ELECTRONIC SUPPLEMENTARY INFORMATION

Rutin-modified silver nanoparticles as a chromogenic probe for the selective detection of Fe^{3+} in aqueous medium

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Experimental

General

All reagents and solvents were acquired from reliable commercial sources and used without further purification. Stock solutions were prepared in ultrapure water (AA, NaOH and $AgNO_3$) or in ethanol HPLC grade (RU). UV-vis analyses were performed in an Ocean Optics YSB – 650 Tide spectrophotometer, using 1cm length quartz cuvette. Transmission electronic microscopy (TEM) analyses was performed in a JEOL JEM-1011 microscopy operating in transmission mode at 100 kV. Photos for both naked eye and image analysis were taken using a Samsung Galaxy S8 smartphone. Infrared analysis were performed in Brucker FT-IR Vertex 70 instrument.

Synthesis of RU-AgNPs and cation sensing assays

A solution of 500 µL of AA 1.00 mmol L^{-1} and 500 µL of NaOH 1.00 mol L^{-1} was added to solutions containing 500 µL of RU (0.10 – 0.50 mmol L^{-1}), 10 µL of $AgNO_3$ 100.00 mmol L^{-1} and 3490 µL of ultrapure, at room temperature. For the preparation of final solutions, 500 µL of RU-AgNPs were combined with 2500 µL of ultrapure water. Photos and UV-Vis spectra of each solution were recorded after 30 minutes.

The cation sensing study was performed by separately adding 10 µL of different cations (10 mmol L^{-1}; Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, Cr^{3+}, Sr^{2+}, Ba^{2+}, Cu^+ and Al^{3+}) to 3990 µL of RU-AgNPs solutions (using 0.1 mmol L^{-1} of RU). For the preparation of final solutions, 500 µL of RU-AgNPs were combined with 1500 µL of ultrapure water. Photos and UV-Vis spectra were recorded after 50 minutes.

TEM analysis

Images were acquired from the addition of 4 µL of colloidal suspension ti copper grid covered with formvar®. A minimum of 100 nanoparticles were measured using ImageJ® software. The average nanoparticle size and distribution were determined by a Gaussian adjustment using OriginPro® 2016 software.

Image data treatment

The raw picture files from cuvettes were captured in triplicate using a smartphone. Data processing consisted of cropping, pre-processing, and image processing. Firstly, Regions of Interest (ROIs) were cropped to squares (50 x 50 pixels) using GIMP 2.8.18 software (GNU) that contained the picture region with the highest light intensity and saved it as jpeg format. Second, images were filtered using Perreault's modern constant time median filtering algorithm for speckle noise removal with R statistics version 3.6.0 platform[1] and EBImage package[2] (bioconductor.org) version 4.26. The

image processing step consisted in extracting the RGB channels of the digital images and averaging the respective values. Finally, the colorimetric absorbance for each RGB channel was calculated following the Beer-Lambert Law. Multiple Linear Regression (MLR) and Second Order Regression routines were implemented in R with 60 images of Fe^{3+} standards from 1 to 8 µM to compare the iron (III) chromogenic probe observed and theoretical model.
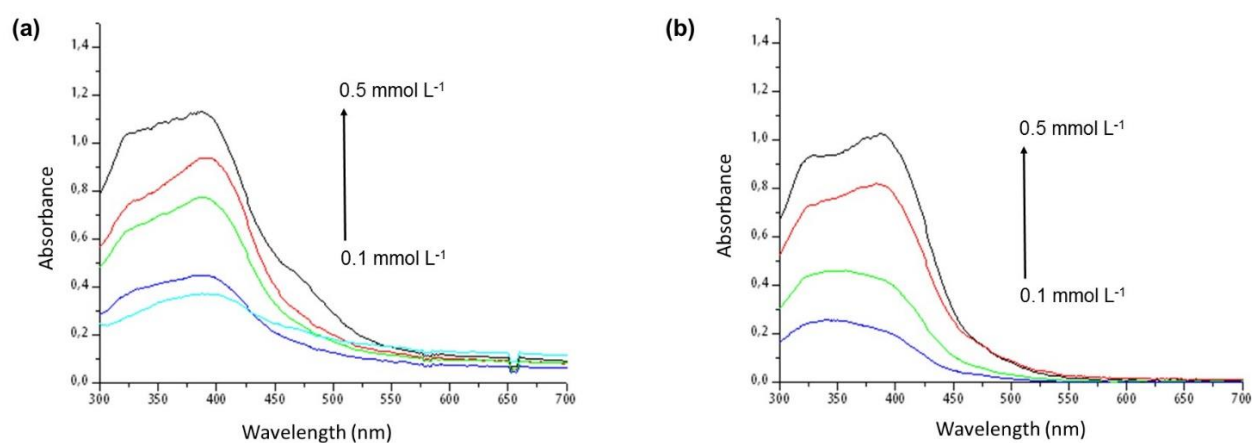

Fig. S1. Effect of reagent addition: UV-vis analysis of RU-AgNPs under different experimental condition: (a) addition of RU, AA, and NaOH to $AgNO_3$ solution; (b) addition of RU and NaOH to a solution of AA and $AgNO_3$. In both cases, concentration of RU ranged from 1 to 5 mM while concentrations of other components were fixed at 0.2 mM $AgNO_3$, 0.1 mM AA and 0.1 M NaOH
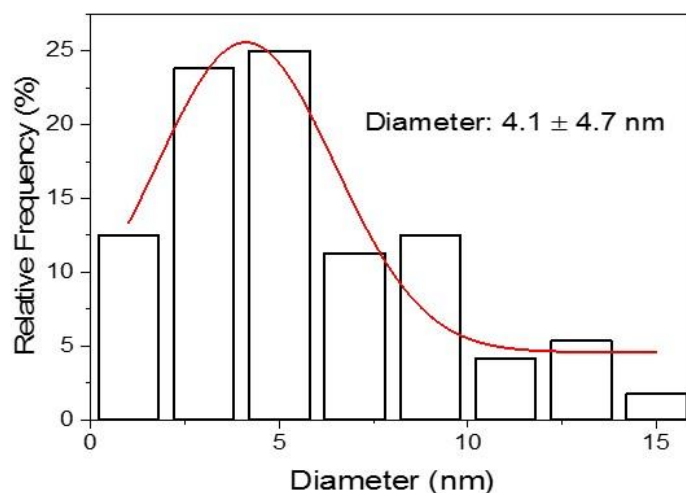

Fig. S2. Histogram obtained from TEM analysis for RU-AgNPs under selected condition.
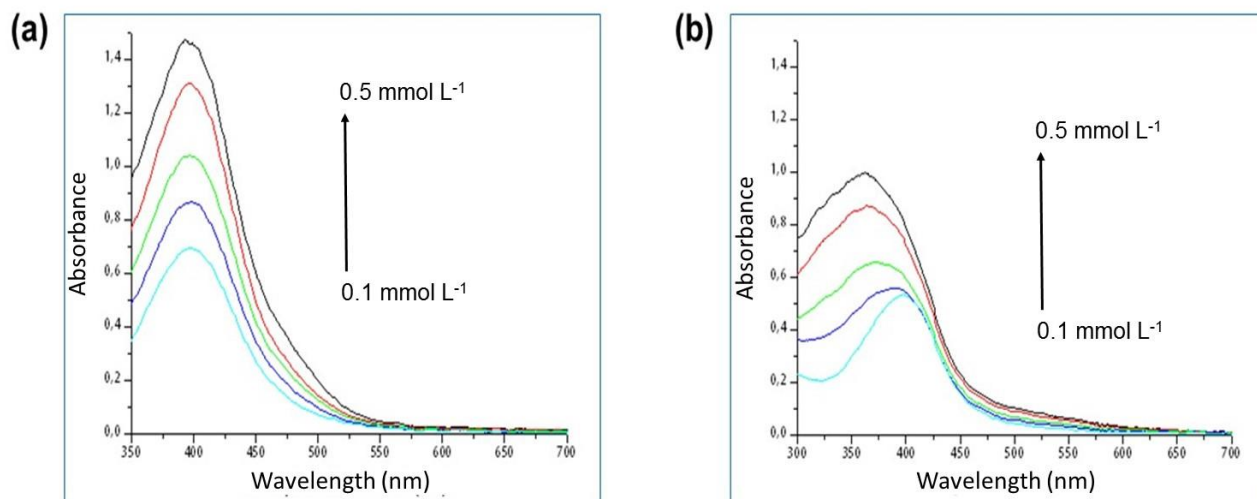
Fig. S3. Stability of RU-AgNPs over the time: UV-vis analysis of RU-AgNPs at initial time (a) and after 24h (b) under best experimental condition (RU, 0.1 mmol L^{-1}; AgNO$_3$, 0.2 mmol L^{-1}; AA, 0.1 mmol L^{-1}; NaOH, 0.1 mol L^{-1}).
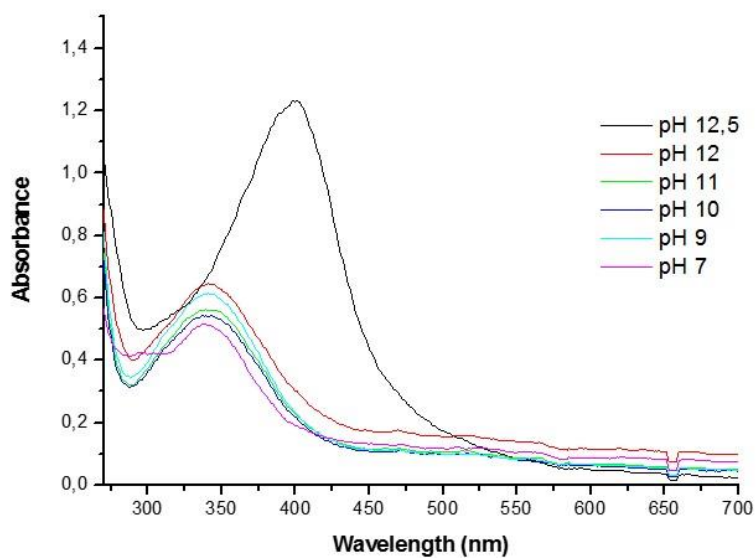
Fig. S4. UV-vis analysis of RU-AgNPs under best experimental condition (RU, 0.1 mmol L^{-1}; AgNO$_3$, 0.2 mmol L^{-1}; AA, 0.1 mmol L^{-1}; NaOH, 0.1 mol L^{-1}) under different pH values.
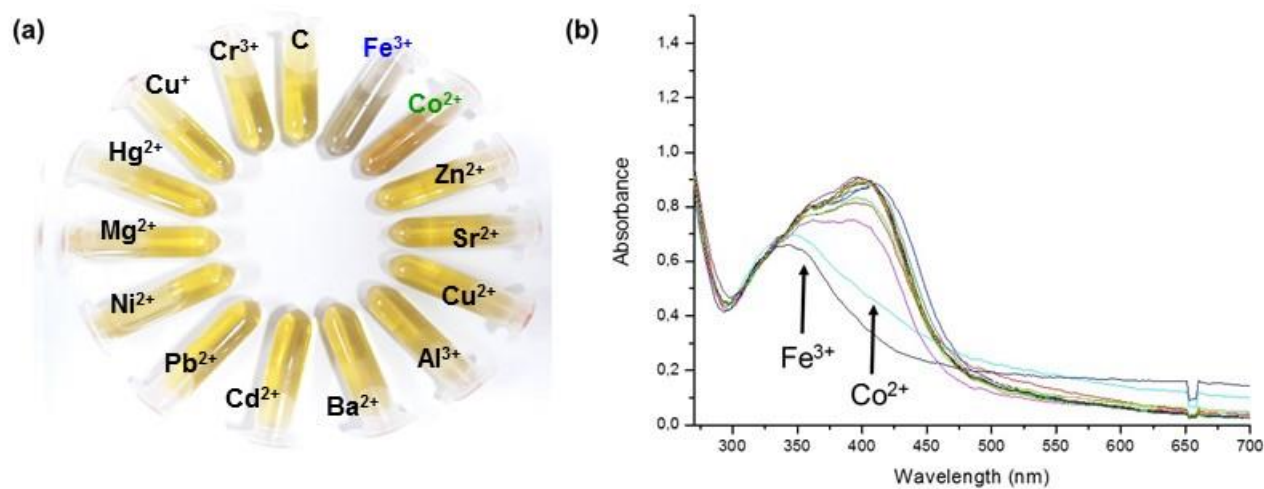
Fig. S5. Naked-eye (a) and UV-Vis (b) analysis of Ru-AgNPs in absence (control) and presence of 10 µmol L^{-1} of selected metal cations (Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, Cr^{3+}, Sr^{2+}, Ba^{2+}, Cu$^+$ and Al^{3+}) after 120 min. Experiments, RU-AgNPs were prepared in the absence of ascorbic acid.
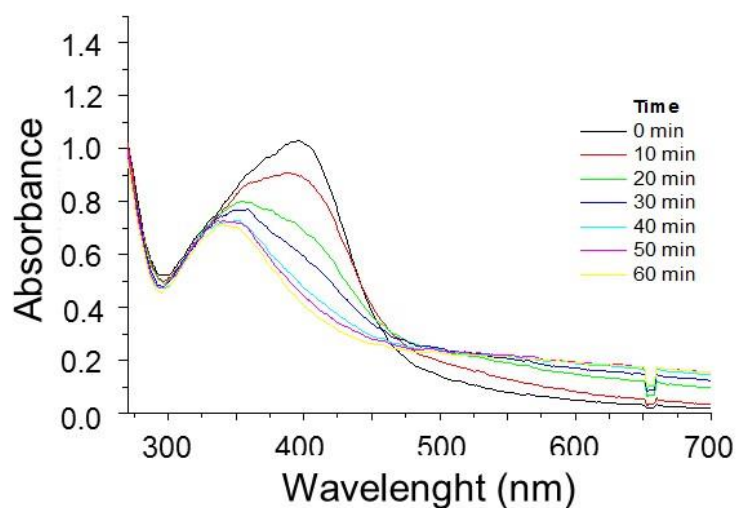

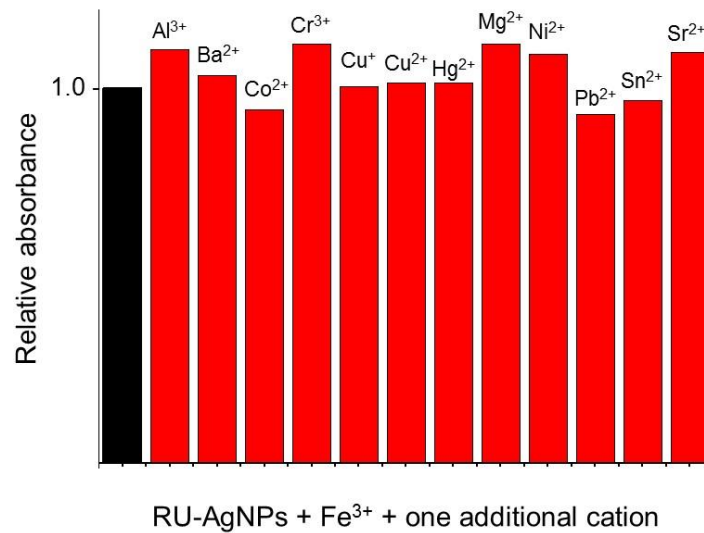**Fig. S6.** Time-dependence in solutions of RU-AgNPs in the presence of Fe^{3+} (10 µmol L^{-1}).

Fig. S7. Normalized absorbances at 404 nm for equimolar mixtures of Fe^{3+} and one more metal ion, both 10 $\mu mol.L^{-1}$, in the presence of RU-AgNPs. Normalization was based on absorbance of the solution containing only and Fe^{3+} and RU-AgNPs (black bar).
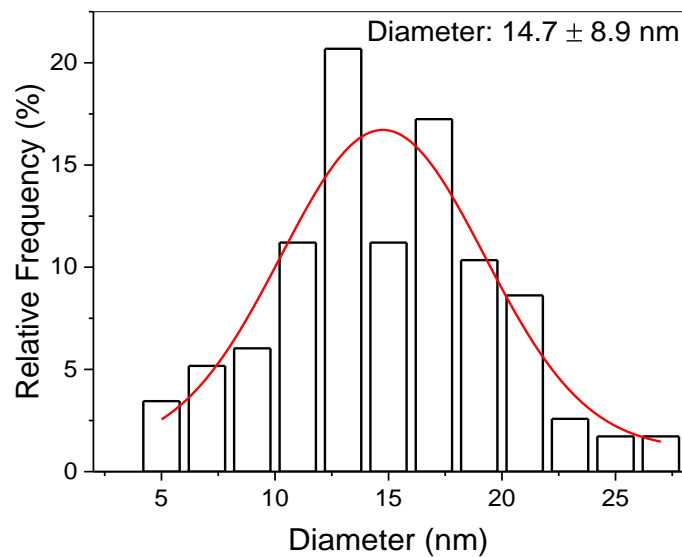

Fig. S8. Histogram obtained from TEM analysis for RU-AgNPs after addition of Fe^{3+} (10 $\mu mol\ L^{-1}$).
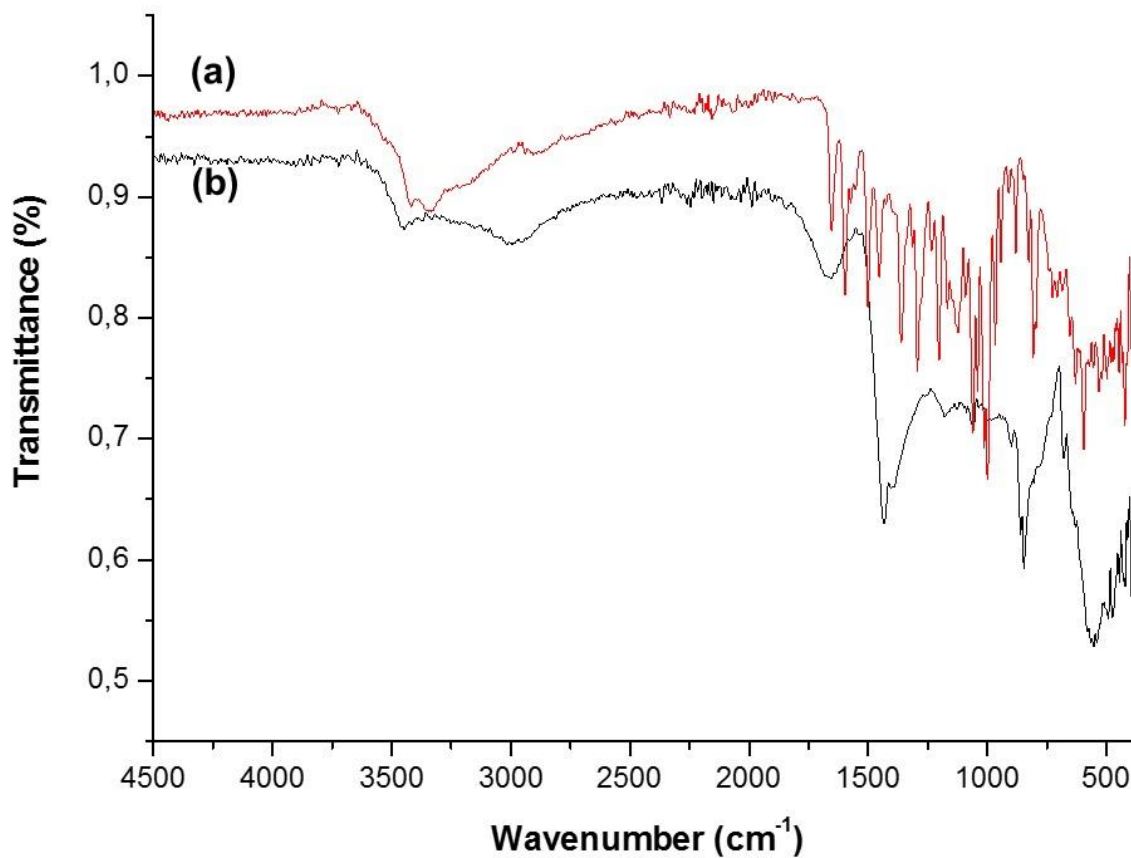
Fig. S9. Infrared spectra of RU (a) and RU-AgNPs (b).

References

1. R Core Team, R: A Language and Environment for Statistical Computing, Vienna, Austria, 2019.

2. G. Pau, F. Fuchs, O. Sklyar, M. Boutros, W. Huber, *Bioinformatics*, 2010, **26**, 979.