adsorption is one remarkable property considering their high SSA, rich adsorbing active species, and ideal components affording extra lone pairs of electrons to meet the unoccupied electronic levels of some metal ions. The component has a direct impact on the removal efficiency. For example, Zhang et al. reported the fast Cr(VI) removal from waste water by iron oxide submicron wires and confirmed most of the Cr(VI) was reduced by Fe(0) in Fe_2O_3 wires to Cr(III) rather than adsorption on wires.[43]

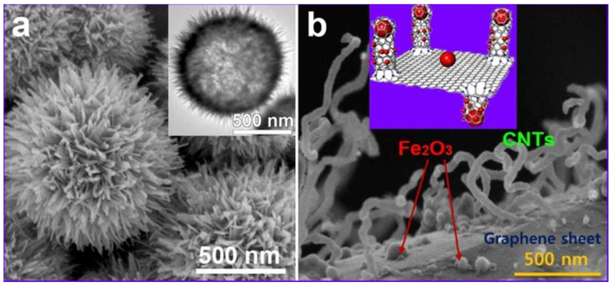

Fig. 8 (a) SEM and TEM (the inset) images of urchin-like α-FeOOH hollow spheres (ref.12, copyright 2012 Wiley-VCH), (b) 3D nanostructures with CNTs vertically grown on graphene and iron oxide NPs decorated. The corresponding structure model was inserted. (ref.15, copyright 2013 American Chemical Society).

Many pollutants such as heavy metal ions, radioactive waste, toxic gas, and organic dye molecules can be adsorbed and removed by choosing suitable nanostructures.[12,15] Mesoporous, hierarchical, and hollow structures, are usually used as their high SSA. Nowadays, continuous efforts have being made to prepare complex adsorbents with 3D nanostructures assembled by low-dimensional building blocks, which could give adsorption cavity, avoid aggregation of NPs, and remain long-time service life. The 3D structures can be directly prepared. For instance, urchin-like α-FeOOH hollow spheres were synthesized in quasi-micro-emulsion system with a high surface area of 96.9 m^2g^{-1} as shown in Fig. 8a, showing excellent water treatment performance towards organic dyes and heavy metal ions.[12] We can also combine extra materials (low-toxic, stable and high-SSA, such as CNTs and graphene) to fabricate 3D structures. Oh and his coworkers prepared 3D structures by CNTs standing on graphene sheets with iron oxide NPs decorated on both carbon materials (Fig. 8b), which showed excellent absorption for As(III) removal from contaminated water due to its high surface-to-volume ratio and the open pore network of the 3D nanostructures.[15]

Furthermore, to improve the adsorbing capability, organic functional groups, polymers, and some biomolecules rich in elements of N, C, O, S and X (X= Cl, Br, I) with lots of lone pairs could be modified on the surfaces of the adsorbents. Sometimes, iron oxide NPs were coated by silica for further covalently grafting. Harwood et al. synthesized neocuproine-functionalized SiO_2-coated maghemite NPs with an extraction efficiency of Cu(II), ~up to 99% from 12 ppm aqueous solution at pH=2.[44] Thanks to the fast development of CNTs and graphene, surface modification of carbon materials can be simply achieved by covalent linkage and non-covalent interaction (π-stacking).[45] Iron oxides NPs can also be immobilized on CNTs or graphene to prevent themselves from aggregation during adsorption.[2]

Using or mixing magnetic nanomaterials as absorbents for degradation of heavy metal ions or organic pollutants, a big reward is that we can apply magnetic separation instead of filtration or centrifugation for the collection of the adsorbents.[2,15]

4.2.2 Adsorbents and catalysts for organic pollutants

Fe(0) nanomaterials have been used in removing chlorinated hydrocarbons (4-chlorophenol, pentachlorophenol, phenol, etc.) for many years, not only as reducing agents but also as active agents to produce molecular oxygen in air by anaerobic removal. In order to prevent Fe(0) NPs from oxidization, Fe@Fe_2O_3 NPs were used instead.[46] Ni(0) nanomaterials are also popular in removing organic molecules (nitrophenol, nitrobenzene, etc.) by hydrogenation. Besides, iron oxide and cobalt oxide are common adsorbents and photocatalysts for the degradation of dye and other organic molecules (rhodamine B, methylene blue, isopropanol, etc.).[47]

Similarly to adsorbents, better catalysts should provide considerable contact interfaces with pollutants. Accordingly, nanostructures with high SSA are more suitable for nanocatalysts, and that is why so many tiny NPs, hollow, mesoporous and hierarchical nanomaterials were used as catalysts. Comparing with preparing complex hierarchical structures, a simple way is to mix (grow) nanocatalysts with (on) some kind of materials with high SSA (graphene is always the best choice).

Sometimes, other materials can be used to form multi-component heterostructure to improve catalytic properties. For example, Fe_2O_3/SnO_2 hollow particles fabricated by Kinkendall effect showed enhanced photocatalytic activity than pure Fe_2O_3 or commercial SnO_2, owing to the effective electron hole separation at the interfaces of Fe_2O_3 and SnO_2.[48] Nobel metals (Pt, Ag, Pd, etc.) are also used to form alloy NPs even polyhedrons to improve the catalysis of the iron triad. For example, Pt-Ni nanodendrites showed high hydrogenation activity while multiply twinned AgNi NPs showed excellent catalytic activity in reduction of 4-nitrophenol and 4-nitroaniline to amines. [49,50] Besides, ferromagnetic components (Fe, Co, Ni, Fe_3O_4 and γ-Fe_2O_3) play important role in collecting pollutants by magnetic separation.[3]

5. Conclusions and outlook

Iron triad nanomaterials show great potential in future industrialization due to their low cost, nature abundance, flexible synthesis, and versatile applications. In this review, we introduce typical approaches for fabricating three kinds of nanostructures with high specific surface area (hollow and porous structure, ultrathin 2D sheets, and complex 3D structures) based on iron triad nanomaterials (summary of SSA values for three typical nanostructures, see ESI), such as the galvanic replacement method and the nanoscale Kirkendall effect. Moreover, hybridization and surface functionalization, such as forming 3D complex structures and heterostructure hybrid nanomaterials, are summarized to further improve their properties and overcome their intrinsic disadvantages with better conductivity, enhanced structural stability, shortened electron-transfer path, or more adsorption sites for the applications in the fields of energy and environmental protection. Combing with recent intriguing work, these strategies are discussed and analyzed in detail. Energy and environmental protection are two hot issues nowadays. Studies on structures and functionalization will promote the further application of nanomaterials.

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Electronic Supplementary Information (ESI) available: list of abbreviations, details about the galvanic replacement reaction and the nanoscale Kirkendall effect, and summary of specific surface area (SSA) values for three typical nanostructures. See DOI:10.1039/b000000x/

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TUTORIAL REVIEW

Biography

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