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Cetyltrimethylammonium bromide – Oleic acid (CTAB-OA) bilayer coated iron oxide nanocrystals for enhanced chromium (VI) photoreduction via ligand-to-metal charge transfer mechanism



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ABSTRACT

Photoactive cetyltrimethylammonium bromide-oleic acid (CTAB-OA) bilayer coated iron oxide nanocrystals (IONCs) were precisely synthesized and demonstrated for photo-enhanced hexavalent chromium (Cr(VI)) treatment. For these materials, an outward facing, CTAB layer offers specific affinity for Cr(VI), while the core IONC (8-25 nm, as Fe₃O₄ single domain) surface participates in Fe(II)/Fe(III) redox cycling. Further, at the coating-particle interface, the OA layer alters material photoactive dynamics (near UV and visible light) via a ligand-to-metal charge transfer (LMCT) mechanism, significantly enhancing Cr(VI) reduction. To delineate process variables, we first quantified photo-catalytic Cr(VI) reduction rates under UVA irradiation (sunlight mimic intensities) as a function of IONC core size, which correlates with the amount of surface available ferrous ion (Fe(II)). It was observed that 25 nm CTAB functionalized IONC showed outstanding Cr(VI) sorption and photoreduction performance compared with other IONC explored and controls (e.g. TiO2 nanocrystals). We systematically explored the photoreduction mechanism(s) through a matrix of control experiments, considering solution pH, dissolved gas (air, O₂, and CO₂), along with hydroxyl and superoxide radicals. Results indicate that Fe(II) (at the IONC interface) acts as the primary Cr(VI) reductant and that Fe(III) (oxidized from Fe(II)) (re) cycles via a photocatalyzed pathway. Taken together, this work presents a clear physical and mechanistic description of CTAB-OA bilayer IONCs which, when optimized, are highly effective for Cr(VI) treatment under UVA irradiation. In addition to potential broad application for other contaminant targets that are reactive with Fe(II), which are many, this work also highlights the need for precise interfacial understanding of nano composite materials towards process optimization.

1. Introduction

Environmentally relevant chromium (Cr) oxidation states are Cr(0), Cr(III), and Cr(VI) [1]. While Cr(III) is the most common form naturally existing, Cr(0) and Cr(VI) occurrence and exposure are typically observed as a function of anthropogenic activities [1–3]. Cr(VI) treatment has received wide industry interest and regulatory attention due to realtively high aqueous solubility, thus mobility, along with strong evidence of negative health effects [4–6]. For Cr(VI) treatment, a number of processes have been explored and demonstrated including membrane filtration, adsorption (including ion exchange), and redox reactions [7–12].

Considering advanced water treatment processes, a potential feasible

treatment option is a photo-Fenton redox-based process, in the presence of hydrogen peroxide (H_2O_2), ferrous ion (Fe(II)), and UV radiation [13]. For this reaction, Fe(II) is used as a catalyst, and its oxidation (to ferric iron (Fe(III)) is the rate-governing step [14]. Hydroxyl radial (·OH) and superoxide (O_2 ·) can also act as reactive intermediates, as they have been reported to occur during Fe(II)/Fe(III) photoreduction cycling under UV irradiation. Interestingly, ligand-to-metal charge transfer (LMCT) processes have been demonstrated to shift interfacial photo activity toward the visible spectrum. In particular, ferric carboxylate complexes, comprised of an iron species with low-molecular weight carboxylic acids (LMWCAs) including citric-, oxalic-, and malic acids, among others, have been demonstrated to facilitate LMCT [15]. Based on this phenomena, solid state photo-Fenton reactions, utilizing

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Fig. 1. TEM micrographs and size histograms of synthesized iron oxide nanocrystals (IONCs). TEM-based diameter measurements were (a) 8 nm, (b) 12 nm, (c) 19 nm, and (d) 25 nm.

magnetite/carboxylate-rich carbons (MCRCs), have been proposed and demonstrated [16,17]. Such an approach (i.e. solid state based) has advantages in terms of packaging and reaction control (stability) at circumneutral pH [16,17]. In contrast, for Fenton reactions in water, solution pH must be low (below 4) to prevent oxyhydroxide precipitation [18,19].

Engineered, monodispersed, iron oxide nanocrystals (IONCs), including single domain Fe₃O₄, have been widely proposed for numerous advanced applications such as magnetic resonance imaging (MRI) contrast agents, drug delivery, and bioseparations, among others, due to low toxicity and unique magnetic properties [20,21]. For environmental applications, IONCs have been demonstrated for broad treatment technologies, for which commercial scale-up is feasible due to low material cost(s) [22]. More recently, organic (surface) functionalized IONCs have been developed and investigated for environmental applications, allowing for a number of advantages compared with uncoated materials [23–27]. Organic coatings can be tuned with deliberate functionality to provide additional/favorable binding sites for target contaminants (i.e. specificity) [24–26]. Further, such coatings also have been demonstrated to stabilize nanocrystal core with regard to dissolution and significantly improve colloidal stability (thus high surface-tovolume ratios) by creating an electrostatic double layer (EDL) and elastic-steric repulsion [24,28,29]. Despite these potential material advantages, to date, few studies have reported IONCs themselves as photocatalysts [30-32]. Specifically, ligand-to-metal charge transfer for enhanced Fe(II)/Fe(III) photoreduction cycling under sunlight irradiation (i.e. red shifted), via IONC surface associated carboxyl groups, has

not been evaluated for pollutant reduction/treatment despite considerable application potential [16,17].

In this work, we explore such potential, evaluating organic surface functionalized (carboxylate-rich) IONCs to reduce Cr(VI) through an enhanced Fe(II)/Fe(III) photoreduction cycle under UVA irradiation. For this, a bilayer coating was designed with the first, (inner) surface layer, to consist of oleic acid, aligning carboxyl groups at the crystal interface, with the goal of altering light absorption properties, via a LMCT mechanism. The second layer is comprised of cetyltrimethylammonium bromide (CTAB) with a net positively charged quaternary amine group (facing outward), offering strong affinity for Cr(VI) anions (above pH 2.2), thus creating a high concentration gradient at the particle interface. The CTAB-OA bilayer was stabilized by hydrophobic tail-tail overlap. Cr(VI) photoreduction performance and mechanism(s) were explored for precisely synthesized core IONCs (8, 12, 19, and 25 nm) by controlling the dissolved gas (i.e. air, oxygen, and CO₂), hydrogen peroxide, hydroxyl radical, and superoxide radical concentrations. Results indicate that Fe(II) (on the surface) acts as the primary Cr(VI) reductant, and that Fe(III) (oxidized from Fe(II)) (re)cycles via LMCT photoreduction under UVA irradiation through a superoxide radicalbased reaction. LMCT phenomenon is observed at the OA-NC interface, shifting the photoactivity, thus enhancing reduction rates. IONC core size was determined to be critical, as larger NCs have a higher relative abundance of surface stable Fe(II).



Fig. 2. IONC characterization. (a) The oxidation state of iron (Fe) on the surface of IONCs (8, 12, 19, and 25 nm) as measured by 2P iron binding energy (via XPS). (b) Tauc plots with linear extrapolation (dashed line) of the four different IONC sizes (8, 12, 19, and 25 nm). (c) Number of surface associated molecules for 25 nm IONC@SDS and four different sizes (8, 12, 19, and 25 nm) of IONC@CTAB.

2. Materials and methods

2.1. Materials

The chemicals including iron oxyhydroxide (FeOOH), oleic acid (OA, 90% and 99%), 1-octadecene (1-ODE, technical grade, 90%), cetyl-trimethylammonium bromide (CTAB, 95%), sodium dodecyl sulfate (SDS, 99%), ethanol (99.9%), acetone (99.5%), hexane (98.5%), hydrogen peroxide solution (H₂O₂, 30%), tert-butanol (99.7%), super-oxide dismutase bovine recombinant (expressed in E. coli), and potassium chromate (K₂Cr₂O₇) were purchased from Sigma-Aldrich. TiO₂ NCs (AERODISP® W 740 X, 70 nm) and SiO₂ NCs (SISN20, 22 nm) were purchased from Evonik Industries and NanoComposix, respectively. The ultra-high purity (UHP) grade argon (99.999%), N₂ (99.999%), CO₂ (99.999%), and Air (95% N₂ and 5% O₂) was purchased from Airgas Inc.

2.2. Iron oxide nanocrystals (IONCs)

Highly monodisperse IONCs were synthesized by decomposition of iron oxyhydroxide (precursor) with OA (surfactant) in the 1-ODE (solvent) at 320 °C under argon gas purging condition [33–35]. The surface of synthesized IONCs was organic functionalized by encapsulation methods using CTAB and SDS [33,35–37]. Synthesis and encapsulation method details were described by our previous studies and others [33–37].

2.3. Cr(VI) photoreduction experiment

The Cr(VI) photoreduction experiments were performed in the customized reactor with two side monochromatic UVA irradiation ($\lambda =$ 351 nm, BHK Inc). Intensity of each lamp was fixed to $950 \pm 50 \,\mu\text{W/cm}^2$. Heat was controlled with reactor installed four fans. We used a customized quartz bottle (Technical Glass Products) with 20 mL of test sample at room temperature (20.0 \pm 1.0 °C). The initial Cr(VI) concentration was 10 ppm, and test solution pH was adjusted using HNO₃ and NaOH. For gas purging conditions (closed system), each quartz bottle was sealed with Teflon crimp-sealed caps (Wheaton Industries Inc.). The Cr(VI) concentration was measured using a UV-vis spectrophotometer (Varian Bio 50), as presented in Fig. S1 [38]. Kinetic data sets were supported by several parallel experiments (performed at least in duplicate, but with slightly varied sampling times), and thus presented as representative data sets, as noted. For all kinetic data sets using synthesized IONCs, experimental variability (experimental error by rate constant) was less than 7.2% for identical reaction conditions. Experimental error of kinetic data sets for TiO2 NCs and SiO2 NCs was 13.8% and 8.7%, respectively. Total Cr concentration was measured in triplicate by using an inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima 7300DV).

2.4. Characterization of NCs

The hydrodynamic diameter and zeta potential were measured at least five times using a Zetasizer Nano ZS (Malvern) in the presence of 1



Fig. 3. Kinetic data, as $\ln(C_0/C)$ versus time, for a matrix of experimental variables. (a-b) 64 ppm of NCs (25 nm IONC@CTAB and 25 nm IONC@SDS, commercial TiO₂, and SiO₂) and a blank (without NCs) at pH 5.0 under (a) UVA irradiation and (b) the dark. (c) Role of pH (5.0, 7.0, and 9.0) using 25 nm IONC@CTAB (64 ppm) under UVA irradiation and dark. (d) Varying 25 nm IONC@CTAB concentration under UVA irradiation and dark. All experiments were performed in an open system with 10 ppm of initial Cr(VI). Experimental error of kinetic data sets for all IONCs, TiO₂ NCs, SiO₂ NCs was less than 4.5%, 13.8% and 8.7%, respectively.

mM NaCl at 22 °C. Transmission Electron Microscope (TEM, Tecnai G2 Spirit, FEI) size was obtained using Image Pro Plus 6.0 software (Media Cybernetics) by counting over thousand particles [39]. Total Organic Carbon (TOC) was measured in duplicate with a TOC analyzer (Shimadzu Scientific Instrument). X-ray Photoelectron Spectroscope (XPS) analysis was conducted using XPS spectrometer PHI 5000 VersaProbe II Scanning ESCA Microprobe (Physical Electronics). The band gap energy (E_g) was measured using a UV–vis spectrophotometer (Varian Bio 50) with Tauc's relation ($(\alpha h\nu)^2 = h\nu - E_g$); where α is the absorption value in the UV–vis spectrum, h is the Plank constant, and ν is the frequency [40].

3. Results and discussion

3.1. Synthesis and characterization

Monodisperse IONCs were synthesized through the thermal decomposition of ferric oxyhydroxide in organic solvent at 320 °C [33,35]. IONC size was precisely controlled by the ratio of iron precursor to oleic acid (OA), which surface stabilized the particles (OA hydrophobic tail outward into the organic solvent). As presented in Fig. 1, as prepared IONC size ranges were 7.9 ± 0.9 , 12.3 ± 1.0 , 18.7 ± 1.0 , and 24.8 ± 1.4 nm, respectively, as single domain magnetite (Fe₃O₄) [23,37]. Particle surface composition and corresponding oxidation state was characterized via XPS with results shown in Fig. 2a. It was observed that only the outermost (atomic layer(s)) Fe(II)/Fe(III) ratio varied depending on IONC size, as the core structures remain identical, as magnetite (Fe₃O₄) [41]. As a function of increasing particle diameter, the Fe(II)/Fe(III) ratio was observed to increase: 0.06, 0.59, 0.75, and 2.28 for 8, 12, 19, and 25 nm IONCs, respectively. This observation is consistent with Park et al. who reported that synthesized IONCs are more surface Fe(II) rich as a function of NC size [41]. NC band gap properties vary as a function of composition, crystalline structure, and size, due to quantum confinement and it is well known that nanoscale magnetite has a small band gap of ca. 0.2 eV at the Fermi level, which is equivalent to ca. 6200 nm wavelength [42-45]. As synthesized, the first organic layer of IONC is OA, which when coordinated with the carboxylic acid group at the iron oxide interface, alters (net) material light absorption within the UV to visible light range (200-700 nm) [16,17]. For these, optical band gap (E_q) measurements are presented using a Tauc plot with linear extrapolations (Fig. 2b). The E_g of IONC (8 to 25 nm) was in the range of 3.15-3.0 eV (394-413 nm), decreasing slightly with increasing particle size, as expected [46,47].

The second layer of the organic bilayer coating was explored with positively charged cetyltrimethylammonium bromide (CTAB) and negatively charged sodium dodecyl sulfate (SDS) via ligand encapsulation method [36,37]. The bilayer organic structure consists of a hydrophilic head group (of the surfactants) facing outwards, into the aqueous phase. In water, the hydrodynamic diameter (D_H), as measured by dynamic light scattering (DLS), for bilayer stabilized particles was 22.7 \pm



Fig. 4. (a-b) Kinetic data, as $ln(C_0/C)$ versus time, for 64 ppm of 8, 12, 19, and 25 nm IONC@CTAB with 10 ppm of Cr(VI) in an open system, under UVA irradiation and dark. (a) Initial pH was adjusted to 5.0 using HNO₃ and NaOH. (b) pH was fixed to 5.0 using an acetate buffer. For all, experimental error was less than 4.5%. (c) Oxidation state of iron (Fe) of 25 nm IONC before and after the experiments as measured by XPS (2P iron binding energy).

1.5, 26.2 \pm 3.4, 31.4 \pm 2.6, and 33.8 \pm 1.9 nm for CTAB functionalized 8, 12, 19, and 25 nm core IONC (IONC@CTAB), respectively, and 33.3 \pm 1.0 nm for SDS coated 25 nm IONC (IONC@SDS). Zeta potential for 8, 12, 19, and 25 nm IONC@CTAB and 25 nm IONC@SDS was measured to be 35.4 \pm 0.7, 35.5 \pm 2.0, 36.7 \pm 1.0, 38.1 \pm 1.0, and $-26.9 \pm$ 3.3 mV, respectively. Additionally, the number of organic molecules per IONC was measured by TOC. Surface loadings for 8, 12, 19, and 25 nm IONC@SDS were 780 \pm 160, 4,670 \pm 480, 26,420 \pm 5,170, 102,650 \pm 12,630, and 116,520 \pm 740 molecules per NC, respectively (Fig. 2c), increasing with IONC diameter. This is due to relative steric hindrance easing (comparatively less surface curvature) when the NC size is increased (i.e. relatively flatter), as discussed previously [48,49].

3.2. Cr(VI) photoreduction

Cr(VI) photoreduction performance was explored with 25 nm IONCs (IONC@CTAB and IONC@SDS), a positive control (70 nm sphere shaped TiO₂ particle), and negative control (22 nm sphere shaped SiO₂ particle), for 64 ppm of NC (pH 5.0 \pm 0.1) under both UVA irradiation and dark. Observed reaction rates are first order, showing linear ln(C_0/C) as a function of time (Fig. 3a). Under UVA, IONC@CTAB (positively charged) demonstrated considerably enhanced Cr(VI) photoreduction compared to other materials; rate constants for IONC@CTAB, IONC@SDS, and TiO₂ NCs were 0.018, 0.00040, and 0.0015 min⁻¹, respectively. In contrast, for negative controls and blanks, observed

rates were minimal. In addition to favorable surface chemistry, colloidal stability is a crucial aspect, as a surface-based reaction is proportional to the available surface area. Here, both synthesized IONCs (IONC@CTAB and IONC@SDS) maintained their initial D_H after observed reactivity, due to high steric repulsion, as observed previously [28,29,50,51]. Control materials, TiO₂ and SiO₂ NCs showed significant aggregation (up to 1750 nm and 1047 nm, respectively). In the dark (absence of UVA), Cr(VI) sorption was also explored (Fig. 3b). Here, Cr(VI) sorption performance for positively charged IONC@CTAB was significantly higher than negatively charged IONC@SDS, SiO₂ NCs (-7.9 mV), and TiO₂ NCs (4.8 mV). As Cr(VI) exists as an anionic form over the pH range of interest (above pH 2.2) and preferentially associates with oppositely charged (positively) surfaces [52–54]. This affinity is also hypothesized to enhance (photo)reduction processes, based on high(er) surface Cr concentration gradients.

The effect of solution pH was explored with 25 nm IONC@CTAB (64 ppm) at pH 5.0, 7.0, and 9.0 (Fig. 3c). In the absence of UVA irradiation (dark), Cr(VI) sorption for IONC@CTAB decreased with increasing solution pH. Effective Cr(VI) removal (C/C_0) was 0.58, 0.28, and 0.21 at pH 5.0, 7.0, and 9.0, respectively over 500 min. As the pH of the solution increased, the zeta potential of 25 nm IONC@CTAB decreased: 38.1, 30.0, and 16.6 mV at pH 5.0, 7.0, and 9.0, respectively, and thus enhanced electrostatic interaction improved Cr(VI) sorption at lower pH values. Photocatalytic reduction of Cr(VI) also increased with decreasing pH: 0.018, 0.0035, and 0.0025 min⁻¹ at pH 5.0, 7.0, and 9.0, respectively. In addition to higher Cr surface concentrations, we



Fig. 5. (a-c) Kinetic data, as $\ln(C_0/C)$ versus time, for 64 ppm of 25 nm IONC@CTAB and 10 ppm of Cr(VI) under the UVA irradiation at pH 5.0. (a) Reactions were explored as a function of H_2O_2 concentration (0, 0.5, 5.0, and 10 ppm) in an open system. (b) Reaction rates with or without H_2O_2 (0 and 10 ppm) and tert-butanol (0 and 1.0 %) in an open system. (c-d) Reaction rates in an open system with or without superoxide scavenger, and in a closed system considering three headspace (purged) gases (as N_2 , CO_2 and Air (95% N_2 and 5% O_2)). Experimental error for all was less than 7.2%. (d) Percentage of Cr(III) insolution and on the surface of 25 nm IONC@CTAB after reaction under UV irradiation.

hypothesize that higher proton concentration (acidic conditions) enhances reduction processes, as observed by others [55-58]. We also explored the role of IONC concentration in the presence and absence of UVA at pH 5 using 16, 32, and 64 ppm of 25 nm IONC@CTAB (Fig. 3d). For all, Cr(VI) removal performance was linearly related to ION-C@CTAB concentration (Fig. S2).

To better understand the role of IONC size, 8, 12, 19, and 25 nm IONC@CTAB suspensions were evaluated under UVA and dark at pH 5.0, with the same NC concentration (64 ppm). Presented in Fig. 4a, size of IONC did not significantly affect Cr(VI) sorption in the dark though the total surface of NCs increases with decreasing the size. The Cr(VI) removal (C/C₀) for 8, 12, 19, and 25 nm IONC@CTAB was 0.55, 0.58, 0.44, and 0.59 for 500 min, respectively. We attribute this to the fact that despite having lower surface area, larger NCs have higher grafting density, and thus a sorption capacity tradeoff, as presented in Fig. 2c. In our previous study, we also reported the higher CTAB grafting density for larger NC [35]. For these, under UVA, 25 nm IONC show enhanced photocatalytic reduction of Cr(VI) compared to other NC sizes. Pseudo first order reaction rate constants for 8, 12, 19, and 25 nm IONC@CTAB were 0.0029, 0.0015, 0.0020, and 0.018 min^{-1} , respectively. It should be noted that, despite adjusting the initial solution pH to 5.0 (unbuffered), the final solution pH of the 8, 12, 19, and 25 nm IONC was 5.74, 6.19, 6.18, and 5.49, respectively. To address pH drift, we fixed the pH

at 5.0 using an acetate buffer (Fig. 4b). In the dark, the sorption capacity of IONC@CTAB was considerably low due to the charge screening (shielding) effects related to acetate being present [59-61]. Cr(VI) photoreduction performance for 25 nm IONC@CTAB also decreased under the buffered system; pseudo first order reaction rate constants for 8, 12, 19, and 25 nm IONC@CTAB were 0.0035, 0.0018, 0.0039, and 0.0072 min⁻¹, respectively. Further, for buffered systems, 25 nm IONCs still showed the highest Cr(VI) photoreduction performance; however, the results were not as clearly size dependent as observed for nonbuffered reactions. To further investigate this, we re-plotted size dependent Cr(VI) photoreduction results as a function of IONC surface area in Fig. S3. Rate constants per surface area of IONCs clearly increase with increasing size of IONCs. As discussed above, we hypothesize two reasons for this: 1) the surface of IONC became Fe(II) rich as the size of IONCs increased (as determined by XPS (Fig. 2a)); and 2) larger IONCs have higher ligand (surface) grafting density which both enhances Cr (VI) sorption (thus the concentration gradient) and relative LMCT activity (per surface area).

3.3. Photoreduction mechanisms

For 10 ppm Cr(VI), we applied 64 ppm (as Fe_3O_4) of IONC@CTAB, which is equivalent to 46 ppm of Fe ions. To specifically assess the role of



Fig. 6. (a) Proposed (primary) Cr(VI) reduction mechanism by IONC@CTAB in the presence of UVA (b) Kinetic data, as $ln(C_0/C)$ versus time, for 64 ppm of 25 nm IONC@CTAB and10 ppm of Cr(VI) at pH 5.0 in an open system under the UVA irradiationover fiveprocess cycles. (c) Normalized Cr(VI) reduction rate constants as a function cycle number. (d) Hydrodynamic diameter of 25 nm IONC@CTAB as a function of cycle number.

iron oxidation state, Cr(VI) photoreduction performance for 46 ppm of ferrous ions (Fe²⁺) and ferric ions (Fe³⁺) ions was evaluated using iron chloride (FeCl₂ and FeCl₃, both dissolved) under the UVA irradiation at pH 5.0 (Fig. S4). As expected, in the presence of only Fe^{3+} there was no Cr(VI) reduction. Based on a stoichiometric reaction calculation, 46 ppm of Fe²⁺ can reduce 14 ppm of Cr(VI); however, Fe²⁺ reduced 4.5 mg/L (45%) of Cr(VI) in the initial stage of reaction (t < 1 min). This difference is attributed to Fe²⁺ oxidized via dissolved oxygen in a competing reaction. Compared to these dissolved Fe²⁺ concentrations, the number of Fe(II) ions on the surface of IONC is considerably lower, and thus Fe (II) on the surface of IONC must be regenerated (after reducing the Cr (VI) in an open system). To explore this, the oxidation state of iron on the surface of 25 nm IONC was measured using XPS by measuring 2P iron binding energy (Fig. 4c) before and after a (photo)reaction. The portion of Fe(II) on the surface of 25 nm IONC was 69.5% before the experiment, and after UVA irradiation, the portion of Fe(II) was decreased to 60.2%. For this, we hypothesize two possible iron redox cycling pathways (Eqs. (1) and (2)).

$$Fe(III)(OA (carboxyl rich)) + H_2O \xrightarrow{UVA(LMCT)} Fe(II) + \bullet OH + H^+$$
(1)

$$Fe(III) + O_2 \cdot^- \to Fe(II) + O_2$$
(2)

With carboxyl associated (here functional group of OA), Fe(III) is reduced via an iron photoreduction reaction under UVA irradiation as a result of a LMCT process (Eq. (1)) [16,17,31,62,63]. Additionally, Fe(III) is also reduced by a superoxide radical produced by dissolved oxygen under UVA irradiation (Eq. (2)), through a photo Fenton-like pathway [64,65].

To determine the pathway for Fe(II) regeneration, a series of control experiments were performed. Cr(VI) photoreduction performance of 25 nm IONC@CTAB (64 ppm) was evaluated under UVA irradiation at pH 5.0 with systematic control of hydroxyl and superoxide radicals, along with dissolved oxygen (Fig. 5). OH radical (•OH) effects on Cr(VI) photoreduction were explored by adding 0, 0.5, 5, and 10 ppm of hydrogen peroxide (H₂O₂) [66,67]. As presented in Fig. 5a, the Cr(VI) photoreduction rate actually decreased with increasing H₂O₂ concentration. Rate constants for 25 nm IONC@CTAB with 0, 0.5, 5, and 10 ppm of H_2O_2 were 0.018, 0.016, 0.013, and 0.012 min⁻¹, respectively. As •OH is the product of equation (1) reaction, increasing •OH concentration likely hinders iron photoreduction [31]. To further explore this, 0.1% tert-butanol was applied as an •OH scavenger (Fig. 5b). In the absence of H₂O₂, the Cr(VI) photoreduction rate for 25 nm IONC@CTAB decreased slightly in the presence of tert-butanol. Whereas, in the presence of 10 ppm H₂O₂, photoreduction rate for 25 nm IONC@CTAB remains virtually unchanged the same scavenger. In the presence tertbutanol, rate constants for 0 ppm of H2O2 and 10 ppm of H2O2 were 0.016 and 0.015 min⁻¹, respectively. Based on these observations, we conclude that •OH does not have a significant effect on the photocatalytic reduction of Cr(VI) for these systems.

To evaluate the role of superoxide radical, we explored the Cr(VI) photoreduction for 25 nm IONC@CTAB (64 ppm) in the presence of 100 ppm of superoxide radical scavenger (superoxide dismutase bovine recombinant) at pH 5.0. As shown in Fig. 5c, the rate constant declined 39% with the superoxide scavenger; rate constants were 0.011 and 0.018 min⁻¹ with and without superoxide control, respectively. Additionally, we controlled the dissolved oxygen through the gas purging

(closed system) to suppress superoxide radical formation. Three types of gases (sparged and headspace controlled), N2, CO2 and modified air (consisting of 95% N2 and 5% O2) were evaluated. With modified air purging, the reaction rates were quite similar to that in an open system (0.017 min^{-1}) . However, without dissolved oxygen (N₂ and CO₂ purging), Cr(VI) reduction performance dramatically increased. Pseudo first order reaction rate constants were 0.044 min⁻¹ for N₂ purging and 0.163 min^{-1} for CO₂ purging. For both, reaction rates increased by about one order of magnitude due to the absence of dissolved oxygen (O₂). CO₂ purging showed faster Cr(VI) reduction than for N2 purging due to lowered solution pH. The final pH was 7.0 for the N₂ purging compared to 4.3 for CO₂ purged. At the end of gas purging experiments, we measured the portion of Cr(III) in the system, both on the surface of NCs and in solution (Fig. 5d), and found the majority of Cr(III) in solution with 4.7%, 1.4%, 2.3%, and 3.6% located at particle interface(s) for open system, N₂, CO₂, and modified air purging, respectively. Based on these results, we propose a primary Cr(VI) reduction mechanism by IONC@CTAB under UVA irradiation (Fig. 6a), whereby Cr(VI) is reduced by Fe(II), and Fe(III) is mainly cycled back to Fe(II) via LMCT at/near the carboxyl rich-iron oxide surface. For this, dissolved oxygen significantly hinders the iron photo-redox cycle.

3.4. Recycling

The regeneration performance of 25 nm IONC@CTAB was evaluated for five cycles at pH 5.0 (Fig. 6b). As shown in Fig. 6b, pseudo first order rate constants were 0.018, 0.010, 0.007, 0.005, and 0.003 min⁻¹ in order of the cycles, indicating photoreduction performance decreases with cycle number. For comparison, normalized Cr(VI) photoreduction rate constants are presented in Fig. 6c. Three factors are likely to affect Cr(VI) photoreduction performance of IONC@CTAB for these systems. First, the IONC surface oxidation state; second, adsorbed Cr on the surface of IONCs; and third is colloidal stability of IONCs. Based on XPS analysis, Fe(II) ions on the surface of IONC are not fully regenerated (Fig. 4c) over time. This is attributed to Cr deposition on the surface and likely coating degradation over time, as reported for other carboxylate (surface) rich magnetite materials [16]. As presented in Fig. 5d above, we observe up to 6.1% (average 4.7%) total Cr adsorbed on IONC surface (after photoreduction). Adsorbed Cr on the surface of IONC likely decreases the additional Cr(VI) sorption thus reducing photocatalytic activity. In addition, we observed coating alteration as measured by decreasing colloidal stability. As shown in Fig. 6d, the H_D of 25 nm IONC@CTAB increased as a function of cycling number; the H_D of the NCs was 29.4, 30.0, 45.9, 54.9, and 58.6 nm, in order of reuse cycles.

4. Conclusion

We have demonstrated precisely engineered CTAB-OA bilayer IONCs for highly effective Cr(VI) photo-based reduction. By controlling key reaction variables, including solution pH, dissolved gas(es), and oxygen based radicals, we provide a mechanistic analysis of the photo-enhanced Cr(VI) reduction process. For this, Fe(II) is the primary Cr(VI) reductant, and Fe(III) (oxidized from Fe(II)) (re)cycles via interfacial LMCT photoenhanced process, including a superoxide radical-based reaction. The observed LMCT phenomenon at the OA-NC interface, shifting the photoactivity into the UVA, not only significantly enhances reduction rates but allows for direct sunlight to be used as a light source. IONC core size was determined to be critical, as larger NCs have a higher relative abundance of surface stable Fe(II) in addition to surface ligand coating density, which provides for higher Cr sorption capacities (per surface area), higher LMCT activity (per surface area), and additional colloidal stability. Taken together, this work details a straightforward process to engineer IONC photoactivity, which is typically not considered for environmental applications, via precise surface modification. Further, and in contrast to Fenton-like reactions (in water), this interfacial-based system offers a number of advantages, including process stability at circumneutral pH and magnetic susceptibility, which should be further explored to treat other redox active contaminants.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.133938.

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