Preparation of Alkanethiolate-Functionalized Core/Shell Fe₃O₄@Au Nanoparticles and Its Interaction with Several Typical Target Molecules

Xiaoli Zhao, Yaqi Cai,* Thanh Wang, Yali Shi, and Guibin Jiang

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

This paper reports the synthesis of alkanethiolate-functionalized core/shell Fe₃O₄/Au nanoparticles (Fe₃O₄@Au NPs) that combine the advantages of core/shell magnetic nanoparticles with self-assembled monolayers (SAMs). The alkanethiolates, having carboxylic acid (COOH) and methyl (CH₃) terminal groups, can be easily self-assembled on the Fe₃O₄@Au NPs substrates. The surface composition and structure of 11-mercaptopundecanoic acid (11-MUA) and 1-dodecanethiol (11-DDT) SAMs were characterized in detail using energy-dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS). To further study the surface properties of the SAMs, hydrophobic, ionic, and nonionic organic compounds were selected as probe molecules. The results indicated that the hydrophobic interaction caused strong retention of analytes, whereas the repulsive electrostatic interaction between the negatively charged 11-MUA SAMs surface and the negatively charged probe molecule would lead to the decrease of adsorption affinity.

In the past few years, nanocomposite materials have been subjected to extensive research as the combination of different nanoscale functionalities are capable of endowing the substrate with enhanced properties and thus have great application potentials in various fields.^{1–11} The core/shell nanostructure is an ideal

composite system that combines the advantages of “core” and “shell” and has shown enhanced physical and chemical properties. The shell layer not only protects the core from oxidation but also provides a platform for surface modification and functionalization. Generally, magnetic materials are the most commonly selected substrates because they can readily be isolated from sample solutions by the application of an external magnetic field. However, magnetic particles suffer from several inherent limitations as they are likely to aggregate and lose magnetic properties when applied in complex environmental and biological systems. Thus, there have been extensive reports on the synthesis of magnetic core/shell nanoparticles in which the core is Fe₃O₄ and the shell consists of a metal or metal oxide such as Au,^{2–5} SiO₂,^{1,6} TiO₂,⁷ Al₂O₃.⁸ Among them, Au has been considered as one of the best materials for protecting Fe₃O₄ NPs due to simple reductive preparation, reliable chemical stability, biocompatibility, and versatility in surface modification. Au nanoparticles have a shortcoming for practical application when applied in the adsorption and separation of target molecules from a sample solution as centrifugation is generally required, which is usually time-consuming and might not be suitable for biological samples. It is anticipated that incorporation of Au coating on a magnetic core could attain both the advantages of chemical stability and biocompatibility of Au and the magnetic properties of Fe₃O₄. The Au layer can be expected to protect the magnetite from etching in harsh environments, and another attribute is that the Au surface can be readily functionalized through Au–S bindings.

Several recent papers have reported the synthesis of different structured Fe₃O₄/Au composites such as the formation of core/shell Fe₃O₄@Au nanomaterials of spherical morphology;^{2–5} Yu et al. synthesized dumbbell-like Au–Fe₃O₄ nanoparticles,¹² and Caruntu et al. reported the attachment of gold nanoparticles onto colloidal magnetite nanocrystals through a two-step chemically controlled procedure.¹¹ Up to now, most of the research works focus on the preparation of Fe₃O₄@Au magnetite nanoparticles and there are only a limited number of literatures about its surface modification capabilities and its practical application.^{13,14}

Self-assembled monolayers (SAMs) of alkanethiolates on gold surfaces have been extensively studied and widely applied in

* Corresponding author. E-mail: caiyaqi@rcees.ac.cn. Phone: (086) 010-62849239. Fax: (086) 010-62849182.

- (1) Deng, Y. H.; Qi, D. W.; Deng, C. H.; Zhang, X. M.; Zhao, D. Y. *J. Am. Chem. Soc.* **2008**, *130*, 28–29.
- (2) Xu, Z. C.; Hou, Y. L.; Sun, S. H. *J. Am. Chem. Soc.* **2007**, *129*, 8698–8699.
- (3) Cho, S. J.; Idrobo, J. C.; Olamit, J.; Liu, K.; Browning, N. D.; Kauzlarich, S. M. *Chem. Mater.* **2005**, *17*, 3181–3186.
- (4) Wang, L. Y.; Luo, J.; Fan, Q.; Suzuki, M.; Suzuki, I. S.; Engelhard, M. H.; Lin, Y. H.; Kim, N.; Wang, J. Q.; Zhong, C. J. *J. Phys. Chem. B* **2005**, *109*, 21593–21601.
- (5) Zhang, H. R.; Meyerhoff, E. M. *Anal. Chem.* **2006**, *78*, 609–616.
- (6) Zhao, W.; Gu, J. L.; Zhang, L. X.; Chen, H. R.; Shi, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 8916–8917.
- (7) Chen, C. T.; Chen, Y. C. *Anal. Chem.* **2005**, *78*, 5912–5919.
- (8) Chen, C. T.; Chen, W. Y.; Tsai, P. J.; Chien, K. Y.; Yu, J. S.; Chen, Y. C. *J. Proteome Res.* **2007**, *6*, 316–325.
- (9) Bao, J.; Chen, W.; Liu, T. T.; Zhu, Y. L.; Jin, P. Y.; Wang, L. Y.; Liu, J. F.; Wei, Y. G.; Li, Y. D. *ACS Nano* **2007**, *1*, 293–298.
- (10) Jordan, A.; Scholz, R.; Wust, P.; Fahling, H.; Felix, R. *J. Magn. Magn. Mater.* **1999**, *201*, 413–419.
- (11) Caruntu, D.; Cushing, B. L.; Caruntu, G.; O'Connor, C. J. *Chem. Mater.* **2005**, *17*, 3398–3402.

- (12) Yu, H.; Chen, M.; Rice, P. M.; Wang, S. X.; White, R. L.; Sun, S. H. *Nano Lett.* **2005**, *5*, 379–382.
- (13) Xi, D.; Luo, X. P.; Lu, Q. H.; Yao, K. L.; Liu, Z. L.; Ning, Q. *J. Nanopart. Res.* **2008**, *10*, 393–400.
- (14) Larson, T. A.; Bankson, J.; Aaron, J.; Sokolov, K. *Nanotechnology* **2007**, *18*, 325101.

molecular recognition, protein adsorption, and chemical and biological sensing.^{15–21} In comparison to traditional surface modification strategies, the favorable merits of thiolate bond (Au–S)-based SAMs can be considered as threefold: (a) They have a well-defined structure and are easy to prepare; Au substrates can be immersed into corresponding alkanethiolate ethanol solutions and left overnight, resulting in the formation of self-assembling monolayers.¹⁵ (b) They have the capacity to incorporate a wide range of functional groups; the structure and chemical properties of SAMs can be conveniently tuned by choosing proper alkanethiolates with different chain lengths or terminal functional groups. For example, methyl (CH₃)- and hydroxyl (OH)-terminated SAMs are used to model hydrophobic and hydrophilic neutral surfaces, whereas carboxylic acid (COOH)- and amine (NH₂)-terminated SAMs are used, respectively, to mimic negatively and positively charged surfaces.¹⁶ (c) They have high stability, reproducibility, and reusability; SAMs are very stable due to the strong covalent sulfur–gold bonds. The SAMs can be used repeatedly, and they are easy to regenerate by reimmersion of the Au substrates into the alkanethiolate ethanol solution.

Great advancements have been achieved in the field of organothiol-functionalized Au materials recently. Especially, studies on alkanethiolates/Au monolayer-protected clusters (MPCs) have attracted a great deal of interest since, as highlighted by Murray and co-workers,^{22–26} Whetten and co-workers,^{27,28} and Negishi et al.,²⁹ MPCs with alkanethiolates (RS) can be functionalized with R'S groups;²² Murray and co-workers described a versatile synthesis of ω -functionalized alkanethiolate MPCs based on place-exchange reactions occurring when an ω -substituted alkanethiol was added to an alkanethiolate-cluster solution.²⁵ Furthermore, the crystal structure and surface properties of the thiolate-protected Au NPs have been systemically studied. With Au coating, the Fe₃O₄@Au NPs can be readily functionalized through the well-developed Au–S chemistry.² Those constructive studies have undoubtedly proven that magnetic Au NPs have great

potential in areas such as catalysis, chemical sensing, and nanoscale electronics.^{23,30}

Furthermore, the structural and chemical properties of SAMs can be conveniently tuned by varying the composition of the adsorbate. Thus, SAMs have been effectively employed as a model system to investigate the structural and chemical properties of organic interfaces and thin films.³¹ Umezawa et al.¹⁸ developed a number of ion channel sensors (ICSs) based on thiol-anchored charged molecules self-assembled on gold electrodes. Electrostatic repulsion between the charged receptors and analytes with the same charge prevents the analytes from reaching the electrode surface. These works provide an important indication, since carboxylic acid (COOH)- and amine (NH₂)-terminated SAMs can be used to mimic negatively and positively charged surfaces. If core/shell Fe₃O₄@Au NPs modified with charged alkanethiolates could be used instead of gold electrodes, a novel magnetic material with similar property to the ICSs is obtained. This will not only extend the scope of application of magnetic carrier technology (MCT) but also offer several new potentials, for example, as selective sorbents in solid-phase extraction (SPE) of trace-level contaminants from complex samples.

In this work, 11-mercaptoundecanoic acid (11-MUA) and 1-dodecanethiol (11-DDT) were self-assembled on the surface of Fe₃O₄@Au NPs, forming sulfur-based monolayers with different terminal groups. Furthermore, in order to study the structure and surface properties of the SAMs, we selected several compounds, roughly representing different classes of typical environmental relevant pollutants, as probe molecules: hydrophobic compounds (environmental estrogens—bisphenol A (BPA), 4-*tert*-octylphenol (4-OP), and 4-*n*-nonylphenol (4-NP)), ionic compounds (anion surfactants—sodium dodecyl sulfate (SDS)), and nonionic compounds (polycyclic aromatic hydrocarbons (PAHs)—phenanthrene). The interaction between the alkanethiolate SAM surfaces and target compounds was accordingly investigated in detail.

EXPERIMENTAL SECTION

Materials. All reagents were of analytical reagent grade and were used as supplied. 4-OP and 4-NP were obtained from Tokyo Kasei Kogyo Co., Ltd., Japan. BPA, phenanthrene, 11-MUA (SHC₁₁H₂₂CO₂H, 95%), and 11-DDT (SHC₁₁H₂₂CH₃, 99%) were obtained from Acros Organics, New Jersey. Ferric chloride (FeCl₃·4H₂O) and ferrous chloride (FeCl₂·6H₂O) were purchased from Beijing Chemicals Corporation (Beijing, China). Chloroauric acid hydrated (HAuCl₄·4H₂O), SDS, sodium citrate, and tetramethylammonium hydroxide pentahydrate (TMAOH) were purchased from Beijing Chemical Reagents Company (Beijing, China). HPLC-grade acetonitrile and methanol were obtained from Merck (Darmstadt, Germany). Aqueous solutions used in all of the experiments were prepared using Milli-Q water by Milli-Q system (Millipore, Bedford, MA).

Preparation of Core/Shell Fe₃O₄@Au Nanoparticles. The Fe₃O₄ nanoparticles were prepared by chemical coprecipitation methods as reported in our previous works,^{31–33} and the core/shell Fe₃O₄@Au NPs were synthesized according to previous reported methods with minor modification.^{2,34} A solution of 0.1%

- (15) Baralia, G. G.; Duwez, A. S.; Nysten, B.; Jonas, A. M. *Langmuir* **2005**, *21*, 6825–6829.
- (16) Wang, H.; Chen, S. F.; Li, L. Y.; Jiang, S. Y. *Langmuir* **2005**, *21*, 2633–2636.
- (17) Gorham, J.; Smith, B.; Fairbrother, D. H. *J. Phys. Chem. C* **2007**, *111*, 374–382.
- (18) Umezawa, Y.; Aoki, H. *Anal. Chem.* **2004**, *76*, 321A–326A.
- (19) Dubrovsky, T. B.; Hou, Z. Z.; Stroeve, P.; Abbott, N. L. *Anal. Chem.* **1999**, *71*, 327–332.
- (20) Diao, P.; Gao, M.; Hou, Q. C.; Xiang, M.; Zhang, Q. J. *J. Phys. Chem. B* **2006**, *110*, 20386–20391.
- (21) Venkataraman, N. V.; Zürcher, S.; Spencer, N. D. *Langmuir* **2006**, *22*, 4184–4189.
- (22) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27–36.
- (23) Templeton, A. C.; Hostetler, M. J.; Warmoth, E. K.; Chen, S. W.; Hartshorn, C. M.; Krishnamurthy, V. M.; Forbes, M. D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 4845–4849.
- (24) Murray, R. W. *Chem. Rev.* **2008**, *108*, 2688–2720.
- (25) Hostetler, M. J.; Green, S. J.; Stokes, J. J.; Murray, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 4212–4213.
- (26) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. *J. Am. Chem. Soc.* **2008**, *130*, 3754–3755.
- (27) Akola, J.; Walter, M.; Whetten, R. L.; Häkkinen, H.; Grönbeck, H. *J. Am. Chem. Soc.* **2008**, *130*, 3756–3757.
- (28) Price, R. C.; Whetten, R. L. *J. Am. Chem. Soc.* **2005**, *127*, 13750–13751.
- (29) Negishi, Y.; Nobusada, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2005**, *127*, 5261–5267.

(30) Rosi, N. L.; Mirkin, C. A. *Chem. Rev.* **2005**, *105*, 1547–1562.

(31) Li, J. D.; Zhao, X. L.; Shi, Y. L.; Cai, Y. Q.; Mou, S. F.; Jiang, G. B. *J. Chromatogr., A* **2008**, *1180*, 24–31.

Scheme 1. Schematic Illustration of the Preparation of Core/Shell $\text{Fe}_3\text{O}_4\text{@Au}$ NPs and the Structure of 11-MUA SAMs and 11-DDT SAMs

HAuCl_4 was added dropwise into the Fe_3O_4 NPs, $\text{NH}_2\text{OH}\cdot\text{HCl}$, and TMAOH mixed solution at 80°C , then sodium citrate was added incrementally within 2 h, and the mixture was stirred for 3 h after the addition. The color of the precipitate changed from black to reddish brown, which suggests that the resulting $\text{Fe}_3\text{O}_4\text{@Au}$ NPs have inherited the colorimetric character of gold nanoparticles. A thin and dense Au layer with desired thickness is rather indispensable, while increase of the Au shell thickness results in the decrease of the magnetic strength. Thus, a molar ratio of Fe_3O_4 to Au of 5:1 was selected because of the strong magnetic property and effective protective coating. Detailed information of preparation of Fe_3O_4 nanoparticles and alkanethiolate-functionalized core/shell $\text{Fe}_3\text{O}_4\text{@Au}$ nanoparticles is provided in the Supporting Information. Illustration of the preparation procedure of 11-MUA and 11-DDT self-assembled core/shell $\text{Fe}_3\text{O}_4\text{@Au}$ NPs ($\text{Fe}_3\text{O}_4\text{@Au@11-MUA}$ NPs and $\text{Fe}_3\text{O}_4\text{@Au@11-DDT}$ NPs) can be followed in Scheme 1.

RESULTS AND DISCUSSION

The transmission electron microscopy (TEM) data serves as an important evidence for the formation of $\text{Fe}_3\text{O}_4\text{@Au}$ NPs. Figure 1 shows a typical TEM image of $\text{Fe}_3\text{O}_4\text{@Au@11-MUA}$ NPs, in which most of the composite nanoparticles were quasi-spherical in shape with an average diameter of about 20 nm. Figure S1 (see the Supporting Information) shows the VSM (vibrating sample magnetometer) magnetization curves of Fe_3O_4 NPs, $\text{Fe}_3\text{O}_4\text{@Au}$ NPs, and $\text{Fe}_3\text{O}_4\text{@Au@11-MUA}$ NPs at room temperature. All of the NPs exhibited typical superparamagnetic property due to no hysteresis, remanence, and coercivity, which is essential for applications where magnetic isolation is desired. The resulting superparamagnetic nanoparticles can readily be dispersed into the solution and then conveniently removed from the matrix by applying a magnetic field. Moreover, it is believed that the saturation magnetization is a measure of the maximum magnetic strength.³⁵ Generally, due to the weight contribution from the nonmagnetic Au, the formation of the Au shell results in the decrease in the magnetic strength of the core/shell nanoparticles.

Figure 1. Transmission electron microscopy (TEM) image of 11-MUA coated $\text{Fe}_3\text{O}_4\text{@Au}$ nanoparticles. The morphology of the samples was determined by TEM with an H-7500 (Hitachi, Japan) operating at 80 kV.

The saturation magnetization of Fe_3O_4 NPs and $\text{Fe}_3\text{O}_4\text{@Au}$ NPs were 63.3 and 53.6 emu/g, respectively, and that of alkanethiolate-coated $\text{Fe}_3\text{O}_4\text{@Au}$ NPs was about 49.7 emu/g. The superparamagnetic properties and saturation magnetization did not change significantly when the alkanethiolates SAMs formed on the surface of $\text{Fe}_3\text{O}_4\text{@Au}$ NPs. Ma et al.³⁶ found that a saturation value of 16.3 emu/g is high enough to enable magnetic separation with a conventional magnet. In our experiments, when a Nd–Fe–B strong magnet (rectangular shape ($150 \times 130 \times 50 \text{ mm}^3$) and maximum energy product of 52 MGOe) was deposited at the bottom of the beaker, both $\text{Fe}_3\text{O}_4\text{@Au@11-MUA}$ NPs and $\text{Fe}_3\text{O}_4\text{@Au@11-DDT}$ NPs were quickly isolated from the solution within a few seconds.

The 11-MUA and 11-DDT were self-assembled on the surface of the $\text{Fe}_3\text{O}_4\text{@Au}$ NPs via Au–thiol bonding and formed two types of sulfur-based monolayers with different surface properties. Energy-dispersive spectroscopy (EDS) analysis (Figure S2, Supporting Information) of $\text{Fe}_3\text{O}_4\text{@Au@11-MUA}$ NPs clearly revealed their elemental composition, in which Fe and Au signals confirm the $\text{Fe}_3\text{O}_4\text{@Au}$ NPs, while the S signals prove the presence of 11-MUA on the Au surface. Successful surface modification with 11-MUA and 11-DDT was also verified by infrared spectroscopic analysis. Figure 2 displays the IR spectrum of the $\text{Fe}_3\text{O}_4\text{@Au}$ NPs, $\text{Fe}_3\text{O}_4\text{@Au@11-MUA}$ NPs, and $\text{Fe}_3\text{O}_4\text{@Au@11-DDT}$ NPs. Asymmetric and symmetric stretching vibrations of the $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ of 11-MUA and 11-DDT were observed at 2922 and 2851 cm^{-1} , respectively.³⁷ In comparison to the FT-IR spectrum of $\text{Fe}_3\text{O}_4\text{@Au}$ NPs, the intensities of $\nu_a(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ of the $\text{Fe}_3\text{O}_4\text{@Au@11-DDT}$ NPs FT-IR spectrum were significantly increased. The variation of the intensities was directly related to the mole fraction of the 11-DDT in the SAMs,³⁸ and therefore, the changes observed clearly indicated that the surface of $\text{Fe}_3\text{O}_4\text{@Au}$ NPs was successfully modified with 11-DDT. Carboxy-

(32) Zhao, X. L.; Shi, Y. L.; Cai, Y. Q.; Mou, S. F. *Environ. Sci. Technol.* **2008**, *42*, 1201–1206.

(33) Zhao, X. L.; Shi, Y. L.; Wang, T.; Cai, Y. Q.; Jiang, G. B. *J. Chromatogr., A* **2008**, *1188*, 140–147.

(34) Pang, L. L.; Li, J. S.; Jiang, J. H.; Le, Y.; Shen, G. L.; Yu, R. Q. *Sens. Actuators, B* **2007**, *127*, 311–316.

(35) Tan, C. J.; Tong, Y. W. *Anal. Chem.* **2007**, *79*, 299–306.

(36) Ma, Z. Y.; Guan, Y. P.; Liu, H. Z. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3433–3439.

(37) Jiang, P.; Liu, Z. F.; Cai, S. M. *Langmuir* **2002**, *18*, 4495–4499.

(38) Zhang, H. L.; Chen, M.; Li, H. L. *J. Phys. Chem. B* **2000**, *104*, 28–36.

Figure 2. FT-IR spectra of $\text{Fe}_3\text{O}_4/\text{Au}$ and (a) 11-DDT, (b) 11-MUA, and (c) coated $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles. FT-IR spectra were taken in KBr pressed pellets on a NEXUS 670 infrared Fourier transform spectrometer (Nicolet Thermo, U.S.A.).

lic acid-terminated 11-MUA SAMs have been extensively characterized, and our results were consistent with those previously reported.^{25,28,39–41} The most prominent feature was the carbonyl stretch of the free carboxylic acid group or non-hydrogen-bonded (COOH) at 1740 cm^{-1} , whereas the side-by-side dimeric hydrogen-bonded one was at 1717 cm^{-1} . The carboxylate (COO^-) band at 1400 cm^{-1} indicated that a small number of the 11-MUA molecules were in deprotonated form.

Even though FT-IR unambiguously confirmed the successful surface modification, X-ray photoelectron spectroscopy (XPS) was also employed as a useful method to acquire more quantitative data on the structure of self-assembled thiol monolayers. Since XPS generally provides elemental information of the surface atomic composition, it is routinely applied to characterizing surface modification.⁴² Binding energies and high-resolution regions of

XPS spectra of the various elements such as C (1s), O (1s), and S (2p) can provide considerable rich information on the structure of SAMs. The XPS survey spectra of $\text{Fe}_3\text{O}_4/\text{Au}@11\text{-MUA}$ NPs and $\text{Fe}_3\text{O}_4/\text{Au}@11\text{-DDT}$ NPs are shown in Figure 3. Nonlinear least-squares fit of the high-resolution XPS spectrum at the S (2p) region (Figure 3, parts a and c), resulted in two peaks at 162.2 and 163.1 eV for 11-MUA SAMs and 162.7 and 163.5 eV for 11-DDT SAMs. These were assigned, respectively, to the S ($2p_{3/2}$) and S ($2p_{1/2}$) photoelectrons. The S ($2p_{3/2}$) peak of $\text{Fe}_3\text{O}_4/\text{Au}@11\text{-MUA}$ NPs and $\text{Fe}_3\text{O}_4/\text{Au}@11\text{-DDT}$ NPs were close to the S ($2p_{3/2}$) binding energy for alkanethiolates on Au, which is further a supporting evidence for the formation of a thiolate-bound SAMs. Thiols bound to Au surface as thiolates have S (2p) binding energies of about 162 eV, whereas unbound thiols have binding energies of 164–165 eV.^{16,43} None of the alkanethiolates SAMs showed any traces of unbound thiols. According to their chemical configuration, an 11-MUA molecule contains 11 carbon atoms at different valence states and two oxygen atoms, whereas an 11-DDT molecule contains 12 carbon atoms at the same valence state but contains no oxygen atom. Thus, for 11-MUA SAMs in the C (1s) region (see Figure 3b), there were two distinct components at 284.6 and 289.1 eV, which were assigned to the methylene carbon and the carboxyl carbon, respectively. The small discrete peak at higher binding energy, arising from the carbon atom in the carboxylic acid group, indicated the presence of the 11-MUA monolayers. For 11-DDT SAMs in the C (1s) region (see Figure 3d), there was only a single sharp peak at 284.8 eV evidencing the aliphatic hydrocarbon chains. Furthermore, for 11-MUA SAMs in the O (1s) region (data not shown), curve fitting resulted in two peaks at 533.1 and 532.0 eV for the hydroxyl and

Figure 3. X-ray photoelectron spectroscopy (XPS) high-resolution spectra of S (2p) and C (1s) for 11-MUA SAMs (a and b) and 11-DDT SAMs (c and d). XPS measurements were conducted by using an ESCA-Laboratory-220i-XL spectrometer with monochromatic Al $K\alpha$ radiation (1486.6 eV). C (1s) peaks were used as an internal standard calibration peak at 284.7 eV. XPS data processing and peak fitting was performed using a nonlinear least-squares fitting program (XPS peak software 4.1, Raymund W. M. Kwork).

Scheme 2. Illustration of the Structures of the 11-MUA SAMs on a Fe₃O₄@Au NPs Surface under Different pH Values and Their Interaction with Different Target Compounds

the carboxyl oxygen, respectively.⁴⁴ All of the XPS data agreed well with the results previously reported.^{21,37,42–45} On the basis of above results, it can be concluded that 11-MUA and 11-DDT monolayers were successfully formed on the surface of Fe₃O₄@Au NPs.

To further study the structure and surface properties of the SAMs, different types of organic compounds were selected as probe molecules. The outer surface of 11-DDT coated Fe₃O₄@Au NPs contains hydrophobic long chains, whereas that of 11-MUA coated Fe₃O₄@Au NPs contains hydrophobic long chains with an ionizable terminal group (carboxylic acid groups). For the 11-DDT coated Fe₃O₄@Au NPs system, the mercapto groups anchor on the Au surface while the hydrophobic tail groups protrude into the solution, which causes retention of analytes by strong hydrophobic interactions. For the 11-MUA coated Fe₃O₄@Au NPs system, when the pH of solution is above the pK_a of 11-MUA, the terminal group (carboxylic acid) of 11-MUA is deprotonated and becomes negatively charged (Scheme 2), and electrostatic repulsion between the same charged polar groups of SAMs and analytes will lead to the decrease in retention.

Figure 4, parts a and b, shows that both of the nanomaterials had strong adsorption capability toward the target compounds, which can be explained by the hydrophobic interactions between the target molecule and alkanethiolates SAMs that mainly govern the retention. Generally, Log K_{ow} is used extensively to demonstrate the hydrophobic properties of a compound and pK_a is used to estimate the deprotonation condition. Supporting Information Table S1 lists the Log K_{ow} and pK_a of the probe molecules. For the 11-DDT coated Fe₃O₄@Au NPs system, the relative adsorption of the five analytes closely correlated with the Log K_{ow} values

(Figure 4). With increasing Log K_{ow} value, the amount of adsorbed analytes increased markedly, which further proved that the adsorption ability mainly depends on the hydrophobic interactions.

Figure 4. Effect of solution pH on the adsorption of target compounds on 11-DDT SAMs Fe₃O₄@Au NPs (a) and 11-MUA SAMs Fe₃O₄@Au NPs (b). Operation was in batch mode. Sample volume: 2 mL. Amount of nanoparticles: 20 mg. Analyte concentrations: 4 mg/L BPA, 4-OP, 4-NP, and phenanthrene, 10 mg/L SDS. Equilibrium time: 30 min. Equilibrium temperature: 25 ± 1 °C. Batch experiments were performed on three replicates, and the standard deviation is represented as the error bar.

(39) Frey, B. L.; Corn, R. M. *Anal. Chem.* **1996**, *68*, 3187–3193.

(40) Palma, R. D.; Peeters, S.; Bael, M. J. V.; Rul, H. V.; Bonroy, K.; Laureyn, W.; Mullens, J.; Borghs, G.; Maes, G. *Chem. Mater.* **2007**, *19*, 1821–1831.

(41) Nakano, K.; Yoshitake, T.; Yamashita, Y.; Bowden, E. F. *Langmuir* **2007**, *23*, 6270–6275.

(42) Tan, C. J.; Chua, H. G.; Ker, K. H.; Tong, Y. W. *Anal. Chem.* **2008**, *80*, 683–692.

(43) Vogt, A. D.; Han, T., Jr. *Langmuir* **1997**, *13*, 3397–3403.

(44) Yam, C. M.; Zheng, L.; Salmann, M.; Pradier, C. M.; Marcus, P.; Jaouen, G. *Colloids Surf., B* **2001**, *21*, 317–327.

(45) Li, X. H.; Li, Y. C.; Yang, C. H.; Li, Y. F. *Langmuir* **2004**, *13*, 3734–3739.

BPA showed lower relative adsorption due to its less hydrophobic nature compared with the other analytes. For the 11-MUA coated $\text{Fe}_3\text{O}_4/\text{Au}$ NPs system (Figure 4b), the adsorption characteristics of the five analytes not only is consistent with their $\text{Log } K_{\text{ow}}$ value but also correlated with the $\text{p}K_{\text{a}}$ values. When the solution pH was above 4.8 (the $\text{p}K_{\text{a}}$ of 11-MUA is about 4.8), the surface of 11-MUA coated $\text{Fe}_3\text{O}_4/\text{Au}$ NPs was mainly in the negatively charged form. The pH of solutions in the range of 3–11.5 has significant influence on the adsorption of phenolic compounds and SDS. In detail, the relative adsorption of BPA, 4-OP, and 4-NP decreased at $\text{pH} > 10$ (the $\text{p}K_{\text{a}}$ of three phenolic compounds were all below 10.0), which can be ascribed to the electrostatic repulsion between the negatively charged 11-MUA SAMs surface and the analytes with the same charge. Following this finding, typical ionic and nonionic compounds such as SDS and phenanthrene were selected to further illuminate the existence of this electrostatic repulsion. For SDS, which is ionic with negative charge in the whole pH range, the adsorption amount decreased dramatically as pH increased above 5 (above the $\text{p}K_{\text{a}}$ of 11-MUA). The adsorption of phenanthrene, a nonionic compound, did not change significantly with the increase of pH. All of the results indicated that the surface properties of 11-MUA@ $\text{Fe}_3\text{O}_4/\text{Au}$ NPs, similarly to the ICSs, could selectively adsorb target compounds by combining the functions of hydrophobic interactions and electrostatic repulsions.

CONCLUSIONS

In this work, we reported the synthesis of core/shell $\text{Fe}_3\text{O}_4/\text{Au}$ NPs that can be functionalized by alkanethiolates. These novel

nanosize materials combine the advantages of SAMs and core/shell $\text{Au}/\text{Fe}_3\text{O}_4$ NPs with magnetic separability and surfaces flexibility, which provide distinctive advantages such as well-defined structure and easy preparation, capable of incorporating a wide range of functional groups and exhibiting high stability and high reproducibility. When 11-MUA coated $\text{Fe}_3\text{O}_4/\text{Au}$ NPs and 11-DDT coated $\text{Fe}_3\text{O}_4/\text{Au}$ NPs system are compared, it can be concluded that, beside hydrophobic interactions, repulsive electrostatic interaction between the charged alkanethiolate terminal groups and the same charged groups of analytes played an important role in the selective adsorption of target molecule on the SAMs surface. Given these findings, it is likely that core/shell $\text{Fe}_3\text{O}_4/\text{Au}$ NPs with different alkanethiolate SAM modifications can be a useful tool in enhancing the analytical performance in biological and environmental monitoring.

ACKNOWLEDGMENT

This work was jointly supported by the National Natural Science Foundation of China (20621703, 20577058, 20475060).

SUPPORTING INFORMATION AVAILABLE

Preparation of alkanethiolate-functionalized core/shell $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles and batch adsorption test and characterization of $\text{Fe}_3\text{O}_4/\text{Au}$ nanoparticles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Received for review July 28, 2008. Accepted September 26, 2008.

AC801581M