Tryptophan-Stabilized Au–FeₓOᵧ Nanocomposites as Electrocatalysts for Oxygen Evolution Reaction

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Supporting Information

ABSTRACT: Au–FeₓOᵧ nanocomposites with a variable gold-to-iron ratio were stabilized with l-tryptophan. The synthetic methodology is based on the facile redox reaction between Au(III) and Fe(0) in the presence of gold nanoparticle as a seed at room temperature in an aqueous medium. The synthesis results in the deposition of Au nanoparticles on the surface of iron oxide layers. Composition variation in the nanocomposites was obtained by controlling the seed amount and reducing agent. These nanocomposites are used as electrocatalysts for the thermodynamically unfavorable oxygen evolution reaction (OER) from water. Among the nanocomposites, the most efficient OER activity was observed from the nanocomposite 12. The content of iron with respect to gold is at the maximum in the nanocomposite, which was obtained from the reaction with a minimum seed concentration and maximum reducing agent.

INTRODUCTION

Electrochemical splitting of water into hydrogen and oxygen is no doubt a matter of significant interest for the scientific community recently because of its potential applications in renewable energy technology.1 Water oxidation reaction is mainly controlled by the oxygen generation step; a four electron transfer process, which is thermodynamically less favorable.2 Therefore, devices or materials capable of generating oxygen from water are the current forefront research area.

In this regard, metal nanocomposites have attracted considerable attention because of their tunable physical and chemical properties.3–8 So far, the combination of Au nanoparticles (AuNPs) with three first row transition metal oxides (Co, Ni, and Mn) has been reported to exhibit promising OER activity in recent literature.9–14 To the best of our knowledge, Au–FeₓOᵧ nanocomposite has been explored only once by Jaramillo’s group as an OER catalyst.15 However, a handful of Au–FeₓOᵧ nanocomposites with interesting catalytic and magnetic properties has been well explored recently.14–20

Syntheses of Au–FeₓOᵧ nanocomposites usually involve the attachment of gold and iron oxide nanoparticles with organic or inorganic polymeric support followed by modular surface modification.21–23 In situ preparation of Au–FeₓOᵧ nanocomposites generally involves the reduction of Au(III) on the FeₓOᵧ core as the platform followed by stabilization with an appropriate stabilizing agent.24 Alternate routes include the use of iron oxide pentacarbonyl or iron oleate as the iron source at elevated temperature in an inert atmosphere along with the gold nanoparticle as the core in the composite.25 Despite having handful of literature resources for the synthesis of Au–FeₓOᵧ nanocomposites, there is a paucity of generalized methodology at ambient reaction conditions.

This work demonstrates the establishment of the one-pot seed-mediated synthetic method for Au–FeₓOᵧ nanocomposites at room temperature in an aqueous medium using l-tryptophan as a stabilizing agent and iron powder as the reducing agent (Scheme 1). It is noteworthy to mention that tryptophan has been used for the first time to stabilize transition metal oxide and noble metal nanocomposites, considering its strong electron donating properties and water solubility during the stabilization of gold nanoparticles.26–28

Scheme 1. Flow Chart of Au–FeₓOᵧ Nanocomposite Synthetic Process with a Variable Au:Fe Composition Ratio for OER Activity

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activity of the nanomaterials has further been correlated with the variation of iron amounts in these materials.

**RESULTS AND DISCUSSION**

In the current syntheses of Au–Fe$_x$O$_y$ nanocomposites, iron powder has been used as the reducing agent for Au(II) reduction because of its comparable reduction potential [$E^{0}_{\text{Fe(II)/Fe}} = -0.45 \text{ V}$] to that of hydroquinone. Although the redox reaction between Au(III) and Fe(0) is favorable as per their redox properties, a successful reaction requires AuNP (16 ± 3 nm) as the seed and stabilizing agent for the nanocomposites.

The seed-mediated synthesis of the Au–Fe$_x$O$_y$ nanocomposites has been performed in the presence of highly water-soluble l-amino acids to investigate their role as a stabilizing agent for the nanocomposites. Among the 16 different amino acids, only the solution-containing tryptophan develops a violet color accompanied by the formation of surface plasmon resonance (SPR) band at 556 nm, indicating the formation of gold nanomaterials (Figure 1). Out of 21 essential amino acids, 5 amino acids could not be utilized because of their poor solubility in an aqueous medium. Under the same reaction condition, other 15 amino acids except tryptophan do not show any color change even after prolonged reaction time, demonstrating the function of tryptophan as the stabilizing agent.

Furtherly, increment in the tryptophan concentration up to 8 μmol (0.2 mM) tryptophan is required for the development of nanocomposites, from 90 × 10$^{-9}$ to 540 × 10$^{-9}$ mL$^{-1}$, respectively, Figure 2a as confirmed by TEM, FE-SEM images (Figure 2b–e). Energy-dispersive X-ray spectroscopy (EDXS) analyses of FE-SEM images confirm the presence of iron in both of the nanocomposites 1 and 6 (Figure S4). The chemical components within the nanocomposites have been also confirmed from the EDXS mapping and EDXS line scan profile (Figures S5–S8). These results clearly show that the metal powder, which has participated in the redox reaction, serves the role of reagent in the nanocomposite formation. The presence of nitrogen confirms the participation of tryptophan in the nanocomposites. This EDXS analyses show the poor incorporation of iron in the respective nanocomposites (5% for 1 and 16% for 6).

Furthermore, the effect of variation of iron powder compared with the iron amount used for 1 and 6 nanocomposite syntheses has also been explored with two different seed concentrations (Figure 3a). In the absence of iron powder, no amino acids develop the characteristic SPR band, confirming the vital role of metal powder in the reduction process (Figure S9 for tryptophan). With a fixed seed and a tryptophan amount, increasing the iron amount (from 18 μmol to 90 μmol) results in the formation of nanocomposites,
increases from nanoparticles on the iron oxide layer. However, in the case of higher seed concentration of iron amount in the presence of low seed concentration, almost constant from 90 to 109 mL of seed amount, the addition of a different iron amount results in the formation of nanocomposites 1, 9, 10, 11, and 12, and 540 × 10^9 mL^-1 of seed nanocomposites 6, 13, 14, 15, and 16 (Figure S9). ζ potential and monodispersity increases from 9 to 12 (Figure S10) with the increase in the concentration of iron amount in the presence of low seed concentration. However, in the case of higher seed concentration, surface charge densities and polydispersity are almost constant from 13 to 16 (Figure S10) with the increasing concentration of the iron amount. Nanocomposites 12 and 16 have been taken as representative materials for further characterization purpose. The TEM and FE-SEM images (Figure 3b–e) clearly confirm the deposition of gold nanoparticles on the iron oxide layer.

The EDX mapping and EDXS line scan profile (Figures S11–S15) also indicate the formation of tryptophan stabilized Au–FeO_x nanocomposites. According to EDXS analysis of FE-SEM images, a higher amount of iron incorporation with respect to gold takes place in the case of nanocomposite 12 (26%) compared to the nanocomposite 1 (5%). This enhancement of iron content within these two nanocomposites in the presence of lower seed concentration can be correlated to the amount of iron used in the syntheses. However, the iron content with respect to gold shows slight enhancement in nanocomposite 16 (20%) compared to the nanocomposite 6 (16%), where the syntheses have been performed with the higher seed amount.

XPS measurements have been carried out to further investigate the chemical compositions and elemental valence states for nanocomposites 1, 6, 12, and 16. The survey spectra confirmed the presence of gold, iron, carbon, nitrogen, and oxygen atoms in the nanocomposites (Figure S16). The detailed scans for N 1s (Figure S17) for 16 show two peaks around 398.3 and 401.0 eV after deconvolution due to the presence of the indole-based nitrogen atom and amine nitrogen of tryptophan. From high resolution scans for 2p of Fe, two distinct peaks can be identified at 709.88 and 723.3 eV, which can be assigned to the Fe 2P3/2 and Fe 2P1/2 electrons, respectively (Figure S17). The Fe 2P1/2 has associated the satellite peak around 719 eV, indicating the predominance of Fe2O3 in these samples.

The broad peak in IR spectra (Figure S18) with maximum peak intensity at 3423 cm^-1 is due to the stretching vibration of amine group from tryptophan. The small peaks around 2925 cm^-1 are due to methylene protons of tryptophan. The position of carbonyl frequency has been shifted to 1615 cm^-1 because of the interaction of carbonyl oxygen with the gold nanoparticle. In addition to the XPS, the IR spectra within a part of the fingerprint region (400–600 cm^-1) suggest the formation of γ-Fe2O3 in samples 1 and 6 and α-Fe3O4 in samples 12 and 16 (Figure S18). In PXRD, only the peaks due to Au(0) has been observed (Figure S19). The absence of diffraction pattern for iron oxide suggests the similar amorphous nature in the nanocomposites. The 2θ values at 38.3, 44.5, and 64.7 angles are due to (111), (200), and (220) planes, respectively, according to the JCPDS (Joint Committee on Powder Diffraction Standards) no. 04-0784, USA for Au nanoparticles. The crystallite size from XRD using the Scherrer equation for gold has been found to be 15 nm, which is in good agreement to the size of gold nanoparticles obtained from TEM images.

To investigate the electrocatalytic behavior of the synthesized Au–FeO_x catalysts, cyclic voltametric scans for the nanocomposites (1, 6, 12, and 16) have been executed in a 1.0 M KOH solution at 50 mV s^{-1} scan rate. The oxidation and reduction peaks in all the cases correspond to a Fe^3+/Fe^2+ redox couple (Figure S20). The OER activities of the synthesized Au–FeO_x nanocomposites have been investigated by LSV in an alkaline aqueous solution at pH 13.0 with the FTO glass plate coated with different nanomaterials as a working electrode.

The polarization curves in Figure 4a demonstrate the comparative OER activity of the nanocomposites (1, 6, 12, and 16) and the mixture of seeds with commercially available Fe2O3 and Fe3O4 mixtures. In both these mixtures, we have used 25% iron oxide with respect to gold amount. It has been found that all the nanocomposites show better OER activity with respect to control materials. The significant enhancement in the OER activity of the composites is probably due to strong-localized interfacial interactions between Au and FeO_x and the increase in the active surface area after composite formation, which has been observed in the case of gold–manganese oxides. For oxygen evolution reaction, the overpotential at a current density of 10 mA/cm^2 is commonly used as a figure of merit for the catalysts. The overpotential values are 0.53, 0.52, 0.45, and 0.47 V for nanocomposites 1, 6, 12, and 16, respectively. Therefore, compound 12 can be considered the best electrocatalyst among these four Au–FeO_x nanocomposites for OER activity. Overpotentials of the controlled materials are greater than 0.65 V at 10 mA/cm^3 current density. The overpotential values in the presence of gold in the nanocomposites are similar to the reported observation. The observed maximum enhancement in the OER activity of 12 is due to the presence of the highest Au:Fe ratio among the Au–FeO_x nanocomposites. The better OER activity of nanocomposites in comparison to individual gold or iron oxide nanomaterial might be due to the local interaction of Au through its dissolution and deposition onto FeO_x sites. This is similar to the reported case of Au/MnO_x OER activity.
To analyze the comparative electrocatalytic behavior, Tafel slope, which is an important parameter, has been calculated (Figures 4b and S21). It is well-known that the smaller the Tafel slope, the higher the charge transfer coefficient, resulting in lowering of energy barrier of the electrochemical reaction.

Tafel slopes obtained from the four nanocomposites, 1, 6, 12, and 16, from the plot overpotential (η) versus the logarithm of current density are 210, 198, 132, and 159 mV/dec (Table 1), indicating the better electrocatalytic efficiency of 12 and 16 compared to 1 and 6 (Figure 4b). These Tafel slopes are significantly smaller in comparison to the commercially available iron oxide nanomaterials (Figure S21). However, the Tafel slopes for the nanocomposites 1, 6, 12, and 16 are higher in comparison to the core–shell Au–Fe₃O₄ nanoparticles of a much smaller size. The Faradic efficiencies during OER are 84, 86, 93, and 91% for the nanocomposites 1, 6, 12, and 16, respectively. The nitrogen-containing aromatic indole group in tryptophan shows a different one-electron oxidation potential at a different environment. Tryptophan might be also effective in the catalytic activity as it can modulate the electrochemistry of nanocomposites at different concentrations. The nitrogen of indole may contribute in the charge separation because of the electronegativity differences between iron and the nitrogen. This charge separation may enhance the OH⁻ adsorption on the nanomaterial surface, which eventually results in the increase of the OER activity.

To investigate the electron transfer kinetics, electrochemical impedance spectroscopy (EIS) measurements have been performed with the four nanocomposites. Figure 4c describes the Nyquist plots acquired for the nanocomposites at their overpotentials. The charge transfer resistances for 1, 6, 12, and 16 nanocomposites are 298, 250, 78, and 110 Ω, which is again consistent with the OER activity of the catalysts. The electrocatalytic trend of the catalysts may be explained in terms of the iron content in the composites. The order of iron content in the catalysis is 12 > 16 > 6 > 1, which resembles the order of their catalytic activity, that is, the turnover frequency of the catalysts (Table 1). Increase in the iron content might result in the increment of the active sites in the catalysts, which causes enhancement in the OER activity. To check the stability of the materials, a chronoamperometry test (Figure S22) has been carried out for the nanocomposites at their corresponding overpotentials for 5 h, and the current densities have been found to be extremely stable for nanocomposites 1 and 16, indicating a long-term viability of these materials. Ratios of gold and iron in the nanocomposites after electrochemistry have been analyzed with the EDXS analysis of FE-SEM images (Figure S23 and Table S1). Slight losses of iron (within 0.5–5%) with respect to the gold amount have been observed in all the nanocomposites probably because of the formation of FeO₄²⁻ as reported. Because the loss of iron is less than 5%, these materials are sufficiently stable after their electrocatalytic performance.

### CONCLUSIONS

In summary, we have developed a facile room temperature synthetic route for tryptophan-stabilized Au–Fe₃O₄ nanocomposites. These nanocomposites were obtained in the presence of gold nanoparticle seed after the redox reaction between Au(III) and Fe(0). The variation of seed and iron amounts in the reaction mixture leads to form Au–Fe₃O₄, having a different Au:Fe ratio. These Au–Fe₃O₄ nanocomposites were explored for their role as electrocatalysts during the OER from water in a basic condition. The OER activity of the catalysts has been rationalized on the basis of their overpotentials, and we have seen that the catalytic performance directly depends upon the amount of the iron content in the nanocomposites. The stabilities of the materials

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**Table 1. Comparison of Different parameters of Four Au–Fe₃O₄ Nanocomposites: 1, 6, 12, and 16**

| nanocomposites | Au loading (wt %) | overpotential (V) | Rₑ (Ω) | current (mA/cm²) | TOF (s⁻¹) | Tafel slope (mV/dec) |
|----------------|-------------------|------------------|--------|-----------------|-----------|---------------------|
| 1              | 70                | 0.53             | 298    | 123             | 0.17      | 210                 |
| 6              | 59                | 0.52             | 250    | 136             | 0.21      | 198                 |
| 12             | 52                | 0.45             | 78     | 178             | 0.31      | 132                 |
| 16             | 48                | 0.47             | 110    | 166             | 0.29      | 159                 |

*Actual gold loading has been confirmed by EDXS analysis of FE-SEM. Overpotentials at a current density of 10 mA/cm². Rₑ is the charge transfer resistance obtained by fitting the EIS data. Current density was measured at 2.4 V (vs RHE). Turnover frequency (TOF) at 1.44 V vs RHE has been calculated as per the available method.*
have been monitored by chronoamperometry test and the FE-SEM analysis of the nanocomposites after OER performance. The environmentally friendly synthetic modification of Au–Fe₃O₄ nanocomposites with lower overpotentials and Tafel slopes is currently ongoing in our laboratory.

### EXPERIMENTAL SECTION

**Materials.** Gold(III) chloride trihydrate was purchased from Sigma Aldrich. Trisodium citrate dehydrate was purchased from Merck chemicals. Iron powder was purchased from SISCO Research Laboratories Pvt. Ltd. The preparation of the seed solution and concentration per milliliter calculation was performed as per literature methods.⁴⁹ All the synthesized nanocomposites were characterized by absorbance spectroscopy, infrared (IR) spectroscopy, transmission electron microscopy (TEM), field emission scanning electron microscopy (FE-SEM), powder x-ray diffraction (PXRD), and x-ray photoelectron spectroscopy (XPS).

**General Syntheses of Nanocomposites in the Presence of Amino Acids as Stabilizing Agent.** For gold–iron oxide nanocomposites stabilized with different L-amino acids, 16 different solutions were prepared. Each solution contains 10 mg (25 μmol) HAuCl₄, 450 × 10⁻⁹ AuNP seed mL⁻¹ in 100 mL of Millipore water. To these solutions, 5 μmol of 16 different amino acids were added. Finally, 10 mg (18 μmol) of iron powder were added to all the solutions for the syntheses of nanocomposites. The generation of the surface plasmon resonance (SPR) peak was studied in each case to monitor the formation of nanocomposite-containing gold.

**Syntheses of Nanocomposites: 1–8.** For gold–iron oxide nanocomposites with variable seed concentration, nine different solutions were prepared. Each solution contains 10 mg (25 μmol) HAuCl₄ in 100 mL Millipore water. To these solutions, eight different seed amounts, 90 × 10⁻⁹, 180 × 10⁻⁹, 270 × 10⁻⁹, 360 × 10⁻⁹, 450 × 10⁻⁹, 540 × 10⁻⁹, 630 × 10⁻⁹, and 720 × 10⁻⁹ mL⁻¹ were added for the syntheses of nanocomposites 1–8, respectively. In each of these solutions, an additional 50 μL solution of tryptophan (5 μmol in 1:1 mixture of water and ethanol) and 10 mg (18 μmol) iron powder were added. All these reaction mixtures were stirred at room temperature for 60 min and then filtered. The filtrate was concentrated by evaporation and 1–8 nanocomposites were obtained as solid materials from the filtrate after 3 days. After discarding the supernatant solutions, the solid nanocomposites were further dried under vacuum before characterization. One-negative control reaction was prepared without any iron powder.

**Syntheses of Nanocomposites 9–16.** For gold–iron oxide nanocomposites with variable iron concentration, five different reactions were prepared. Each solution contains 10 mg (25 μmol) HAuCl₄, 540 × 10⁻⁹ AuNP seed mL⁻¹, and a 50 μL solution of tryptophan (5 μmol in 1:1 mixture of water and ethanol) in 100 mL Millipore water. Iron powder amounts of 20 mg (36 μmol), 30 mg (54 μmol), 40 mg (72 μmol), and 50 mg (90 μmol) were added for the syntheses of nanocomposites 9–12, respectively. All these reaction mixtures were stirred at room temperature for 60 min and then filtered. The filtrate was concentrated by evaporation, and 9–12 nanocomposites were obtained as solid materials from the filtrate after 3 days. After discarding the supernatant solutions, the solid nanocomposites were further dried under vacuum before characterization. One-negative control reaction was prepared without any iron powder.

**Electrochemical Measurements.** The electrochemical experiments were performed in a three-electrode electrochemical cell at room temperature with a 660D CH Instrument potentiostat. A Standard calomel electrode (SCE) was used as the reference electrode. The working electrode was nanomaterial-coated FTO plates. Pt wire was used as the counter electrode. A KOH amount of 1.0 M (pH ~13.0) was used as the electrolytes. The nanomaterial/FTO working electrode was prepared as follows: 1 mg of nanomaterials was added into 0.2 mL EtOH; 0.2 mL water and 0.06 mL 5% Nafion solution and ultrasonicated for 30 min to prepare the ink; and then 20 μL of ink was loaded onto the FTO plate. The catalyst loading area was maintained as ~1 cm². Then, the plate was dried at room temperature for 24 h. Linear scan voltammograms (LSV) were recorded at a scanning rate of 50 mV/s. The electrochemical impedance spectroscopy (EIS) tests were carried out in a N₂-saturated 1 M KOH (pH ~13.0) solution at 0.5 V (vs SCE). Potentials were converted to RHE for comparison. The EIS spectra were obtained in a frequency range of 0.1–10⁹ Hz with an amplitude value of 5 mV. The charge transfer resistance (Rクト) was determined by fitting the Nyquist plot to a Randles equivalent circuit. Faradaic efficiency was calculated on the basis of the volume of the oxygen collected per area of electrode at their corresponding onset potentials for 5 h (Figure S24a), and the theoretical number of moles of the gas per area of electrode was calculated using the

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ideal gas law \( (n_\text{O}_2 = PV/RT) \). Finally, the \( n_\text{O}_2 \) was converted to photocurrent density (using photocurrent density \( = 4 \times n_\text{O}_2 \times F \), where \( F \) is the Faraday constant, which is 0.096487 \( C/\mu\text{mol} \)). Amounts of oxygen produced were 45.3, 47.4, 60.3, and 56.3 mmol for 1, 6, 12, and 16, respectively (after blank subtraction), which was obtained from the calibration curve in Figure S25. The total accumulated charge during 5 h of electrolysis was found to be 20.8, 25.3, 25.3, and 23.9 \( \mu\text{C} \) (after blank subtraction) for 1, 6, 12, and 16, respectively (Figure S24b).

■ ASSOCIATED CONTENT
- Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03549.

Electronic absorption, TEM, FE-SEM images, EDX plots with elemental mapping and EDX line scanning, XPS, PXRD, and IR data of the nanocomposites (PDF)

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Notes
The authors declare no competing financial interest.

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