

# (Super)paramagnetic nanoparticles as platform materials for environmental applications: From synthesis to demonstration

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## HIGHLIGHTS

- The fabrication of monodisperse, (super)paramagnetic nanoparticles is summarized.
- Monolayer and bilayer surface coating structures are described.
- Mono/bilayer coated nanoparticles showed high sorption capacities for U, As, and Cr.

## ARTICLE INFO

### Article history:

Received 27 January 2020

Revised 6 April 2020

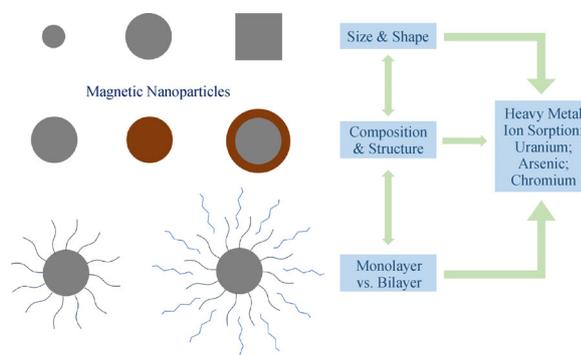
Accepted 6 April 2020

Available online 16 May 2020

### Keywords:

Superparamagnetic nanoparticles  
Surface functionalization  
Environmental sensing  
Heavy metal ion sorption

## GRAPHIC ABSTRACT



## ABSTRACT

Over the past few decades, engineered, (super)paramagnetic nanoparticles have drawn extensive research attention for a broad range of applications based on their tunable size and shape, surface chemistries, and magnetic properties. This review summarizes our recent work on the synthesis, surface modification, and environmental application of (super)paramagnetic nanoparticles. By utilizing high-temperature thermo-decomposition methods, first, we have broadly demonstrated the synthesis of highly monodispersed, (super)paramagnetic nanoparticles, via the pyrolysis of metal carboxylate salts in an organic phase. Highly uniform magnetic nanoparticles with various size, composition, and shape can be precisely tuned by controlled reaction parameters, such as the initial precursors, heating rate, final reaction temperature, reaction time, and the additives. These materials can be further rendered water stable via functionalization with surface mono/bi-layer coating structure using a series of tunable ionic/non-ionic surfactants. Finally, we have demonstrated platform potential of these materials for heavy metal ions sensing, sorption, and separation from the aqueous phase.

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## 1 Introduction

Access to clean drinking water remains a considerable global challenge (Ambashta and Sillanpää, 2010; Adeleye et al., 2016). In particular, the remediation of metals and metalloids, such as uranium and arsenic, among others, presents an urgent and challenging need (Ambashta and Sillanpää, 2010; Xu et al., 2012; Dave and Chopda, 2014).

In the United States, drinking water regulations provide enforceable maximum contaminant levels (MCL) for such elements (arsenic (10 µg/L) and uranium (30 µg/L)) (U.S. EPA, 2001; Li et al., 2016d). With this, a range of significant resource limitations/pressures require new methodologies and technologies to meet regulatory limits and resource demand(s).

It has been demonstrated that bulk magnetic metal oxide, such as iron oxides and manganese oxides, show high affinities for heavy metals, which makes them an ideal candidate for water treatment (Ambashta and Sillanpää, 2010; Tang and Lo, 2013). In addition to arsenic and uranium, other dissolved contaminants as well as benign species (e.g., phosphates, silicates) can be effectively

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Special Issue—Accounts of Aquatic Chemistry and Technology Research (Responsible Editors: Jinyong Liu, Haoran Wei & Yin Wang)

removed by adsorption to these metal oxide based materials (Chowdhury and Yanful, 2010; Yuan et al., 2010; Gupta et al., 2011). Despite these advantages, bulk metal oxide-based sorbents remain relatively underdeveloped at the commercial scale, especially with regard to maximizing sorbate sorption capacities, material control, interferences, and material cost(s).

Recently, developments in advanced materials, particularly at the sub-microscale, have increased the potential for such materials to impact the pathway of water treatment and environmental remediation in a number of ways (Tang and Lo, 2013; Wei et al., 2019; Gupta et al., 2020). Such materials, especially those with tunable size at the nanoscale, can be engineered to have unique properties including high surface area-to-volume ratio, tunable size, structure, and surface chemistry (Tang and Lo, 2013; Su, 2017). For instance, when compared with bulk counterparts, nanoparticles exhibit far higher sorption capacities due to specific surface area enhancement, which can be two to three orders of magnitude (Tang and Lo, 2013; Su, 2017). Another interesting aspect to be considered for metal oxide (e.g. iron oxide) is that when size decreases to the nanoscale, magnetic properties change significantly. Magnetism is generally defined by how materials respond to an externally applied magnetic field. There are five basic types of magnetism: diamagnetism, paramagnetism, ferromagnetism, ferrimagnetism, and antiferromagnetism (Cornell and Schwertmann, 2003). Diamagnetic materials display a weak repulsion to the applied magnetic field. In fact, most materials are diamagnetic. All the other types of magnetic behavior originate from the unpaired electrons in atomic shells, often in the 3d or 4f shells of the atom. Materials are defined as paramagnetic if the magnetic moment produced, partially aligns with, and further enhances, the applied magnetic field. Paramagnetic materials possess nonzero and non long-range order magnetic moments. Superparamagnetic materials have aligned magnetic moments in the presence of an external applied field but lose this orientation once the field is removed. Ferromagnetic materials have aligned atomic magnetic moments of equal magnitude and sustain a magnetic field even when no magnetic field is applied (i.e. permanent magnets). For antiferromagnetic materials, the equal atomic magnetic moments are aligned in an antiparallel fashion, thus, remaining no net magnetization. In ferrimagnetic materials, the antiparallel atomic magnetic moments are not equal in magnitude, leading to a net magnetization in the absence of external magnetic field. Vibrating sample magnetometry (VSM) and SQUID (superconducting quantum interference device) magnetometry are two common and powerful tools used to measure the sample's magnetism (Lu et al., 2007). In particular, superparamagnetic regimes are interesting as particles respond to an exerted magnetic field, yet they remain no magnetization when the external magnetic field is removed, which is ideal for magnetic separation and

recovery (Adeleye et al., 2016; Su, 2017). However, these properties strongly depend on particle size and atomic order (below 25 nm), and thus necessitate the precise synthesis control. Towards this, nanoparticles can be precisely engineered (e.g. size, density, morphology, surface coating strategies, etc.) for desired magnetic-based recovery applications (Trivedi and Axe, 2000; Hyeon et al., 2001; Wiltshire et al., 2001; Kim et al., 2008; Chandra et al., 2010; Hsu et al., 2010). In addition, for successful aqueous-based environmental applications, such nanoparticles should also have high stability/dispersity in relevant environmental matrixes. In this short review, we will detail successful strategies to address these challenges based on our recent research progress.

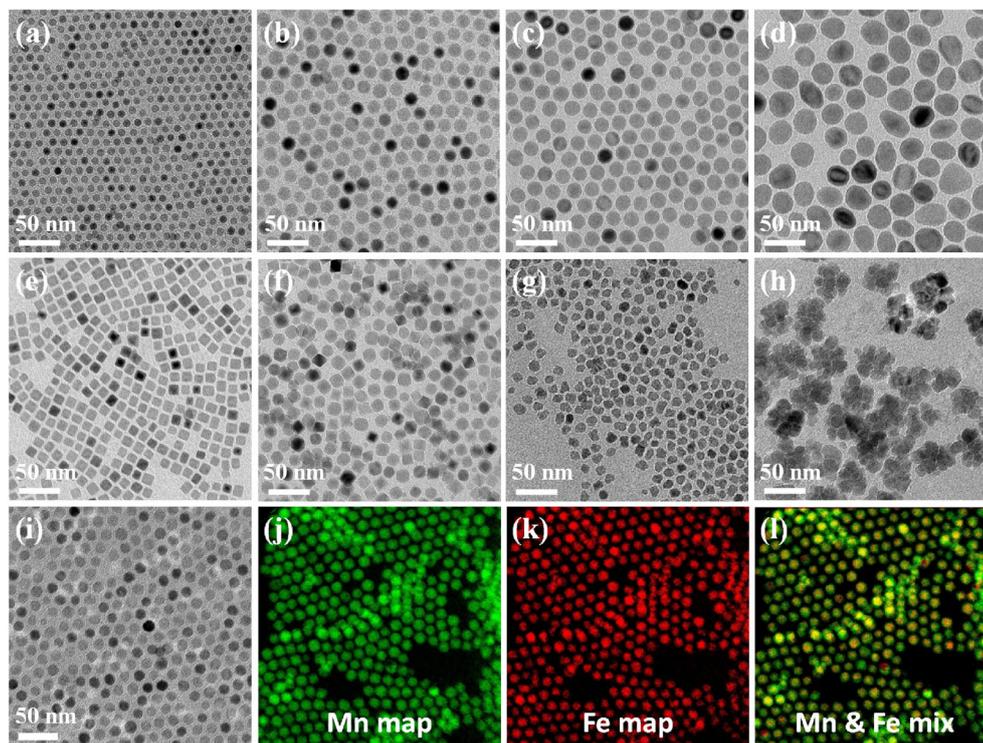
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## 2 Synthesis of (super)paramagnetic nanoparticles

Although most of magnetic nanoparticles can be obtained simply by top-down methods (e.g. mechanical grinding/milling), the product is often lack of size control and quality (i.e. consists of mixtures of phases) (Lu et al., 2007). Alternatively, a number of bottom-up synthesis methods for magnetic nanoparticles have been developed, such as chemical co-precipitation, microemulsion, thermal decomposition, and hydrothermal synthesis processes (Lu et al., 2007; Su, 2017). Take iron oxides for example, the most traditional way of producing magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles is via the coprecipitation of ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ) ions by a base in an aqueous solution. This approach, however, can lead to poor crystalline and/or polydisperse nanoparticles (Zhou et al., 2001; Li et al., 2005). Recently, organic phase decomposition of iron precursors at high temperatures has been pursued to yield high quality of monodisperse magnetic nanoparticles with controlled sizes and narrow size-distribution (Sun and Zeng, 2002; Yu et al., 2004; Park et al., 2005). As particle size is crucial for desired magnetic properties, thermal decomposition methods will be the focus for the synthesis of magnetic nanoparticles (Yavuz et al., 2006) as they allow for precise shape and size control that is reproducible. Material libraries, focused here on size (from 5 to 50 nm as diameters), composition (Mn, Fe, Co, and Ni), and shape (sphere, cubic, core-shell, etc.), of mono-, binary-, and ternary- nanocrystalline magnetic metal oxides can be achieved through high temperature metal precursor(s) decomposition in an organic media under varied reaction time, temperature, heating rates, metal precursor concentrations, and particular reaction additives (Fig. 1).

### 2.1 Iron oxide nanoparticles

Single domain, superparamagnetic iron oxide nanoparticles were synthesized via controlled thermal decomposition of iron carboxylate salts in mixtures of oleic acid/co-



**Fig. 1** Magnetic nanoparticles: (a–d) TEM micrographs of iron oxide nanoparticles with different sizes, (e–h) TEM micrographs of iron oxide nanoparticles with different shapes, and (i–l) TEM micrograph of core-shell structured iron oxide-manganese oxide with Gatan Image Filter (GIF) analysis shows mapping position of Mn/Fe. Reproduced with permission from refs. (Li et al., 2016c; Kim et al., 2018b).

surfactant and 1-octadecene (1-ODE) at 320°C (Yu et al., 2004; Li et al., 2016c). For a typical synthesis of spherical iron oxide nanoparticles, a certain amount of ferric hydroxide oxide (FeO(OH)) was mixed with oleic acid and 1-ODE and gradually heated to 320°C under the protection of Ar. Here, the FeO(OH) first reacted with oleic acid to generate iron oleate as the iron precursor, which then further decomposed at 320°C. The size of nanoparticles can be tuned from 6 to 30 nm by increasing the monomer concentration added to the reaction system. When 2 mmol FeO(OH) and 8 mmol oleic acid were added, the product size was 8 nm, while the addition of 5 mmol FeO(OH) and 20 mmol oleic acid led to the formation of 20 nm iron oxide nanoparticles. Once the burst nucleation step is completed, excess monomer acts as the building block for the continuous growth of nanoparticles (Li et al., 2016c; Li et al., 2017a).

Compared with the size control, engineering shape is not as well understood (Li et al., 2016c). Recently it was reported that additives, during synthesis, played an important role with regard to the final shape of product (Cabot et al., 2007; An et al., 2008; Koo et al., 2012). Through the inclusion of additives to the reaction system, iron oxide nanoparticles with other shapes, such as cube, octahedra, potato, and even flower-shape can be obtained (Li et al., 2016c). For instance, the inclusion of sodium

oleate, sodium decanoate, sodium myristate, and sodium stearate will generate cubic nanoparticles with sharp, faceted edges. For octahedral shape, 0.1–0.5 mmol trioctylammonium bromide (TOAB) can be added to the initial reaction system. The size of cubic and octahedral nanoparticles can be changed by varying the concentration of additives. Interestingly, the addition of L-arginine and L-arginine monohydrochloride results in iron oxide nanoparticles with irregular potato-like and flower-like shape, respectively (Li et al., 2016c).

## 2.2 Manganese oxide nanoparticles

Similarly, decomposition of manganese oleate in the presence of surface stabilizer (e.g. oleic acid) at high temperature forms monodisperse manganese oxide nanoparticles. In contrast to the synthesis of iron oxide nanoparticles, where iron oleate was in situ generated from the reaction of ferric hydroxide oxide with oleic acid at 200°C, manganese oleate was first prepared by reacting manganese salts with oleic acid in the mixture of ethanol, water, and hexane (Lee et al., 2015a). The rest of the preparation method is similar to that of iron oxide nanoparticles described above, whereby a certain amount of manganese oleate and oleic acid were added to high boiling point organic solvent (e.g. 1-ODE) and cooked at

high temperature. When reaction temperature increased from 290°C to 320°C, the particle size increased from ca. 7 nm to 12 nm accordingly. The concentration of precursor, the ratio of surfactant to manganese oleate, and reaction time are all critical variables with regard to final particle size. Manganese oxide nanoparticles with sizes from 12 nm to 28 nm can be obtained by carefully adjusting these reaction parameters (Lee et al., 2015a).

### 2.3 Ferrites nanoparticles

Libraries of monodisperse magnetic ferrite ( $MFe_2O_4$ : ferrites;  $M = Mn, Co, Ni, \text{ and } Zn$ ) nanoparticles can also be precisely synthesized through thermal decomposition of transition metal precursor(s) with mixed ratios and/or doping (ionic metal salts and organometallic precursors) in organic solvents (Liu et al., 2000a; Liu et al., 2000b; Chinnasamy et al., 2001; Hyeon et al., 2002; Kang et al., 2004; Sun et al., 2004; Zeng et al., 2004; Ashiq et al., 2011). Depending on desired ferrite compositions, serial libraries of monodisperse binary or even ternary metal oxide nanoparticles with varying size from 5 to 50 nm ( $\sigma < 10\%$ ) can be synthesized (Yu et al., 2004; Lee et al., 2012; Lee et al., 2015b; Kim et al., 2020). For instance, the mixture of iron and manganese oleate precursors results in the formation of manganese iron oxides (ferrites). By changing the ratio of iron oleate to manganese oleate, either iron-rich or manganese-rich ferrite can be produced (Lee et al., 2015b). For ternary metal oxide synthesis, such as the preparation of cobalt nickel iron oxide nanoparticles, the combination of cobalt, nickel, and iron precursors were mixed and heated in a similar way (Kim et al., 2020).

### 2.4 Core-shell nanoparticles

Additionally, a simple metal precursor addition in the presence of starting seed nanomaterials (iron oxides) at high temperatures (over 300°C) in organic solvent, can result in core-shell structured nanoparticles (Kim et al., 2018b). Here, starting seed material concentration in organic media has been found to be crucial for the formation of reproducible core-shell nanostructure. Depending on the ratio of manganese oleate to iron oxide seeds, the Mn/Fe ratio in the produced core-shell nanoparticles ranges from 0.28 to 0.73. The resulting core-shell structured magnetic metal oxides showed altered physicochemical and magnetic properties induced by structural and compositional characteristics (Kim et al., 2020).

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## 3 Surface functionalization

As aforementioned materials are synthesized in organic solvents, they possess an outer layer terminating in organic

moieties (e.g. oleic acid), which limits the direct application in aqueous environment (Lu et al., 2007; Hao et al., 2010; Li et al., 2016a). Without a passivating layer, nanoparticles tend to agglomerate due to the large specific surface area and high surface energy (Tang and Lo, 2013). Therefore, it's imperative to transfer and stabilize these particles in aqueous phase via appropriate surface coatings, as the stability of magnetic nanoparticles is crucial to maintain desired physical and chemical properties. Generally, there are four types of forces that govern the particle stability in the solution: van der Waals forces, electrostatic forces, magnetic dipolar forces, and steric repulsion forces (Laurent et al., 2008; Tang and Lo, 2013). Thus to prevent the agglomeration of particles, an increase in the electrostatic repulsion or/and steric stabilization forces by means of surface coating/modification is required (Faraji et al., 2010). Through balancing the attractive and repulsive forces, stable nanoparticles in aqueous suspension can be successfully accomplished.

Nanoparticles can be coated during the synthesis process, with the tradeoff that particle growth will be limited. There are also post-synthesis coating approaches, including polymer grafting or incorporation of additional surfactant(s) onto particle surfaces immediately after synthesized (Ngaboni Okassa et al., 2005; Lu et al., 2007; Hao et al., 2010). Nanoparticle surface coatings can be simply classified as organic coatings, which include surfactants and polymers, and inorganic coatings, typical examples of which are metal oxides, precious metals, silica, and carbon (Lu et al., 2007; Tang and Lo, 2013; Dave and Chopda, 2014). Through modification of surface chemistry (coatings and functional groups), these particles can remain monodispersed and stable in water, as demonstrated previously (Li et al., 2016a). For this, we have successfully demonstrated a number of coating strategies, including organic-based monolayer and bilayers. Examples are shown in Fig. 2.

### 3.1 Monolayer coatings

Sterically stable, hydrophilic nanoparticles have been achieved using polyethylene glycol (PEG) and polyethyleneimine (PEI) (Lee et al., 2015a; Pan et al., 2019). The introduction of PEG and PEI replace the original oleic acid layer around the nanoparticles; thus, the particle cores are fully warped with the hydrophobic and hydrophilic groups from PEG and PEI, resulting in a monolayer coating structure. PEG with molecular weight (MW) of 200, 1K, and 10K have been demonstrated for the phase transfer of nanoparticles, with transfer yields over 60%. After phase transfer into water and purification, dynamic light scattering (DLS) was used to measure the hydrodynamic size of these nanoparticles. The hydrodynamic sizes of PEG 200, PEG 1K, and PEG 10K coated 12 nm manganese oxide nanoparticles were 21.5 nm, 31.5 nm, and 46.6 nm,



suspensions has been evaluated as a function of surfactant chain length, functional group, surface charge, etc. The hydrodynamic size of mono or bi-layer coated nanoparticles showed negligible change within 3 months, and particles remained stable for up to 1 year, highlighting the developed mono/bi-layer coating strategies are effective and robust method platform for aqueous-based nanoparticle surface modification (Li et al., 2014; Lee et al., 2015a; Li et al., 2016a).

## 4 Environmental applications

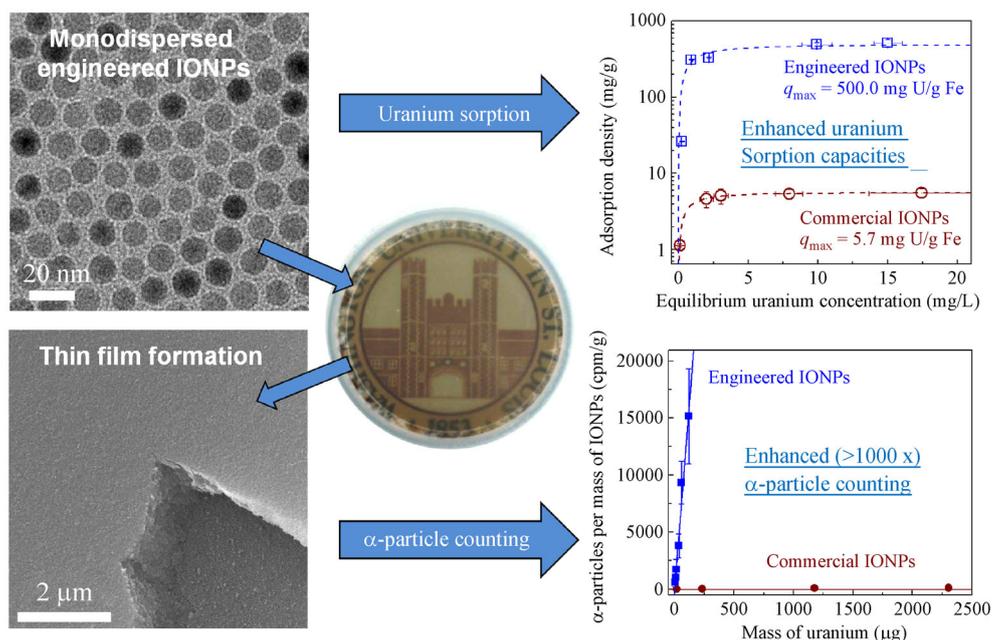
The vision of applying engineered nanoscale materials as platform materials to address environmental challenges is compelling. Here, we briefly explore recent reports of engineered magnetic particles for environmental sensing and the treatment of metal/metalloids in water.

### 4.1 Environmental sensing

Selective sorption, magnetic separation, and sensing strategy for radionuclide (e.g. uranium) have been developed and demonstrated using truly tunable, combinatorial magnetic nanoparticles. The approach described here centers on superparamagnetic, nanocrystalline iron oxide nanoparticles with variable (tunable) surface coatings, to bind and separate water-stable uranium species (as uranyl,  $\text{UO}_2^{2+}$ ) and complexes from solution(s) (Fig. 3) (Li et al., 2016d). First, the high surface area to volume ratios of the oleic acid bilayer coated nanoparticles coupled with favorable enthalpic surface interactions allow for enhanced

sorption capacities (ca. 50 wt.% sorption capacity), compared with polydisperse, aggregated commercial iron oxide materials (0.6 wt.% sorption capacity). Second, the (super)paramagnetic properties of the core materials facilitate low-field magnetic separation of these materials from heterogeneous and complicated aqueous matrixes. During the final separation step, high particle stability leads to homogenous, sub-micron films, which can minimize radiation ( $\alpha$ -particle) self-absorption (shielding), thus allowing for optimized sensitivity/detection with a hand-held Geiger counter (in the case of radioactive materials) (Li et al., 2016d). Further, such films can also be analyzed via (field deployable) X-ray / fluorescence / Raman-based techniques, among others, for non-radioactive analytes. As a result, the detection sensitivity for uranium has increased by a factor of 1000 compared with a bulk approach. These advantages have also been clearly demonstrated for real world samples for the case of low-level uranyl sensing (Li et al., 2016d).

While such reports are certainly promising, the ultimate success for such a material-based approach to environmental uranium (and other metal/radionuclide) separation and analysis will depend on whether the sorption capacity remains high under more complicated (realistic) water and soil conditions. In addition to favorable enthalpic interactions with target species, overall material stabilities under field conditions will be equally as important, especially when considering recovery processes. Environmental samples contain a range of interfering constituents (NOM, ions, and etc.) and solid phases that could, in principle, affect the concentration factors through a variety of mechanism (Li et al., 2016d; Li et al., 2017a).



**Fig. 3** Monodispersed iron oxide nanoparticles for uranium sorption, separation, and low-level sensing using a hand-held Geiger counter. Reproduced with permission from ref. (Li et al., 2016d)

## 4.2 Metal and metalloid treatment

For magnetic nanoparticles investigated, such as iron oxide, manganese oxide, and ferrites, all have shown high sorption capacities toward uranium, once the optimized material design is achieved (Lee et al., 2015a; Lee et al., 2015b; Li et al., 2016b; Li et al., 2017a; Kim et al., 2018b). The surface coating is demonstrated to greatly affect the uranium (here as uranyl cation,  $\text{UO}_2^{2+}$ ) sorption capacity. For 12 nm manganese oxides, PEG monolayer coated particles exhibited lower uranium sorption capacity (227.3 mg/g) compared with that of bilayer coated particles (256.4 mg/g to 625.0 mg/g) at/under pH 5.6 (Lee et al., 2015a). For bilayer coated nanoparticles, coating structures (saturated vs. unsaturated, chain length, and head group) from the second layer play a vital role on the uranium sorption capacity (Lee et al., 2015a; Lee et al., 2015b; Li et al., 2017a). It was found that generally unsaturated fatty acid coated particles had higher sorption capacity compared with saturated fatty acid coated particles, due to the enhanced particle stability (at higher ionic strengths). Particles coated by fatty acid with longer chain lengths exhibited higher sorption capacity compared with particles coated by fatty acid with shorter chains. Among carboxylate, sulfate, hydroxyl, quaternary ammonium, and phosphate head groups, a second chain with the negatively charged phosphate group resulted in nanoparticles with the highest uranium sorption capacities (Lee et al., 2015b; Li et al., 2017a). When normalized for the same coating, nanoparticles with smaller core size exhibited higher uranium sorption capacity compared with larger particle – based on enhanced surface area. Further, a comparison between unary and binary/ternary metal oxides suggests the importance of nanocomposite hybridization on uranium sorption. Fe-rich manganese ferrite nanoparticles demonstrated higher sorption capacity than Mn-rich manganese ferrite, manganese oxide, and iron oxide nanoparticles (Lee et al., 2015b; Kim et al., 2018b).

Unlike U(VI) which exists as cationic forms under oxic condition, As(V) and Cr(VI) are usually found in their anionic forms. Nanoparticles with positively charged surface (e.g. PEI or CTAB) demonstrated higher affinity toward As(V) and Cr(VI) compared with nanoparticles with negatively charged surface, which is attributed to the favorable electrostatic interactions between coating and contaminants of concerns (Kim et al., 2018a).

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## 5 Implications

In this review, we have presented recent findings on the synthesis, surface modification of a spectrum of magnetic nanoparticles, followed by their application for environmental sensing and heavy metal removal. Reproducible synthesis of monodisperse magnetic nanoparticles is

critically important as the physicochemical properties depend strongly on their size, order, and dimensions. Non-hydrolytic routes were chosen to synthesize highly crystalline magnetic nanoparticles, allowing for particle size and morphology to be precisely controlled via changing ratio of precursor, organic additive, reaction time, etc. Nanoparticles can be subsequently rendered water dispersible (stable) via newly developed phase transfer strategies using a series of surface engineered monolayer or bilayers, which can be systematically varied with regard to hydrophobic tail (size and properties) and polar head groups. The tunable core materials in addition to the flexible outer surface design, allow for customized strategies for a variety of environmental applications. Highlighting this potential, engineered magnetic nanoparticles demonstrated ultra-high sorption capacities for uranium, arsenic, and chromium. Taken together, this short review provides fundamental understanding that directly expands the current state of the art for engineered magnetic nanoparticles and corresponding behavior, and thus potential environmental application in aqueous systems. Ultimately though, performance optimization, in pilot-scale operations and field-scale demonstrations, is needed to evaluate the technoeconomic feasibility (Jiang et al., 2020). Continued research into this material platform will further improve basic chemical-physical guidelines and corresponding material properties, resulting in attractive performance regimes for advanced environmental sensing and separation technologies, among others.

**Acknowledgements** This work was supported by American Chemical Society's Petroleum Research Fund (#52640-DNI10), the US National Science Foundation (CBET, #1236653 and #1437820), and US Army Corps of Engineers (W912HZ-13-2-0009-P00001).

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