Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Fluorescent Polarization Molecularly Imprinted Polymer and Its Application in the Tetection of Naringin

Chen Zhao (19379886@qq.com)
xi'an techological university
Xiangyan Meng
Xi'an Technological University
Wenzong Lu
Xi'an Technological University
Gun Li
Xi'an Technological University

Research

Keywords: Naringin, molecularly imprinted polymer, fluorescence polarization

Posted Date: August 11th, 2020

DOI: https://doi.org/10.21203/rs.3.rs-53954/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Abstract

Background

A fluorescent magnetic surface molecular imprinting method was used to detect narigin by fluorescence polarization technology.

Method

By using SiO_2-coated magnetic particles as substrate and methlacrylic acid and acrylamide as monomers, a surface molecular imprinting polymer with both fluorescence and magnetic characteristics was prepared and loaded with fluorescein isothiocyanate. The binding ability of the prepared polymer was tested by fluorescence polarization and ultraviolet (UV) spectrophotometry.

Results

Compared two other methods, the fluorescence polarization method was more sensitive, and its limit of detection (LOD) was 0.1 mg/L. The recovery of the fluorescence polarization method was higher than 81.3%.

Conclusion

It was shown that the fluorescent magnetic surface molecular imprinting technique could be a new method to quickly and efficiently detect naringin in food.

Background

Naringin, a kind of dihydroflavonoid compound with multiple biological activities and pharmacological actions [1-2], features activities of antivirus, anti-mutation, anti-allergy, anti-ulcer, anticancer, anti-inflammation, analgesia and blood pressure reduction. It can be applied in the food industry as a flavor modifying agent, natural pigment or bitterant for food and beverage production. However, it may poison human's genes [3] as it is one of the toughest substances for oxidation promotion among flavonoid compounds that are able to resist [4-6] and promote oxidation according to research. Among the Chinese patent medicines, those against coughing contain a certain amount of flavonoid compound, or naringin that is tested for more effective control over medicine quality via the currently-used methods of high performance liquid chromatography (HPLC) and spectrophotometry [7-8]. The latter is easy to present false-positive results due to its lower sample selectivity, while the former is costlier and time consuming in sample testing in spite of higher measuring precision and relatively thorough separation of structural analogues. Therefore, it is necessary to research how to detect naringin rapidly and effectively.

In recent years[9-14], the molecular imprinting technique has been rapidly developing in fields of separation, catalyzing and sensor, owing to its specificity and practicality. Notably, the research on the surface molecular imprinting technique has solved the problems in the traditional molecular imprinting

technique, such as difficulties for elution and recombination of template molecules caused by highly-crosslinked net-structured polymers, and for efficient combination. The surface molecular imprinting technique is to compound molecularly imprinted polymers on the vehicle surface, forming a two-dimension net structure which makes template molecules easy for adsorption and elution, and thus improves the capability of polymers to absorb and select [14-16]. In the meantime, the combination of the magnetic nano-materials and the surface molecular imprinting technique produces magnetic surface molecularly imprinted polymers, which can rapidly separate under external electric field, with merits of active identification and fast separation [17-18]. The fluorescent surface molecularly imprinted polymers produced by marking fluorescent materials on the surface molecularly imprinted polymers have fluorescence properties. Whether the template molecules have or have no fluorescence properties, they can be detected by the fluorescence method that greatly improves the sensitivity and specificity of the detection. The schematic diagram for this process is shown in Fig. 1. As a new popular method in fluorescence detection, fluorescence polarization, based on physical manifestation, is used to study the interaction among molecules in lives. It can simulate, to the most extent, the real life environment, while performing the real-time monitoring on the variation among molecules [19]. This experiment combines the magnetic and the fluorescent surface molecular imprinting techniques to produce naringin fluorescent magnetic surface molecularly imprinted polymers, and adopts a fluorescence polarimeter to carry out real-time inspection on detection signals, thus achieving a new sensitive way to detect naringin rapidly and efficiently.

Results

Magnetic inspection

As shown in Fig. 2, particles disperse in the water which appears to be black and turbid. By absorbing the particles in the water with a magnet, it can be clearly seen that all the particles gather at one side of the magnet, and thus the solution becomes clear again. Therefore, it can be demonstrated that the prepared Fe_3O_4, Fe_3O_4@SiO_2 and fluorescent MIP-Fe_3O_4@SiO_2 are magnetic.

Infrared spectroscopy analysis

By inspecting between 4 000–400cm^{-1} with the infrared spectrometer, as shown in Fig. 3a, it can be seen that there are two characteristic peaks, at 561 cm^{-1} is an absorption peak called the characteristic vibration peak of Fe—O , while that at 1,400 cm^{-1} presents the vibration peak of hydroxide radical. So it is known that the preparation of Fe_3O_4 magnetic nano-particles is correct. As shown in Fig. 3b, at 1,091 cm^{-1} is an absorption peak that is the characteristic peak of Si—O, demonstrating that SiO_2 is successfully covering the surface of Fe_3O_4 particles.

Inspection by fluorescence microscope

A fluorescence microscope with a ten-time magnification is used for fluorescence detection on fluorescent MIP-Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2, as shown in Fig. 4. By comparison of both two, it can be seen in Fig. 4a that fluorescent circles clearly appear on the surface of silica gel, while nothing happens in Fig. 4b. This proves that fluorescent molecules are successfully decorated on the fluorescent MIP-Fe_3O_4@SiO_2.

Results by transmission electron microscope (TEM)

A TEM with a 10,000-time magnification is used for detection on Fe_3O_4, Fe_3O_4@SiO_2 and fluorescent MIP-Fe_3O_4@SiO_2under the accelerating voltage of 75kV. From Fig. 5a, it can be seen that the magnetic particles with an average diameter of about 70nm are relatively even in size, shape and spatial distribution. As for Fe_3O_4@SiO_2, it can be observed from Fig. 5b that the regularly round particles have a diameter increased to about 100nm due to Fe_3O_4@SiO_2 wrapped by SiO_2. From Fig. 5c, it can be clearly seen that the particles are irregular in size, shape and distribution, with a diameter of 100–200nm. This is because the monomer, fluorescent reagent (isothiocyanic acid fluorescer) and cross-linking agent that wrap Fe_3O_4@SiO_2 leave the diameter of fluorescent MIP- Fe_3O_4@SiO_2 increased.

Results of detection on the combining rate of fluorescent MIP-Fe_3O_4@SiO_2 by ultraviolet spectroscopy

The ultraviolet spectrophotometer is used to detect the ultraviolet absorption value of the solution before and after adding fluorescent MIP-Fe_3O_4@SiO_2 and NIP-Fe_3O_4@SiO_2, and the value of Q as the combining amount of fluorescent polymers is calculated according to Equation (1). Taking mass concentration as abscissa and Q as ordinate, the isothermal curve of naringin fluorescent MIP-Fe_3O_4@SiO_2 and NIP-Fe_3O_4@SiO_2 adsorbing naringin can be obtained, as shown in Fig. 6. The capability of fluorescent MIP-Fe_3O_4@SiO_2 to combine naringin is obviously higher than that of NIP-Fe_3O_4@SiO_2, in that the nonspecific absorption of NIP-Fe_3O_4@SiO_2 to combine naringin has a value so small that can be negligible. Therefore, the prepared fluorescent MIP-Fe_3O_4@SiO_2 can combine naringin in a specific way, and its combining capability reaches to the maximum limit when the mass concentration of naringin is at 2.5mg/L. The lower limit of detection by ultraviolet spectroscopy on naringin is 0.5mg/L.

Results of detection on the combining capability of naringin fluorescence magnetic molecularly imprinted polymer by fluorescence polarization

As shown in Fig. 7, the capability of fluorescent MIP-Fe_3O_4@SiO_2 to combine naringin varies in a linear way under the mass concentration ranging 0.1–0.9mg/L. With the increase in the mass concentration of naringin solution, the signal value of fluorescence polarization rises, and thus the combining capability increases. This is because the fluorescence-marked micromolecular fluorescent MIP-Fe_3O_4@SiO_2span pretty fast in the solution, with a small light intensity of fluorescence polarization. After such fluorescence-marked micromolecular fluorescent MIP-Fe_3O_4@SiO_2 were added to the naringin solution, they combined with naringin in the solution to form a kind of macromolecular compound whose

molecules slowed down the rotation, thus leading the light intensity of fluorescence polarization to increase. The higher the concentration of naringin solution is, the more the naringin molecules that combine with fluorescent MIP-Fe3O4@SiO2, the larger the volume of the large molecules, and the stronger the fluorescence polarization integrity. Taking the deionized water as blank control, the fluorescent surface molecularly imprinted polymers in the solution did not combine with naringin molecules at this moment, and the fluorescence polarization value measured was 28.564. It increased with the increase of the mass concentration of naringin solution, due to the combination of the naringin molecules in the solution and the fluorescent MIP-Fe_3O_4@SiO_2. When the combination of both approached the upper limit, or the mass concentration reached to 0.9mg/L, the volume of large molecules became constant, and the fluorescence polarization value tended to be stable. The NIP-Fe_3O_4@SiO_2-add fluorescence polarization signals had no obvious change with the increase of the mass concentration of the solution. This is because the nonspecific interaction of NIP-Fe_3O_4@SiO_2 and naringin molecules by electrostatic adsorption led to a small and constant combining amount that didn't increase with the changing mass concentration of the solution, and had slight impact on the volume of NIP-Fe_3O_4@SiO_2, leading to a pretty small fluorescence polarization value and an almost unchanged curse. By comparison of the two curses in Fig. 7, it can be known that the fluorescent MIP-Fe_3O_4@SiO_2 has a specific impact on the naringin detection. Meanwhile, the limit for fluorescence detection on naringin is 0.1mg/L, with the linear detection range of 0.1 0.9mg/L (R2=0.995 8) and the linear equation of y=94.84x, which is obviously lower than that for ultraviolet spectrophotometry. Therefore, it indicates that the fluorescence method used for detecting the capability of molecularly imprinted polymer to combine naringin is more sensitive.

Results of detecting the recovery rate of naringin in food

As shown in Table 1, the recovery rate of naringin in food by the prepared fluorescent MIP-Fe_3O_4@SiO_2 is 81.3%-92.9%. Meanwhile, NIP-Fe_3O_4@SiO_2 has a lower naringin recovery rate, below 10%. This shows that the prepared naringin MIP-Fe_3O_4@SiO_2 can effectively detect whether the food contains naringin, and this method has specificity.

Table 1 Detection recovery of Naringin in ketchup

		MIP-Fe_3O_4@SiO_2		NIP-Fe_3O_4@SiO_2	
	Adding Naringin (mg)	Testing Naringin (mg)	Recovery (%)	Testing Naringin (mg)	Recovery (%)
Ketchup	0.12	0.10	83.3%	0.01	8.3%
	0.16	0.13	81.3%	0.012	7.5%
	0.25	0.23	92%	0.021	8.4%
	0.31	0.27	87.1%	0.029	9.3%
	0.42	0.39	92.9%	0.033	7.8%

Discussion

This experiment has several steps: first, introduce highly-active group – couple on the surface of silica gel with triethoxyvinylsilane as the coupling reagent through hydroxide radical – by taking Fe_3O_4@SiO_2 as the base and adopting the “grafting to” technology of using the interaction between Fe_3O_4@SiO_2 and hydroxide radical; second, add functional monomers (methacrylic acid and acrylamide) to form polymeric macromolecular chains and couple on the surface of the silica gel; third, add fluorescent reagent for combining with the amide bond of acrylamide; last, add template and cross-linking agent to aggregate into a molecular imprinting layer. The fluorescent MIP-Fe_3O_4@SiO_2 is obtained after the elution of template molecules. Magnetic nano-particles magnetize the surface molecularly imprinted polymers, and make them separate and aggregate rapidly under external electric field, thus simplifying the operating steps. The nano-scale Fe_3O_4@SiO_2 formed by silica-gel-wrapped Fe_3O_4 particles has a higher specific area and surface activity, whose surface can couple with various coupling reagents, and will encounter swelling and resist corrosion in organic solvent due to the thermostability and rigidity of silica gel itself. Therefore, the surface molecularly imprinted polymers made by Fe_3O_4@SiO_2 as the base have an excellent performance.

Meanwhile, this experiment proposed using the fluorescence polarization method to evaluate the combining efficiency of fluorescent surface molecularly imprinted polymers. Due to the fast rotation of the fluorescence-marked nano-scale surface molecularly imprinted polymers in the solution and a small light intensity of fluorescence polarization, the combination of such polymers and corresponding substrates generated new polymers with an increased volume, decreased spinning speed and increased light intensity of fluorescence polarization. The difference of fluorescence polarization values has some bearing on how many fluorescent surface molecularly imprinted polymers in the solution combine with substrates. With the increase of the mass concentration of naringin solution, the combination of the naringin in naringin solution with different mass concentrations and the fluorescent MIP-Fe3O4@SiO2 gradually peaked, while the light intensity of fluorescence polarization increased to a stable value. The

nonspecific combination between fluorescence NIP-Fe3O4@SiO2 and naringin molecules made such a combination inefficient, and thus the fluorescence polarization strength had no obvious change with the increased mass concentration of the solution, with its change having nothing to do with the mass concentration of naringin solution (see Fig. 7). Therefore, it is feasible to use the fluorescence polarization method to detect how fast the naringin fluorescent MIP-Fe3O4@SiO2 can combine naringin. Comparing with the ultraviolet spectroscopy method in detection sensitivity, it is known that the lowest limit of detection for ultraviolet spectroscopy is 0.5mg/L, and that for fluorescence polarization method is 0.1mg/L, with a linear detecting range of 0.1-0.9mg/L (R2=0.995 8). This can demonstrate that the new fluorescence polarization method is more sensitive, efficient and convenient. The recovery rate of naringin in food can reach over 81.3% by using this method.

Conclusion

In conclusion, the prepared fluorescent magnetic surface molecularly imprinted polymers have an excellent recovery rate, and the fluorescence polarization has a higher specificity and sensitivity in detecting naringin in food.

Materials And Methods

2.1 Materials and agents

Self-made ketchup by laboratory; $FeCl_2$•$4H_2O$, $FeCl_3$•$6H_2O$, ethyl alcohol, aqua ammonia, isopropanol, tetraethoxysilane(TEOS), methacrylic acid, acrylamide, acetone, ammonium persulfate, naringin and ethylene glycol dimethacrylate (EDMA) (all of them are analytical pure) from TCI Shanghai; methylsulphonicacid and fluorescein isothiocyanate (FITC) (both of them are analytical pure) from Sinopharm Chemical Reagent Co., Ltd.; vinyltriethoxysilane (analytical pure) from US Sigma-Alorich; chloroform (analytical pure) from Sinopharm Shanghai.

2.2 Instruments and devices

DF-101S Heat-collecting Thermostatic Magnetic Stirrer from Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd.; 101 Electrothermal Blowing Dry Box from Beijing Kewei Yongxing Instrument Co., Ltd.; JEM-2100F Transmission Electron Microscope from JEOL; RE5298A Rotary Evaporator from Shanghai Yarong Biochemical Instrument Co., Ltd.; IRprestige-21 Fourier Transform Infrared (FTIR) Spectrometer from Shimadzu Corporation; 2100UV Ultraviolet Spectrophotometer from Amersham Biosciences Corp.; BX40 Fluorescence Microscope from Olympus Corporation.

2.3 Methods

2.3.1 Preparation of fluorescent magnetic surface molecularly imprinted polymers

1) Preparation of Fe_3O_4 nano-particles

Add 1.72g $FeCl_2$•$4H_2O$, 4.72g $FeCl_3$•$6H_2O$ and 80mL deionized water into a flask, release nitrogen continuously into the flask and then pour the mixture into the DF-101S heat-collecting thermostatic magnetic stirrer to make them dissolved by forceful stirring. Slowly instill 10mL aqua ammonia solution into the flask for reaction for 30min with the temperature rising to 80℃. Separate the product under external magnetic field. Then wash it with deionized water six times to remove the unreacted substances before drying it for storage.

- Preparation of Fe_3O_4@SiO_2

Perform ultrasonic treatment to 300mg magnetic nano-particles, 50mL isopropanol and 4mL ultrapure water for 15min, and then successively add 5mL aqua ammonia and 2mL tetraethoxysilane. Keep stirring to let them react for 12h at room temperature. Collect the product under external magnetic field, and then use ultrapure water to wash it six times before drying it.

- Preparation of fluorescent Fe_3O_4@SiO_2

Activate 20g Fe_3O_4@SiO_2 in the methylsulphonicacid solution (50% of mass fraction). Place the activated Fe_3O_4@SiO_2 and 30mL vinyltriethoxysilane into 400mL mixed solution of ethyl alcohol and water of 1:1 (V/V) to let them react for 31h at 50℃, and wash with ethyl alcohol and distilled water before drying, to get vinyltriethoxysilane-Fe_3O_4@SiO_2. Put 3g vinyltriethoxysilane-Fe3O4@SiO2, 10g methacrylic acid, 1g acrylamide, 200mL distilled water and 0.018g ammonium persulfate into a 200mL round-bottom flask, to let them react for 7h at 70℃, then collect the product under external magnetic field, and wash it with ethyl alcohol and distilled water for several times before drying it. Mix 1g product obtained from the above process, 15mg fluorescein isothiocyanate, 5mL ethyl alcohol and 100mL distilled water, and keep shaking for 5h. Then collect the product under external magnetic field, and wash it before drying it.

- Preparation of fluorescent MIP-Fe_3O_4@SiO_2

Dissolve the synthesized fluorescent Fe_3O_4@SiO_2 and 4mmol/L naringin into 100mL chloroform solution, keep releasing nitrogen into the solution for 5min, shake it for 6h before adding EDMA as the cross-linking agent, and then keep stirring for 8h in 50℃ of water bath kettle. Collect the product under external magnetic field, and then wash it before drying it.

- Preparation of non-imprinted fluorescent magnetic polymer (NIP-Fe_3O_4@SiO_2)

Its preparation is the same as the above 2.3.1.4 section except for the step of adding naringin.

2.3.2 Inspection on the combining capability of naringin fluorescent magnetic surface molecularly imprinted polymers

1) Inspection on the combining capability by ultraviolet spectroscopy

First, prepare naringin solution with varied mass concentrations. Then place 0.05g fluorescent MIP-Fe_3O_4@SiO_2 into such naringin solution for 1h. Then take away the clear liquid on the upper layer, to detect the UV absorption value of the solution after reaction via ultraviolet spectrophotometry. Thus the mass concentration of the solution after reaction can be calculated according to the standard curve. And the Q value is calculated by Equation (1):

$$Q = \frac{v(c_1 - c_2)}{m}$$

(1)

where, c1 is the initial mass concentration (mg/L) of the naringin solution; c2 is the mass concentration (mg/L) of the naringin solution when being in equilibrium; v is the volume (L) of the naringin solution; m is the quality (g) of fluorescent MIP-Fe_3O_4@SiO_2; Q is the content (g/g) of naringin combining with MIP@Fe_3O_4 of unit mass when being in equilibrium.

The method to detect how fast NIP-Fe_3O_4@SiO_2can combine naringin is the same as above. Naringin NIP-Fe_3O_4@SiO_2 is added into the standard solution to calculate the Q value, which will be compared with the detected results of imprinted polymers

- Inspection on the combining capability by fluorescence polarization

Place equivalent fluorescent MIP-Fe_3O_4@SiO_2 and NIP-Fe_3O_4@SiO_2 into the centrifuge tubes with naringin standard solution of different mass concentrations and deionized water, respectively, to make naringin molecules interact with fluorescent MIP-Fe_3O_4@$SiO_2$and NIP-Fe_3O_4@SiO_2. Use a pipette to transfer a small amount of mixed solution in a 384 pore plate. Then place the pore plate in the fluorescence polarimeter for detection.

2.3.3 Results of detection on the recovery rate of naringin in ketchup by fluorescence polarization

Add the naringin of 0.12, 0.16, 0.25, 0.31 and 0.42mg to five helpings of ketchup to make the ketchup have a total mass of 10mg respectively, then take 10mg ketchup without naringin to make solutions of 1,000mL, respectively. Take 5mL solution, respectively, add 0.05g synthesized fluorescent MIP-Fe_3O_4@SiO_2 respectively, and then shake for 2h to make the fluorescent MIP-Fe_3O_4@SiO_2 to combine fully with naringin molecules for achieving the adsorption equilibrium. Use the fluorescence polarimeter to detect for fluorescence intensity. As per the linear relation between the mass concentration of naringin solution and the fluorescence intensity, the mass concentration of naringin in five helpings of solution can be obtained, thus its mass can be calculated. The recovery rate I of naringin in the ketchup can be gained according to Equation (2). In the meantime, NIP-Fe_3O_4@SiO_2 is used to perform fluorescence polarization detection on naringin in the ketchup as the controlled trial.

$$I = \frac{m}{m'} \times 100$$

(2)

where m’ is the mass (mg) of the naringin added in the ketchup; m is the naringin mass (mg) detected by fluorescence polarimeter; I is the recovery rate (%) of the naringin in the ketchup.

Abbreviations

TEM
transmission electron microscopy
UV
ultraviolet
LOD
limit of detection
HPLC
high performance liquid chromatography
MIP
molecularly imprinted polymer
NIP
non-imprinted polymer
FITC
fluorescein isothiocyanate
EGDE
ethylene glycol diglycidyl ether
TEOS
tetraethyl orthosilicate
TTS
triethoxyvinylsilane

Declarations

Availability of data and material

The data sets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Acknowledgements

The authors are grateful to all the study participants.

Funding

This work was supported by the Natural Science Foundation Research Project of Shaanxi Province of China (2018JQ2075, and 2014JQ2-8053) and National students innovation and entrepreneurship training (201610702017). The funding agency had no role in the study design; the collection, analysis, and interpretation of data; the writing of the report; or the decision to submit the article for publication.

Authors information

Affiliation

School of Electronic and Information Engineering of Xi'an Technological University,Xi'an City, Shanxi Province, 710021, Peoples Republic of China

Chen Zhao, Mengxiang Yang, Wenzong Lu, Gun Li

Contributions

All authors have read and agree to the published version of the manuscript. Conceptualization, Chen Zhao; methodology, Chen Zhao; software, Gun Li; validation, Xiangyan Meng and Wenzong Lu; data curation, Gun Li; writing—original draft preparation, Chen Zhao; writing—review and editing, Chen Zhao; supervision, Xiangyan Meng; funding acquisition, Chen Zhao

Corresponding Author

Correspondence to Chen Zhao

Ethics approval and consent to participate: Not applicable

References

1. Wilbur W. Collaborators:. Determination of Naringin and Neohesperidin in Orange Juice by Liquid Chromatography with UV Detection to Detect the Presence of Grapefruit Juice: Collaborative Study[J]. Journal of Aoac International. 2019;5:5.
2. Hongwei Yu,Weina Gu,Na Li. Research Progress of Naringin[J]. Hubei Agricultural Sciences. 2011;50(8):1516–8.
3. Ma X, Chen R, Zheng X, et al. Preparation and Application of Naringin Sensor Based on Molecularly Imprinting Technique[J].Chinese Journal of Analytical Chemistry,2010,38(1):100–104.
4. Li C,Jian Yu,Liang Zeng,et al.Study of antioxidation of Naringin on pork meat[J].Food research and development,200829(10): 20–23.
5. Kontogianni A, Skouridou V, Sereti V, et al. Lipase-catalyzed esterification of rutin and naringin with fatty acids of medium carbon chain[J]. Journal of Molecular Catalysis B Enzymatic. 2003;21(1–2):59–62.

6. Hou GX, Liu X, Ding Y, et al.Synthesis and Antiturnor Activity of Rare Earth Complexes with Naringin [J].Journal of Cannan Medical University,2015,35(1): 31–32.
7. Zeng X, Bai WY, et al. HPLC-MS/MS method for simultaneous determination of naringin and naringenin in human plasma[J]. Acta Scientiarum Naturalium Universitatis Sunyatseni. 2017;56(1):125–30.
8. Lian-jun Luan Zhou-hong, Jiang Song-yuan, Mi, et al. Comprehensive quality control method for total flavonoid of Fructus Aurantii][J]. Journal of Zhejiang University. 2011;40(1):17–22.
9. Yang Q, Wu X, Peng H, Fu L, Song X, Li J, Xiong H, Chen L. Simultaneous phase-inversion and imprinting based sensor for highly sensitive and selective detection of bisphenol A. Talanta. 2018;176:595–603.
10. Udomsap D, Branger C, Culioli G, Dollet P, Brisset H. A versatile electrochemical sensing receptor based on a molecularly imprinted polymer. ChemCommun. 2014;50:7488–91.
11. El Gohary NA, Madbouly A, El Nashara RM, Mizaikoff B. Synthesis and application of a molecularly imprinted polymer for the voltammetric determination of famciclovir. Biosens Bioelectron. 2015;65:108–14.
12. Yang Q, Peng H, Li J, Li Y, Xiong H, Chen L. Label-free colorimetric detection of tetracycline using analyte-responsive inverse-opal hydrogels based on molecular imprinting technology. New J Chem. 2017;41:10174–80.
13. Chen L, Xu S, Li J. Recent advances in molecular imprinting technology: current status, challenges and highlighted applications. Chem Soc Rev. 2011;40:2922–42.
14. Chen L, Wang X, Lu W, Wu X, Li J. Molecular imprinting: perspectives and applications. Chem Soc Rev. 2016;45:2137–211.
15. Chen Z. Wu Daocheng. Rapid detection assay for the molecular imprinting of gossypol using a two-layer PMAA/SiO2 bulk structure with a piezoelectric imprinting sensor[J]. Sens Actuators B. 2013;181:104–13.
16. Chen Z, Guangfeng J, Wenzong Lu, et al. A piezoelectri magnietic molecularly imprinted surface sensor for the detection of Sudan I[J]. Journal of Alloys and Compounds,2017 710,711–716.
17. Zhao C, Ren YM, Lu WZ, et al. Detection of piezoelectric magnetic surface molecularly imprinted sensor to chloramphenicol. Sci Technol Eng. 2016;16:149–53.
18. Chen Zhao G, Jia W, Lu, et al. Detection of Sudan I in food using magnetic molecularly imprinted polymer microspheres. Mod Food Sci Technol. 2016;32:,302–7.
19. Lu Wenzong N, Yuan J, Guangfeng, et al. Rapid fluorescence polarization immunoassay for highly sensitive detection of 2,4,6-Trinitrotoluene[J]. Asian J Chem. 2014;26(3):773–6.

Figures

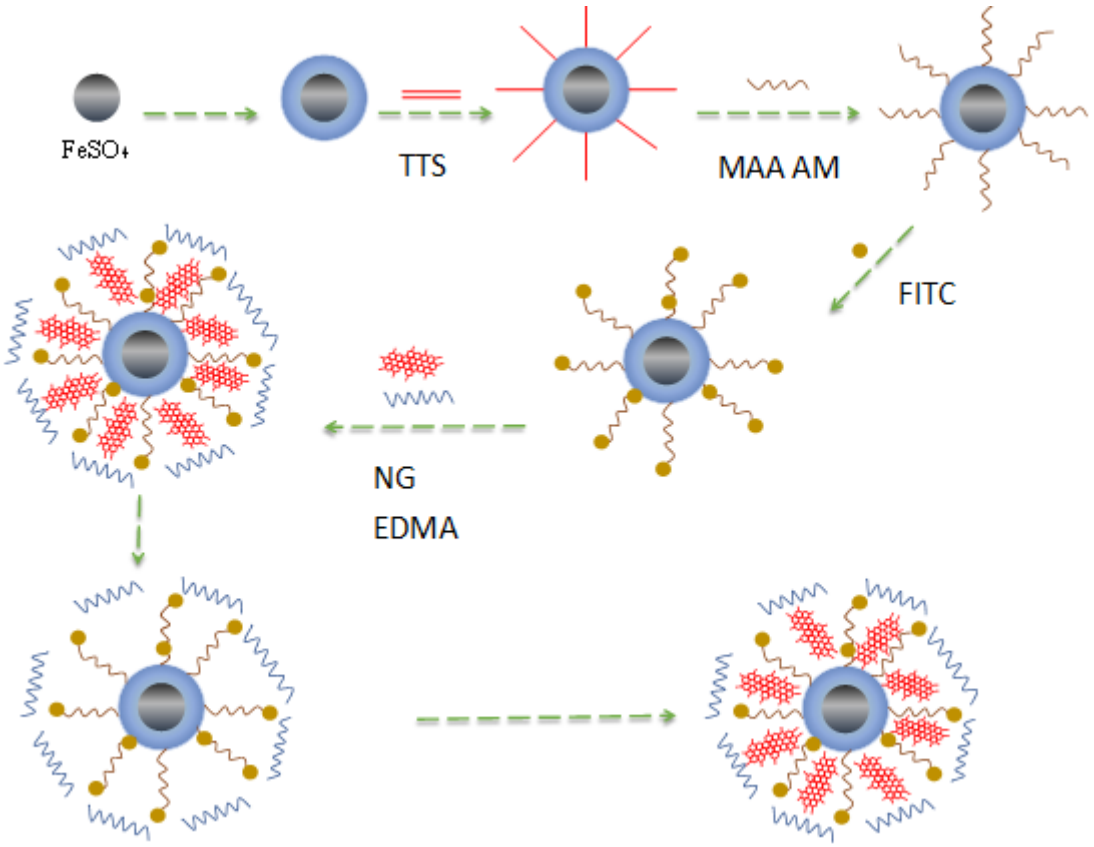

Figure 1

Schematic Diagram of Preparation of Fluorescent Magnetic Molecularly Imprinted Polymers

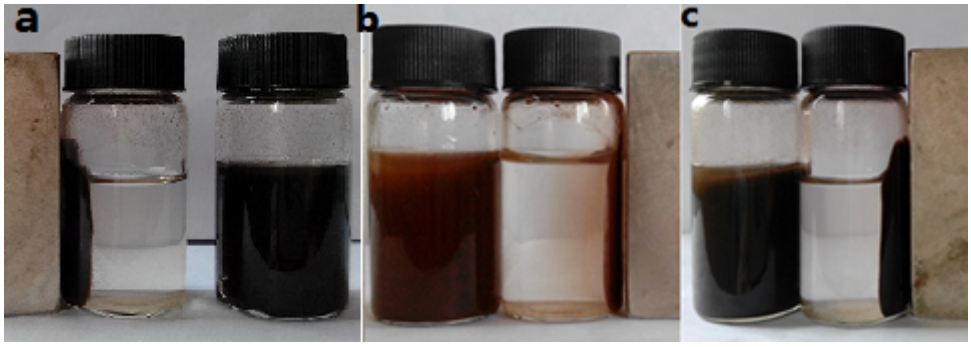

Figure 2

magnetic detection of Fe3O4（a）Fe3O4@SiO2（b）MIP- Fe3O4@SiO2（c）

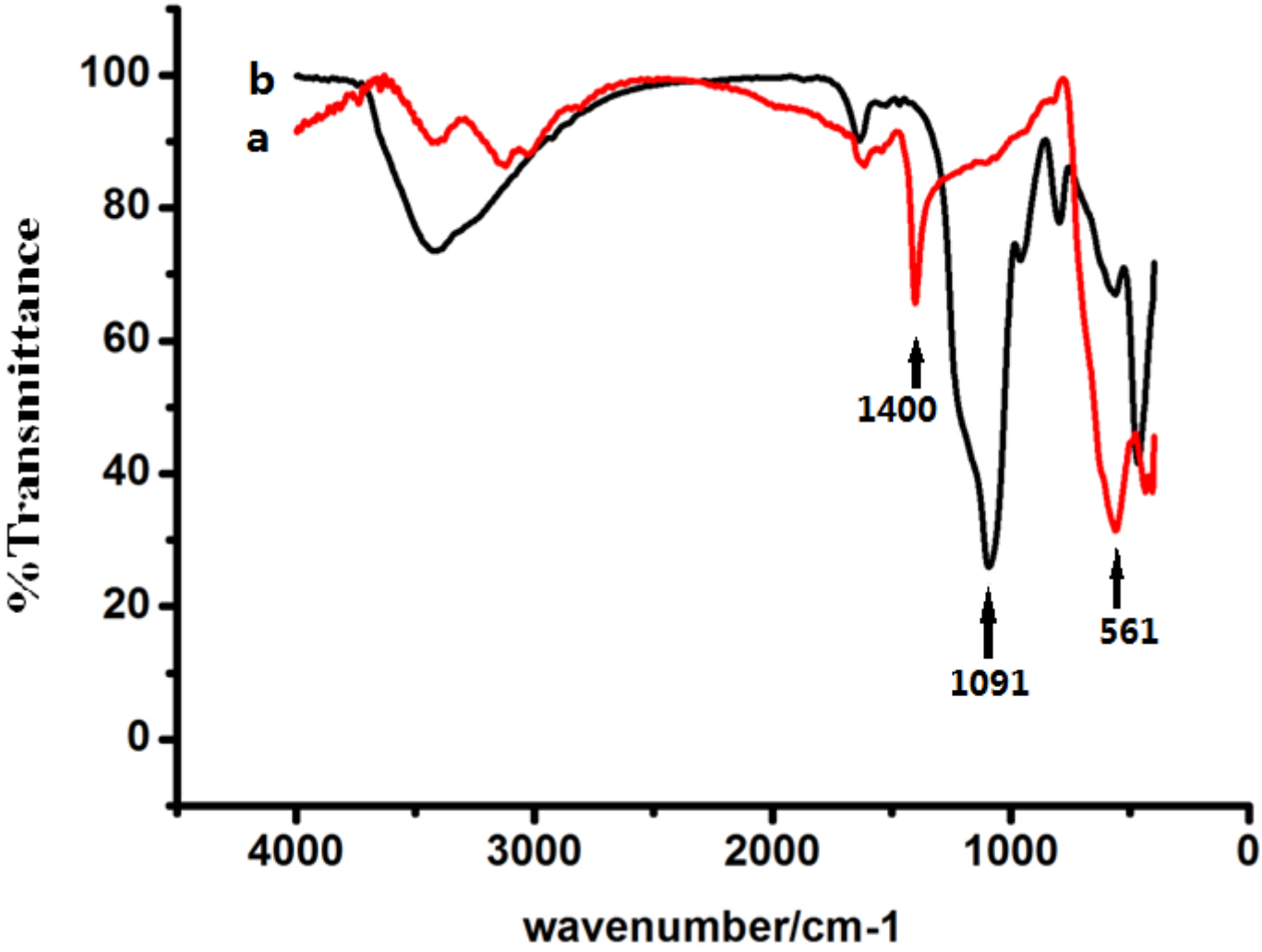

Figure 3

Infrared spectra of Fe3O4（a）and Fe3O4 @SiO2（b）

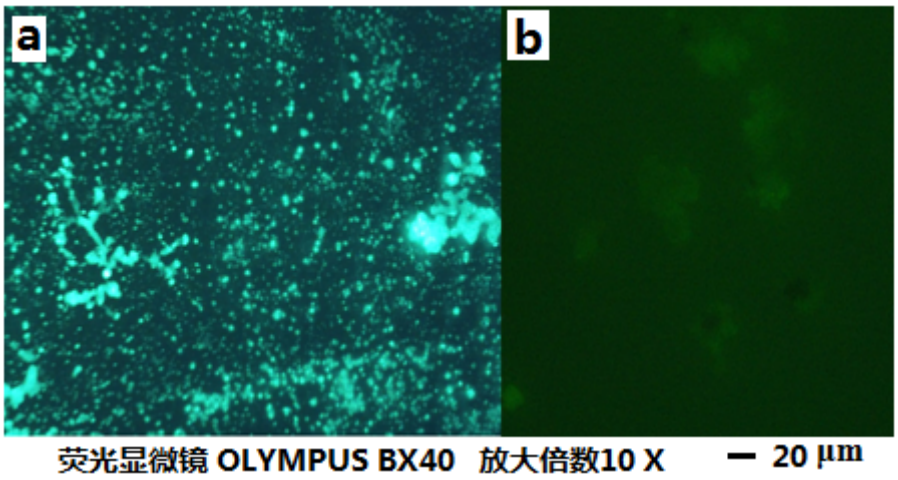

Figure 4

Fluorescence microscope detection of Fluorescence MIP- Fe3O4@SiO2（a）and Fe3O4@SiO2（b）

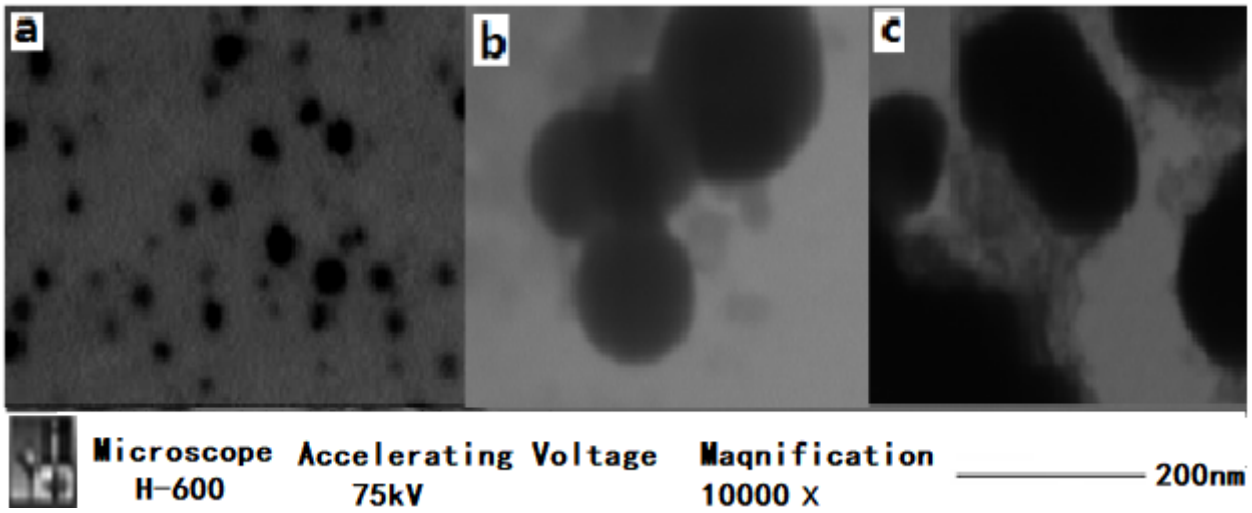

Figure 5

TEM images of Fe3O4 (a) Fe3O4@SiO2 (b) and MIP- Fe3O4@SiO2 (c)

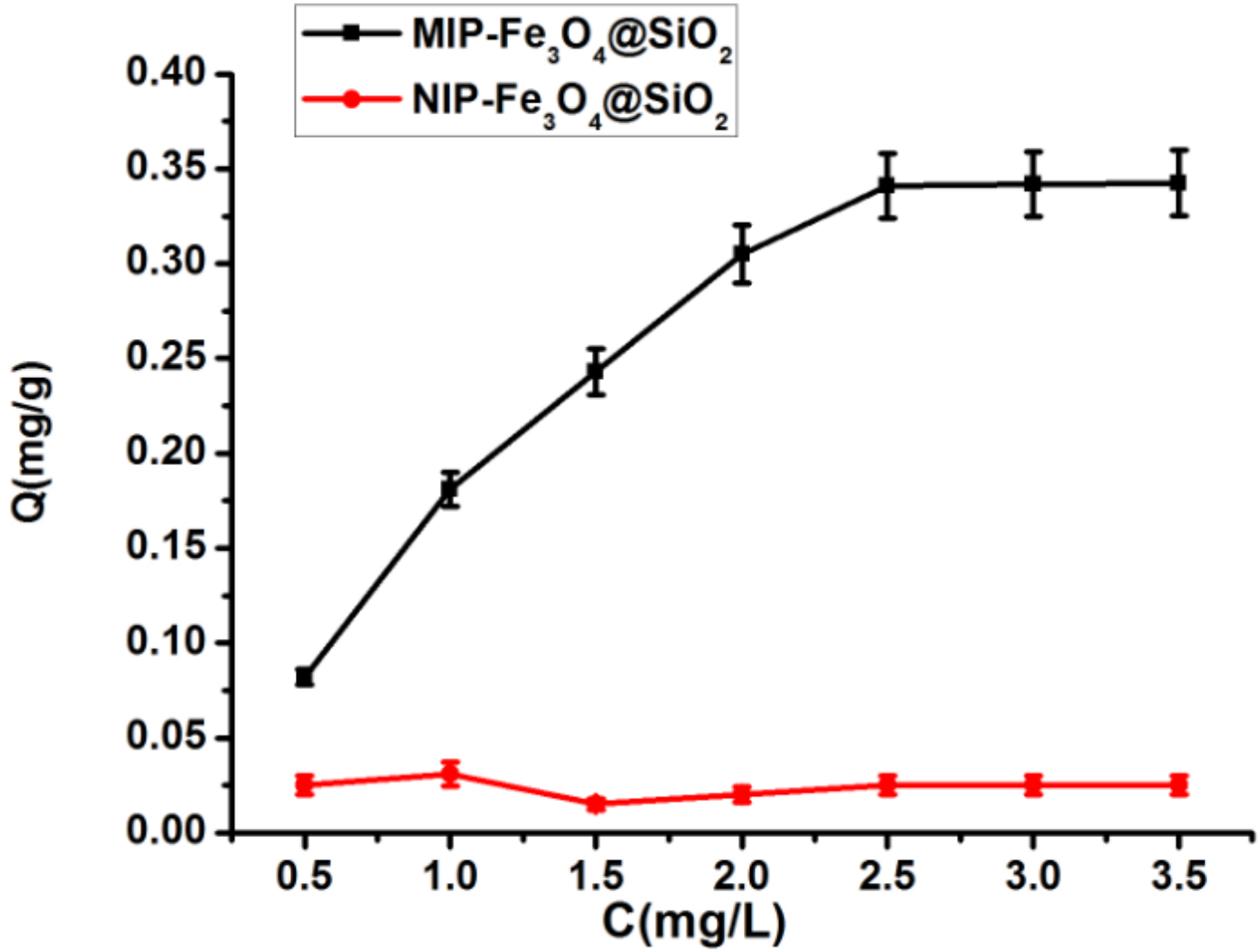

Figure 6

Adsorption isotherm of Naringin for MIP-Fe3O4@SiO2 and NIP-Fe3O4@SiO2

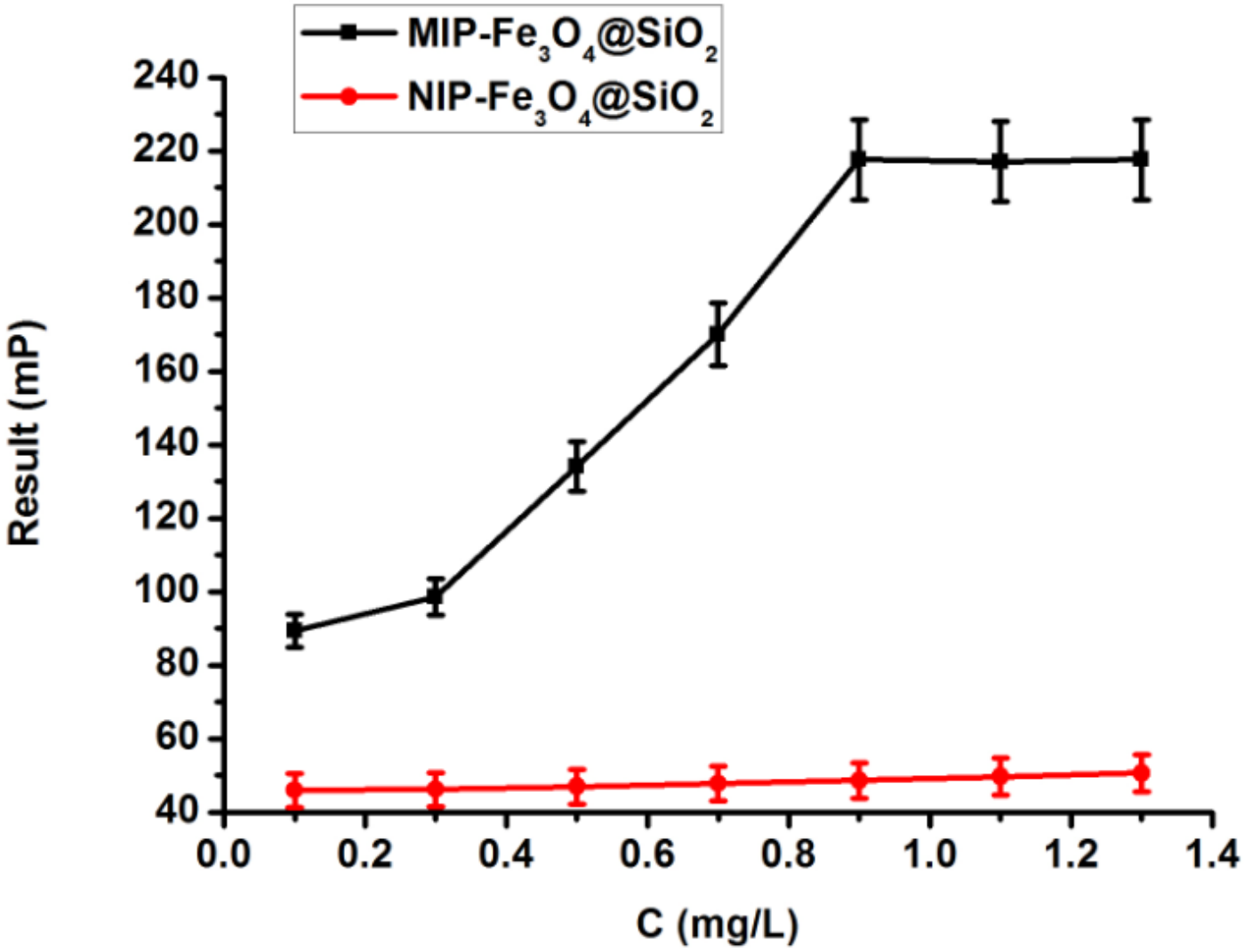

Figure 7

fluorescence polarization detection of naringin for MIP-Fe3O4@SiO2 and NIP-Fe3O4@SiO2