

Guided Assembly of Magnetic Nanocomposite with Open Shell Structure for Water Remediation

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Colloidally stable magnetic nanocomposite with magnetic and catalytic bifunctionalities was constructed by using silica colloids as a building template. The fabrication of the open shell structure of the magnetic nanocomposite was achieved by employing polyelectrolyte as the bridging agent between silica and iron oxide nanoparticles (IONPs). The dimension and composition of the nanocomposite was fine-tuned by altering the number of polyelectrolyte interlayer, constructed by poly-diallyldimethylammonium chloride (PDDA) and/or poly-styrenesulfonate (PSS), from one PDDA layer to three PDDA/PSS/PDDA layers through layer-by-layer assembly. The successful development of nanocomposite from its building blocks was confirmed by dynamic light scattering and zeta potential measurements. With the evidence of surface morphology of nanocomposite examined by transmission electron microscopy (TEM), IONPs were found to be more evenly distributed on the silica colloid surface by single layer of polyelectrolyte and forming ramified structure as the polyelectrolyte layers increased. Additionally, the structure of the assembled films was evaluated by quartz crystal microbalance with dissipation (QCM-D). Experiments showed nanocomposite constructed by single polyelectrolyte was more flexible and promoted better pollutant removal capability than that of three polyelectrolyte layers by taking Methylene Blue and Methyl Orange dyes as the model system. The nanocomposite can be used for water treatment purpose for multiple cycles by magnetic collection at the end of each treatment cycle.

1. Introduction

Composite materials have attracted immense interest in various areas such as for electronic, catalysis and separation processes (Liz-Marzán et al., 1996). The popularity of developing composite materials is due to the improved properties (electrical, optical, magnetic, catalytic, mechanical, etc.) compared to their original counterparts (Imhof and Pine, 1997). IONPs have played an important role in biomedical field (Pankhurst et al., 2009) such as magnetic field controlled target delivery (Lübbe et al., 2001), cell labelling (Tartaj, 2003), bio separation (Guo and Sun, 2004), and magnetic resonance imaging (Bulte et al., 2002), owing to its magnetic property. In addition, magnetic property enables an easy way of separation after water treatment (Baruwati et al., 2007). Besides, IONPs also play a role as an adsorbent or catalyst to remove the contaminants in wastewater such as heavy metals (Xing et al., 2013), inorganic or organic compounds (Che et al., 2014a). Taking advantage of the discovery by Decher (1997) in layer-by-layer assembly, a highly flexible and easy route of electrostatic driven technique for the production of advanced hierarchically ordered composite was established (Decher, 1997). This process entails a stepwise adsorption of oppositely charged different materials such as organic or inorganic molecules, polymers, proteins, clay particles or colloids onto a template in developing a nanocomposite, which is mainly ascribed by the electrostatic interaction for the multilayers build-up (Decher et al., 1998). Particularly, polyelectrolyte is the key building block of hybrid materials by imparting the stability and determining the overall structure of various molecular assemblies (Dunn, 1986). As a consequence of the development of this simple approach (Caruso et al., 1999), fruitful research of film model on solid support constructed by cyclic repetition of adsorption steps with respect to sequential attachment of oppositely charged polyelectrolytes

(Lvov et al., 1999) or nanoparticles/polyelectrolytes (Lvov et al., 1997) have been carried out to prepare multilayers.

It is worth to point out that many works were solely done to claim the successful preparation of multilayers structure by repeating the deposition steps of oppositely charged polyelectrolytes and nanoparticles (Ariga et al., 1999) on charged substrates without further proving the practicability and functionality of the constructed multilayers (Rhodes et al., 2000) for engineering related applications. On top of that, the apparent contribution of the 'soft' layer when employing polyelectrolyte in developing multilayer has been overlooked. Additionally, the practical value of the hierarchically structured polyelectrolyte multilayers is hardly to be found. Hence, the importance of the hierarchically structured polyelectrolyte layers remains a critical challenging issue. Although multilayers constructed via layer-by-layer assembly provides the opportunities to design applicable function-specific films (Lvov et al., 1996), the mechanism and interaction remains unresolved. In fact, understanding the polymer physical chemistry is of utmost importance in order to bring out comprehensive message of the fascinated polyelectrolyte multilayers structure. Hence, the deficiency motivated us to describe the role of polymer interlayer(s) in bridging iron oxide nanoparticles onto like-wise charged silica colloids, guiding the morphology of the IONPs distribution. With an aid of the characterization from quartz crystal microbalance with dissipation (QCM-D), the impact of softness of the polymeric structure towards the synthesis of magnetic core-shell nanocomposite and corresponding application can be investigated. An insightful comprehension of the relationship disclosed a correlation of nanocomposite structure with the macroscopic performance of the hybrid materials. Therefore, with this information available, the desired architecture of hierarchically ordered composite can be designed by having the understanding of the structure-property and its corresponding functionalities.

In this study, silica-polyelectrolyte(s)-IONPs nanocomposite were developed by constructing a layer of polyelectrolyte (poly-diallyldimethylammonium chloride) and three layers of polyelectrolytes (poly-diallyldimethylammonium chloride/ poly-styrenesulfonate/ poly-diallyldimethylammonium chloride) to bridge IONPs deposited onto like-wise charged silica colloids. The evolution of each building block developed into desired nanocomposite was monitored via dynamic light scattering (DLS) and zeta potential measurements (Malvern Instruments, Zetasizer Nano-ZS). The surface morphology of the synthesised nanocomposite was examined under transmission electron microscopy (TEM) (JEOL, JEM-20CX). The conformation of the adsorbed layers onto silica surface was evaluated by quartz crystal microbalance with dissipation (QCM-D) (Q-Sense E1, Sweden). QCM-D is a sensitive tool enables real-time monitoring of the layers build-up on a quartz crystal surface, which provides reliable information of the mass and viscoelastic property of the adsorbed materials (Notley et al., 2005). Hence, in recent years, QCM-D has emerged as a favourable analytical tool to prove the successful build-up of hybrid films, such as the assemblies of polysaccharide (HA) and collagen (Costa et al., 2013), poly-cation and poly-anion (Notley et al., 2005) and nanoparticles (Fatissou et al., 2009). The pollutant removal capability of the synthesised nanocomposite on two different charges of dyes (cationic Methylene Blue and anionic Methyl Orange) was investigated. It is worth to mention that the synthesised magnetic nanocomposite embraced the unique features reminiscent of the building block (IONPs), which allowed the nanocomposite to be magnetically separated after performing catalytic degradation towards the dye molecules. The ability to recover nanocomposite magnetically enables the reusability of nanocomposite in subsequent treatment. In this article, we described the formation of hierarchical polyelectrolyte layers inhibited the penetration of the nanoparticles and targeted pollutants. Additionally, the benefit of having singly polyelectrolyte layer included regularity of IONPs deposition and better pollutant removal capability. This finding allowed us to announce that the open shell structure provided by polyelectrolyte is the key factor in promoting the well distribution of IONPs and enhancing the dyes removal performance.

2. Materials and methods

2.1 Materials

All the reagents in this work were of analytical grade and used as received without further purification. Ethanol (absolute), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2 , 100 volumes >30 %W/V) were bought from Fisher Scientific (M) Sdn. Bhd. Ammonia solution (25 %), Methylene Blue and Methyl Orange were supplied by Merck. Poly-diallyldimethylammonium chloride (PDDA of 100 - 200 kg/mole and 20 W% in water) and poly-styrenesulfonate (PSS with 70 kg/mole) were obtained from Aldrich Chemistry. Tetraethylorthosilicate (TEOS, 98 %), iron (III) chloride ($FeCl_3$, 98 % pure, anhydrous) and iron (II) chloride ($FeCl_2 \cdot 4H_2O$, 99 %) were obtained from Acros Organics. QCM-D silica quartz crystal was supplied by Kulim Hi-Tech Company. Sodium dodecyl sulphate (SDS), approximately 95 % based on total alkyl sulphate content were purchased from Sigma-Aldrich. In all experiments, Milli-Q water was employed from Pure-lab Option-Q with resistivity at $18 M\Omega \cdot cm$ from a potable water source.

2.2 Methods

The preparation and characterization of synthesising IONPs via co-precipitation method, silica colloids via Stöber process, silica-polyelectrolyte and silica-polyelectrolyte(s)-IONPs via directed assembly technique was described in our earlier publication (Che et al., 2014b). In brief, electrostatic interaction is the driving force for the successful sequential attachment among the building blocks, where the polyelectrolyte interlayer played the role of a scaffold for the attachment of IONPs onto like-wise charged silica colloids, forming a fractal structure. In brief, silica colloids were synthesised by Stöber process by mixing ethanol, TEOS, and ammonia in a volume ratio of 30:1:3, where the mixture was magnetically stirred at 500 rpm for 2 h. The synthesised silica colloids were subjected to three cycles of washing with deionized water to remove excess reactants. Later these colloidal particles were further functionalized with polyelectrolyte(s) with a mass ratio of 1:8 in order to have full polymeric coverage on silica surface. For IONPs synthesis, co-precipitation method was employed with the standard 2:1 mole ratio of ferric chloride and ferrous chloride. The reactants were subjected to aeration with argon gas under a magnetic stirring at 700 rpm before the reflux process. Once the reaction mixture reached 70 °C, 2.5 M NaOH was injected and the reaction continued for another 30 min before the black precipitate was collected with a permanent magnet. Lastly, the silica-polyelectrolyte(s)-IONPs nanocomposite was synthesised by adding IONPs to polymeric silica in the ratio of 126 mg/m². It is worth noted that all the synthesised nanoparticles solution was prepared in final concentration of 10 kg/m³ for further usage and all the coating process was subjected to mixing on an end-to-end rotator with mixing speed at 40 rpm for 1 day to achieve complete surface coverage. For QCM-D measurement, the polyelectrolyte and IONPs solutions were prepared in 6.0 mM and 1×10^{-10} kg/m³ to introduce onto silica quartz crystal in a sequential manner at a constant flow rate of 20 μ L/min to construct two different systems of PDDA-IONPs and PDDA-PSS-PDDA-IONPs. It is worth to mention that the AT-cut piezoelectric quartz crystal coated with thin silica electrodes was cleaned in 2 % (W/V) sodium dodecyl sulphate (SDS) solution for 30 min and then rinsed under a stream of running deionized water. The cleaned crystal was blow-dried with nitrogen gas before mounting it into QCM-D flow cell. The initial concentration of dyes (Methylene Blue and Methyl Orange) and nanocomposite (silica-PDDA-IONPs and silica-PDDA-PSS-PDDA-IONPs) was fixed at 2×10^{-11} ppm and 10 kg/m³ for 6 h dye removal experiment.

3. Results and discussion

Hydrodynamic diameter of all nanomaterials involved was evaluated via dynamic light scattering and the associated surface charge was determined by zeta potential measurement with Malvern Zetasizer Nano-ZS. All data obtained were summarised in Table 1. The synthesised silica with initial zeta potential of -48.8 mV experienced surface charge reversal to +65.0 mV upon attachment of PDDA and experienced a hydrodynamic diameter increment of 33.9 nm. Subsequent coating of silica-PDDA with PSS and PDDA consecutively gave rise to a zeta potential shift of -56.0 mV and +66.3 mV, and increased the diameter of the composite to 245.1 nm and 300.9 nm. The introduction of IONPs to silica-PDDA and silica-PDDA-PSS-PDDA registered a zeta potential of +43.6 mV and +24.5 mV with the final composite structure having a hydrodynamic diameter of 233.7 nm and 344.6 nm. The successful charge reversal and hydrodynamic diameter increment confirmed the layer deposition of the polyelectrolyte(s) and IONPs onto silica template.

Table 1: Zeta potential and hydrodynamic diameter of nanoparticles synthesised at each stage.

Synthesised nanoparticle	Zeta potential (mV)	Hydrodynamic diameter (nm)
Silica	-48.8	164.0
Silica-PDDA	+65.0	197.9
Silica-PDDA-PSS	-56.0	245.1
Silica-PDDA-PSS-PDDA	+66.3	300.9
Silica-PDDA-IONPs	+43.6	233.7
Silica-PDDA-PSS-PDDA-IONPs	+24.5	344.6

Images of transmission electron microscopy (TEM) in Figure 1 revealed a core shell structure had been synthesised, with light contrast of silica core, and dark contrast of IONPs shell. TEM pictured a thinner outermost IONPs layered structure with well-organized IONPs distribution on silica colloids with pre-coating of a PDDA layer. On the contrary, a thicker IONPs layer with significant large IONPs agglomerates was observed on PDDA/PSS/PSS layers which were pre-adsorbed on silica colloids.

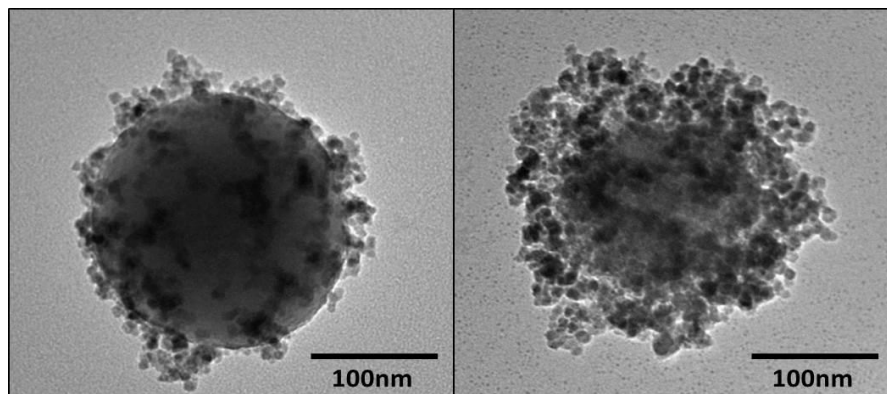


Figure 1: The TEM images of silica-PDDA-IONPs (left) and silica-PDDA-PSS-PDDA-IONPs (right)

In general, QCM-D is a powerful tool to detect the particles deposition by observing the changes in frequency (F) and energy dissipation (D) over time of an oscillating AT-cut quartz crystal in response to the adsorbed materials. A decrease of frequency and an increase of dissipation over time were detected in simultaneous manner upon the successful deposition of polyelectrolyte(s) and IONPs on silica-coated quartz crystal. From QCM-D, the frequency shift at saturation for PDDA-IONPs and PDDA-PSS-PDDA-IONPs films was ~ -175.9 Hz and ~ -95.8 Hz, where the corresponding dissipation values were 63.9×10^{-6} and 22.6×10^{-6} . Since frequency and dissipation factors owned different time dependencies, direct comparison between the two systems can be evaluated by taking into account of the relationship of dissipation over frequency shift (hereafter known as D-f) in order to eliminate time-dependency as an explicit parameter (Höök et al., 2001). On top of that, the combination of both frequency and dissipation factors were generally evaluated together to extract the information of viscoelasticity and conformational changes of the assembled layer (Otzen et al., 2003). In fact, Höök et al. (1998) had suggested that larger ratio of D-f indicated higher flexibility of the adsorbed layer structure (Höök et al., 1998). Therefore, greater value of D-F ($0.36 \times 10^{-6} \text{ Hz}^{-1}$) for PDDA-IONPs system indicated a more flexible adsorbed films had been constructed by single polyelectrolyte layer than the PDDA-PSS-PDDA-IONPs system ($0.24 \times 10^{-6} \text{ Hz}^{-1}$). This result suggested to us that the adsorbed layers constructed by single polyelectrolyte layer were a more flexible structure due to the repulsion of the similar charge among the polymer segment. In contrast, better charge neutralization and compensation was denoted by the three consecutive polyelectrolyte layers, gave rise to a stiffer assembled films.

The practical usage of the different aforementioned magnetic nanocomposite (IONPs integrated into positively charged silica-PDDA and silica-PDDA-PSS-PDDA) was assessed by taking dyes, namely Methylene Blue (MB) and Methyl Orange (MO) as the model system, mainly due to the ease of detection by colorimetric measurement. The removal efficiency of MB and MO was depicted in Figure 2, where silica-PDDA-IONPs performed better in both dyes compared to silica-PDDA-PSS-PDDA-IONPs in the absence or presence of an oxidizing agent, hydrogen peroxide (H_2O_2). The introduction of H_2O_2 boosted the dyes removal efficiency by facilitating advanced oxidation process with IONPs to catalytically degrade the dyes molecules (Andreozzi et al., 1999). It was believed that the three polyelectrolyte layers did not assemble in an absolute-layered manner, but were in interpenetrated network led to complexation within polymer chains (Zhang et al., 2014), resulting in a stiffer structure, evidenced by the lower D-f ratio value in QCM-D measurement. Hence, the stiffer polyelectrolyte multilayers had most likely acting like a firmed physical layer imposed strong steric barrier for the diffusion of IONPs within polymeric matrix (Wu et al., 2014), resulting in larger IONPs agglomerates formed on the outermost surface (see TEM images in Figure 1). By having large IONPs agglomerates has diminished the benefit of large surface-to-volume ratio of IONPs. Together with the restricted migration of dyes molecules into interpenetrated polymeric matrix, were believed to be the two main factors for the lower dye removal efficiency. By placing an external magnet near to the glass vial containing the reaction mixture, nanocomposite can be recollected for the following water treatment cycles (Enayati Ahangar et al., 2014). Dye removal efficiency of both nanocomposite remained reproducibly high in the repetitive dye removal cycles, implying that the magnetic nanocomposite can be potentially used as a catalytic material in wastewater remediation purpose.

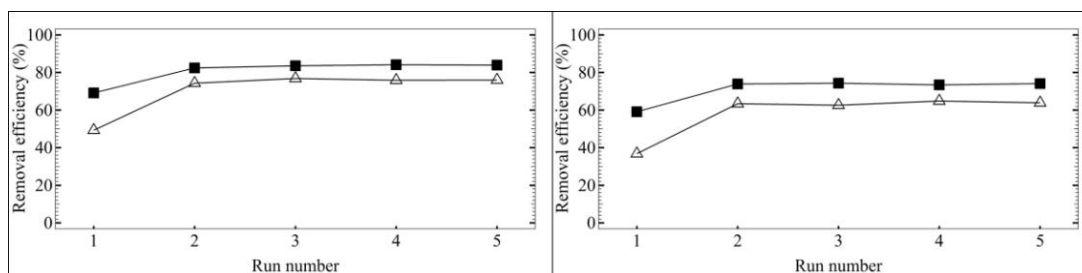


Figure 2: MB (left) and MO (right) dyes removal by silica-PDDA-IONPs (—■—), and silica-PDDA-PSS-PDDA-IONPs (—△—) without H_2O_2 (1st cycle) and with H_2O_2 (recycling run 2-5)

4. Conclusion

Silica-polyelectrolyte(s)-IONPs nanocomposite can be constructed by electrostatic driven adsorption process, where the structural evolution of the nanocomposite was ascertained by size and surface charge measurements and supported by TEM observation. Different layer of polyelectrolyte could dramatically alter the IONPs immobilization on silica colloids. The TEM images demonstrated that single PDDA layer promote a thinner IONPs deposition with orderly IONPs distribution compared to multiple PDDA/PSS/PDDA layer. QCM-D was employed to determine the main feature of conformational structure of the adsorbed layers on silica surface, where one layer of polyelectrolyte was detected to have preserved the soft nature of a flexible macromolecule in the assembled films. Meanwhile, multilayers of polyelectrolyte which experienced interpenetrated polymeric network had induced a stiffer structure, inhibiting the IONPs penetration into the interior multilayers. Hence, a highly irregular IONPs distribution with larger IONPs agglomerates were deposited on silica template pre-coated with polyelectrolytes multilayers. On the contrary, the more flexible structure of nanocomposite constructed by one polyelectrolyte layer was believed to have contributed to the ease of diffusion of IONPs and other particles (dye molecules) into polymeric matrix. Together with high surface-to-volume ratio of IONPs contributed by the more organized IONPs distribution with minor agglomerates, were the main contributing factors for the better MB and MO dyes removal achieved by silica-PDDA-IONPs. The recyclability with reproducible pollutant removal performance enabled the synthesised nanocomposite to be potentially used as water remediation agent. Although it was technologically fascinating to produce polyelectrolyte multilayers, the real value and applicability of having such structure for environmental engineering applications remained questionable and needed further justification. Nevertheless, electrostatic driven assembly has indeed provided opportunities to design composite materials with multilayer films which can be targeted for specific function.

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