Electronic Supplementary Material (ESI) for Analytical Methods

Electronic Supporting Information

A GBI@PPyNWs-based Prototype of Reusable Fluorescence Sensor for the Detection of Fe^{3+} in Aqueous Solution

Meiling Wang,[a] Guowen Meng,[*, a,c] Qing Huang,[*, b] Qiaoling Xu,[a] Guodong Liu[a]

[a] Key Laboratory of Materials Physics, and Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, China

[b] Key Laboratory of Ion Beam Bioengineering, Institute of Physical Science, Chinese Academy of Sciences, Hefei, 230031, China

[c] University of Science and Technology of China, Hefei, 230026, China.

[*]To whom correspondence should be addressed. E-mail: gwmeng@issp.ac.cn, huangq@ipp.ac.cn

The Supporting Information includes:

Electronic Supplementary Material (ESI) for Analytical Methods

Figures S1 to S9

Part S1 Fabrication of the GBI@PPyNWs

Firstly, the AAO template was immersed in 10^{-4} mol/L GBI/ethanol for 2 h, and rinsed with ethanol for several times to remove superfluous GBI molecules on its surface to achieve GBI modified AAO. The electrolyte for PPy electrodeposition contains 0.2 mol/L pyrrole and 0.5 mol/L NaCl in a 1:1(v/v) ethanol/deionized-water mixture, and was purged with N_2 for 30 min prior to the electrodeposition. The electrodeposition was carried out under 1V in a common two-electrode electrochemical cell at ambient temperature.

Part S2 Optical spectra characterization of the GBI@PPyNWs

Infrared (IR) spectra of the PPyNWs, GBI@PPyNWs, and the complex of GBI and Fe^{3+} were recorded on a Perkin-Elmer Fourier transform infrared (FTIR) spectrometer as KBr pellets. Fluorescence spectra measurements were carried out on a FL 4500 Fluorescence Spectrophotometer at ambient temperature. Excitation and emission slits were all set at 5 nm. Nitrates of various metal ions used in experiment were purchased from Aldrich Chemicals. The GBI@PPyNWs were dispersed in water and 1:1 (v/v) ethanol/water solutions to form 34 μg/ml suspensions at pH 7.0. Varied concentrations of Fe^{3+} were titrated to the GBI@PPyNWs solution to form homogeneous medium for fluorescence characterization.

Part S3 Calculation of the average coverage of GBI molecules on the GBI@PPyNWs

As the sensing of GBI to Fe^{3+} is based on the complexation, given that the bare GBI molecules in water and GBI molecules anchored on the surface of the PPyNWs in water have equal quantum efficiency and similar bonding equilibrium with Fe^{3+}, thus inflectional points on the titration curves correspond to the same ratio of Fe^{3+} to GBI, i.e.,

$$\frac{4\times10^{-5}mol/L\cdot V}{10^{-5}mol/L\cdot V}=\frac{7\times10^{-5}mol/L\cdot V}{n\cdot V}$$

where V is the volume of the cuvette used in experiments, and n is the concentration of GBI in 34 μg/ml GBI@PPyNWs solution. Thus 34 μg/ml GBI@PPyNWs corresponds to 1.75×10^{-5} mol/L GBI, and the number of GBI molecules in per microgram of PPyNWs can be calculated to be 3.1×10^{14}.

Part S4 GBI coordination with Fe^{3+}

To study the sensing machenism of the GBI@PPyNWs to Fe^{3+}, we purposely titrated GBI aqueous solution to Fe^{3+} nitrate aqueous solution, and the result shows that there is an obvious color change from orange to dark red for Fe^{3+} nitrate solution (Fig. S7A). This indicates that coordination compounds between Fe^{3+} and GBI are formed. To further prove this, we measured the UV-vis absorption of GBI in E/W solution titrated with Fe^{3+}, and the IR spectra of GBI and its complexation with Fe^{3+}. For the fabrication of the coordination compounds of Fe^{3+} and GBI, 1 and 4 mmol of the Fe^{3+} nitrate and 1 mmol of the GBI ligand were each dissolved in 5 ml ethanol. Then the ligand solution was slowly titrated to the two Fe^{3+} nitrate ethanol solutions, thereby the Fe^{3+} salt solution become cloudy and dark red. After a while, a light yellow precipitate was isolated by filtration. As shown in Fig. S7B, the absorption peak of GBI at 294 nm was blue-shifted to 288 nm, and there appears an isosbestic point at 291 nm, confirming the complex formation. Furthermore, IR spectra of GBI and its complex with Fe^{3+} (Fig. S7C) proves the coordination of the nitrogen atoms of imidazole and guanidine with Fe^{3+}.[1] The IR spectra show that the band coming from ν(NH···N) of the guanidine group of GBI is shifted from 3444 cm^{-1} to 3343 cm^{-1} as a result of the complexation, and there appears a band at 1384 cm^{-1}, which proves the presence of ionic nitrates in the coordination compound. Moreover, in the range of 500–1800 cm^{-1} as shown in the inset of Fig. S7C, the ν(C=N) of the imidazolic ring (1596 cm^{-1}) is shifted to the higher energy compared to the free ligand, indicating the coordination of the imidazole nitrogen atom with Fe^{3+}; while the shift of guanidine ν(C=N) band from 1541 to 1584 cm^{-1} proves the coordination of the guanidine nitrogen atom.[1]

Part S5 Evaluation of the bonding constant *K* and the number of the bonding sites *n*

As the relationship between the fluorescence intensity and [Fe^{3+}] can be described by the following Eq.:

$$Log(\frac{I_0 - I}{I}) = LogK + nLog[Fe^{3+}]$$

where I_0, I, K and n are fluorescence intensity of GBI@PPyNWs in 1:1 (v/v) ethanol/water without and with Fe^{3+}, binding constant and the number of the bonding sites per GBI molecule respectively. Thus K and n can be calculated from the plot of $Log(I_0\text{-}I)/I$ versus $Log[Fe^{3+}]$ shown in Fig. S8.

Figure S1 to S9

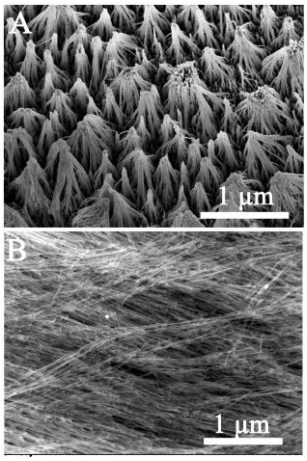

Fig. S1 SEM images of the GBI@PPyNWs.

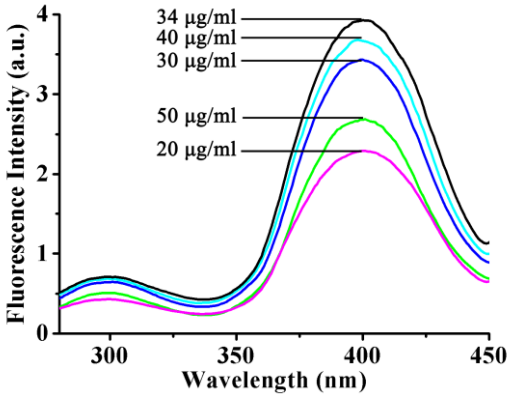

Fig. S2 Fluorescence spectra of different concentrations of GBI@PPyNWs.

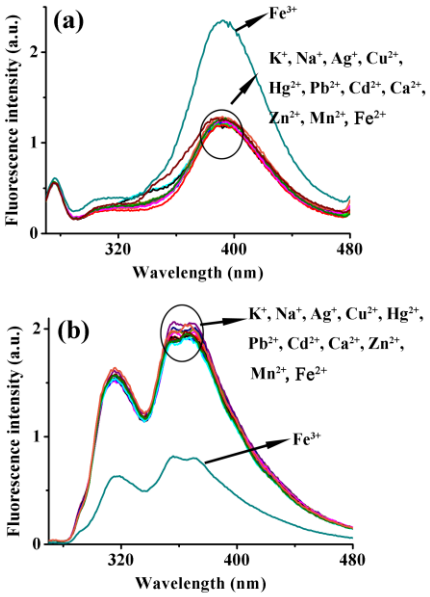

Fig. S3 Fluorescence spectra of the GBI@PPyNWs in (A) water and (B) 1:1 (v/v) ethanol/ water solutions with 10^{-5} mol/L M^{n+}. (λ_{ex}=250 nm)

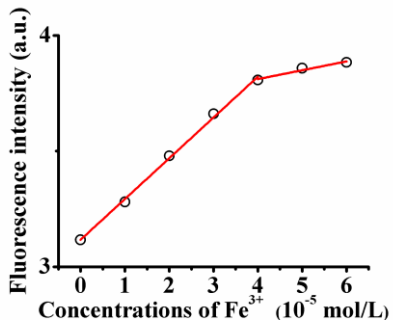

Fig. S4 Titration curve of 10^{-5} mol/L GBI in water solution with Fe^{3+}.

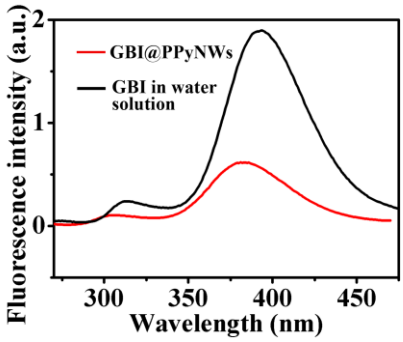

Fig. S5 Fluorescence spectra of the 34 μg/mL GBI@PPyNWs and the 1.75×10^{-5} M GBI in water solutions.

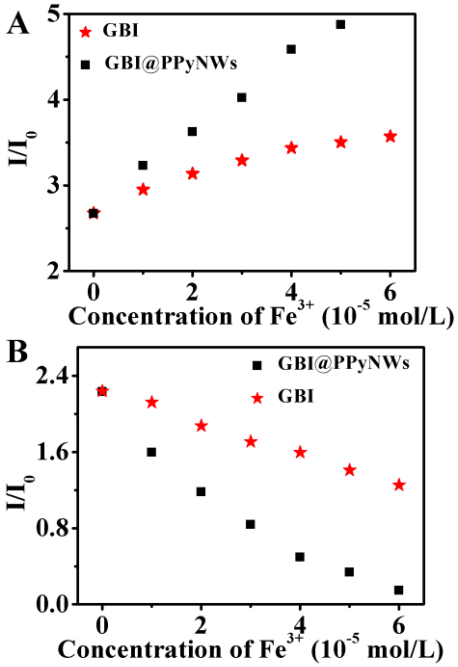

Fig. S6 Comparison of the sensitivity of GBI@PPyNWs (34 μg/ml) and GBI (1.75×10^{-5} mol/L) to Fe^{3+}: (A) in water and (B) in 1:1 ethanol/water respectively. λ_{ex}=250 nm, λ_{em}=400 and 370 nm for water and in 1:1 ethanol/water respectively.

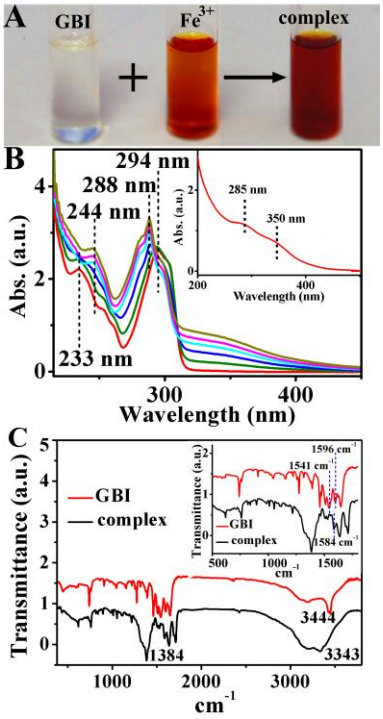

Fig. S7 (A) Color changes before and after complexation. (B) UV-vis absorption spectra of 2 ml 1.1×10^{-4} M GBI in E/W solution in the presence of 0, 2, 4, 6, 8, 10 equiv. Fe^{3+}. Inset: UV-vis absorption spectrum of 10^{-3} M Fe^{3+} in E/W. (C) IR spectra of GBI and the complex of Fe^{3+} with GBI.

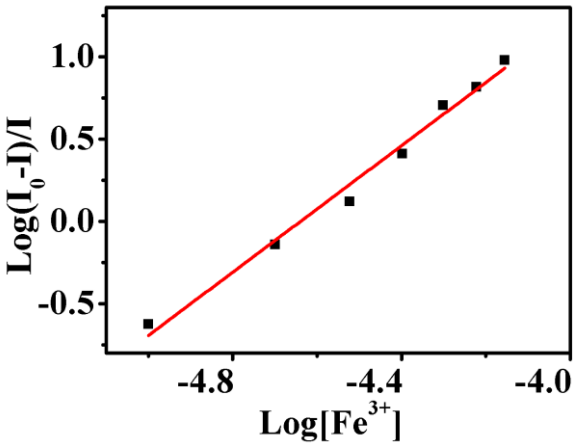

Fig. S8 Bonding equilibrium of GBI and Fe^{3+}.

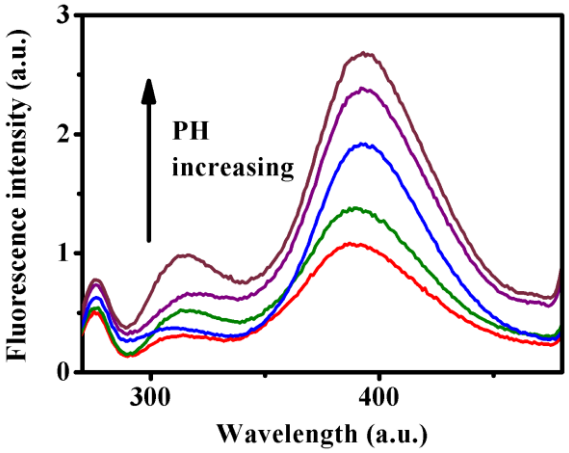

Fig. S9 Fluorescence spectra of 10^{-5} mol/L GBI solution with different pH. (pH=5, 6.5, 7, 9.5, 13 respectively)

Notes and References

[1] M. Hasegawa,F. Renz, T.Hara, Y. Kikuchi, Y. Fukuda, J. Okubo, T. Hoshi, W. Linert. *Chem. Phys.*, 2002, **277**, 21–30.