Electronic Supplementary Information

Ferric reducing reactivity assay with theoretical kinetic modeling uncovers electron transfer schemes of metallic-nanoparticle-mediated redox in water solutions

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Figure S1. TEM images for Au (left) and Ag (right) nanoparticle samples. Images and publication permission are provided by the material manufacture (nanoComposix).

Figure S2. Concentration (molar) of Ag atoms versus the total formed Fe\textsuperscript{II} concentration (molar). The data lining up with a 1:1 ratio line proves the one-to-one stoichiometry of the reaction between Ag\textsuperscript{0} and Fe\textsuperscript{III}, i.e., Ag\textsuperscript{0} + Fe\textsuperscript{III} → Ag\textsuperscript{+} + Fe\textsuperscript{II}. 
Figure S3. The dissipation of the surface plasmon absorbance (414 nm) and the formation of Fe$^{II}$ (reflected by absorbance at 593 nm) in a typical FRAN reaction. The dissipation of the surface plasmon absorbance suggests the dissolution of Ag NPs through the reaction. The data is recorded for a 40-nm Ag NP sample dosed at 200 µg/L.

Derivation of eq (3)

In eq (2), the only $d$ is a variable dependent on $t$, and thus it can be simplified to

$$2\nu_{\lambda_0}\pi\delta d \frac{dd}{dt} = -k\nu_{\lambda_0}\pi\delta d^2,$$

which further leads to
\[
\frac{dd}{dt} = -\frac{k}{2} d. \tag{s2}
\]

Eq (s2) suggests the diameter of a Ag NP reduces as a first-order kinetics in the reaction.

Let \( d_0 \) be the initial size of Ag NPs, and the solution of eq (s2) becomes

\[
d(t) = d_0 \exp\left(-\frac{k}{2} t\right). \tag{s3}
\]

The molarity of Fe\(\text{II} \) yielded from one Ag NP Ag\(^+\) released from is corresponding to those reacted Ag\(^0\) and described as

\[
n_{\text{Fe}^{\text{II}}} = \frac{1}{6} \pi \left( d_0^3 - d(t)^3 \right) \nu_{\text{Ag}}. \tag{s4}
\]

As there are numerous Ag NPs in the solution, the overall Fe\(\text{II} \) concentration in the solution is given by

\[
C_{\text{Fe}^{\text{II}}}(t) = \frac{1}{6} \pi d_0^3 \nu_{\text{Ag}} C_{\text{Ag NP}}^\text{num}. \tag{s5}
\]

Substituting \( d(t) \) in eq (s5) with eq (s3) gives

\[
C_{\text{Fe}^{\text{II}}}(t) = \frac{1}{6} \pi d_0^3 \nu_{\text{Ag}} C_{\text{Ag NP}}^\text{num} \left( 1 - \exp\left(-\frac{3}{2} kt\right) \right). \tag{s6}
\]

Noticing that \( \frac{1}{6} \pi d_0^3 \nu_{\text{Ag}} C_{\text{Ag NP}}^\text{num} \) is the initial Ag\(^0\) molar concentration in the entire solution and replacing \(-\frac{3}{2} k\) with one constant of \( k_{\text{obs}} \), eq(s6) is simplified to

\[
C_{\text{Fe}^{\text{II}}}(t) = C_{\text{Ag}^{0,0}} \left( 1 - \exp\left(-k_{\text{obs}} t\right) \right). \tag{s7}
\]

Thus far eq (3) in the main text is reached.

**Derivation of eq (7)**
Let $Q_0$ be the total electronic charge on Au NPs surfaces in the solution at $t_0$, eq (6) in the main text can be solved:

$$Q(t) = \frac{CRT}{F \alpha} \log \left( \exp \left( \frac{\alpha F Q_0}{CRT} + \frac{k_0 F^2 A \alpha C_{Fe^{in}}}{CRT} t \right) \right). \quad (s8)$$

Noticing the balance of charge in reaction (5) in the main text, one has:

$$C_{Fe^{in}}(t) = -\frac{1}{F V} (Q_0 - Q(t)); \quad (s9a)$$

$$C_{Fe^{in}}(t) = \frac{CRT}{VF^2 \alpha} \log \left( \exp \left( \frac{\alpha F Q_0}{CRT} + \frac{k_0 F^2 A \alpha C_{Fe^{in}}}{CRT} t \right) - \frac{Q_0}{F V} \right). \quad (s9b)$$

It is noteworthy that $Q$ is the charge on NPs; when reaction (4) proceeds, $Q$ becomes more positive and thus increases with $t$. $Q_0 - Q(t)$ is negative.

Eq (7) in the main text is nothing more than a series of mathematical simplification of eq (s9b). First, notice a few replacements of variables:

$$C_s = \frac{C}{A};$$

$$A_{m,AuNP} \times C_{mass}^{AuNP} = \frac{A}{V};$$

$$q_0 = \frac{Q_0}{A}.$$
\[ C_{Fe}(t) = \frac{A_{m,\text{AuNP}} C_{\text{mass}}}{F^2 \alpha} \frac{C_S RT}{F} \log \left( \exp \left( \frac{\alpha F q_0}{C_S RT} \right) + \frac{k_0 F^2 \alpha C_{Fe^{iii}t}}{C_S RT} \right) - \frac{q_0 A_{m,\text{AuNP}} C_{\text{mass}}}{F} \]

\[
= \frac{A_{m,\text{AuNP}} C_{\text{mass}}}{F^2 \alpha} \left( \frac{C_S RT}{C_S RT} \right) \log \left( \exp \left( \frac{\alpha F q_0}{C_S RT} \right) + \frac{k_0 F^2 \alpha C_{Fe^{iii}t}}{C_S RT} \right) - \frac{q_0 \alpha F}{C_S RT} \]

\[
= \frac{A_{m,\text{AuNP}} C_{\text{mass}}}{F^2 \alpha} \left( \frac{C_S RT}{C_S RT} \right) \log \left( \frac{\exp \left( - \frac{q_0 \alpha F}{C_S RT} \right)}{\exp \left( \frac{\alpha F q_0}{C_S RT} \right)} \left( 1 + \exp \left( - \frac{q_0 \alpha F}{C_S RT} \right) \left( \frac{k_0 F^2 \alpha C_{Fe^{iii}t}}{C_S RT} \right) t \right) \right) \]

\[
= L C_{\text{AuNP}} A_{m,\text{AuNP}} C_S \log \left( 1 + K C_{Fe^{iii}t} \right),
\]

where, \( L = \frac{RT}{\alpha F^2} \), and \( K = \frac{k_0}{L C_S} \exp \left( - \frac{q_0}{L FC_S} \right) \). Eq (7) is therefore achieved.