Scalable synthesis of heterostructure of Fe₂O₃–Au nanomaterials for application in biological detection

Shouyi Huang¹, Guoqing Jiang¹, Xinchang Wu¹, Hua Zhang¹, Zhe Chen¹, Anran Chen² and Jin Zhang¹*©

¹ Kunming Vocational and Technical College of Industry, Kunming 680040, People’s Republic of China
² School of Energy, Yunnan University, Kunming 650091, People’s Republic of China

E-mail: 58025574@qq.com

Keywords: heterogeneous structure, nanocomposite, gold nanoparticle, multifunction, FDTD simulation

Supplementary material for this article is available online

Abstract
In terms of developing high-performing, multifunctional hetero-nanostructures, an exact control of the growth dynamics at the interface of metal nanoparticles (NPs) and metal oxides is of great significance. Having this in mind, we reported a facile and efficient approach to anchor and control the growth process of Au NPs on the surface of iron oxide, and to synthesis α–Fe₂O₃–Au heterogeneous structure. The nanocomposite exhibits its outstanding multifunctional performance, the energy absorption rate and energy transfer efficiency of α–Fe₂O₃–Au heterogeneous structure is obviously more than that of α–Fe₂O₃ materials. FDTD simulation results also show that α–Fe₂O₃–Au heterogeneous structure have excellent absorption light property and surface Raman effect compared to the single materials, and exhibit enhanced analysis enhancement factor (to \(5 \times 10^5\)) with R6G molecule probe in SERS measurement. Furthermore, for the electrocatalytic activity of H₂O₂, the sensitivity and detection limit is 42.265 μA mM⁻¹ cm⁻² and 1.166 μM, respectively. This work provides an innovative synthetic route for new heterogeneously structured nanocomposites.

1. Introduction
During the past few decades, heterogeneously structured nanocomposites have attracted significant attention because of its multifunctional properties, which can be applied in SERS [1, 2], magnetic sensors [3, 4], and medical equipment [5]. For metal/metal oxide hetero-nanostructures, which show excellent photocatalytic and electrocatalytic performances, leading to well-defined morphologies are required, which provide reasonable contact areas and strong material synergies [6]. However, the synthesis of heterojunction materials and to tailor their properties is one of the research hotspot and important subjects in the field of nanocomposites, and how to solve the lattice mismatches between metal and metal oxide materials is not only a challenge for developing modern synthetic methodology, but also important for extending their potential applications.

At present, a number of imaging modalities has been applied in disease diagnosis and treatment, such as near-infrared fluorescence (NIRF), magnetic resonance imaging (MRI), photoacoustic imaging (PA), computed tomography (CT), and so on [7, 8]. Nanocomposites integrating multifunction can effectively improve the imaging sensitivity and space resolution to accurately identify the localization and size of the tumor tissue. Surface-enhanced Raman spectroscopy (SERS) as a sensitive non-invasive ‘molecular fingerprint’ technology be able to offer an ideal method for medical diagnoses and therapy [9]. Up to now, various precious metals including Au, Ag and other materials have been employed as SERS-active substrate to obtained the reliable signal from the probe molecules [10, 11]. However, considering the cost and the complicated synthesis process of the precious metals, the main synthetic strategy is focusing on the combination of low cost materials and the precious metals to constructed multifunctional heterojunction materials, which possess electrocatalysis and SERS properties etc, to minimizes the amount of precious metal used and extends the performance from single
material. Hematite is one of the suitable candidate to meet the above-mentioned requirements and exhibits great potential for wide applications in medical treatment, photocatalyst, magnetic sensors and information storage [12, 13]. Ferromagnetic nanoparticles (Fe$_3$O$_4$) is used in a lot of the magnetic separation, imaging and catalytic fields [5, 14]. However, weak magnetic $\alpha$–Fe$_2$O$_3$ nanocomposites has rarely reported, particularly in the research for the structure and morphology of $\alpha$–Fe$_2$O$_3$–Au nanocomposites. Simultaneously, how to exact control the dynamics factor of the growth process and anchoring Au NPs on the surface of iron oxide substrate, it is still a great challenge to develop new facile synthetic strategies to building multifunctional heterojunction materials.

Hence, in the current work, we reported a facile and efficient approach to achieve morphology control of heterogeneously structured $\alpha$–Fe$_2$O$_3$–Au NPs, and obtained the uniform growth of Au NPs on the surface of iron oxide by wet-chemical synthetic strategies. The structure and performance of heterogeneously structured $\alpha$–Fe$_2$O$_3$–Au NPs are discussed in detail. We measured the photothermal, SRES and electrochemical catalysis properties of $\alpha$–Fe$_2$O$_3$–Au NPs, which is obviously improved compared with that of the single materials. As well as it has excellent electrochemical catalysis for H$_2$O$_2$.

2. Experimental

2.1. Chemicals

Ferric chloride (FeCl$_3$·3H$_2$O), chloroauric acid (HAuCl$_4$·3H$_2$O), lysine ($C_{12}H_{22}N_2O_4$), R6G ($C_{28}H_{31}N_2O_3Cl$), hydrogen peroxide (H$_2$O$_2$, 30 wt%) and ascorbic acid ($C_6H_8O_6$L–AA) were obtained from Aladdin Industrial Corporation. Potassium hydrogen phosphate (K$_2$HPO$_4$), sodium sulfate (Na$_2$SO$_4$). Sodium citrate ($C_6H$_7$Na$_2$O$_7$–2H$_2$O) were obtained from Sinopharm Chemical Reagent Co., Ltd. The deionized water used in all of the experiments was 18.25 MΩ·cm, and the chemical reagents used in the preparation were analytical grade and without any further purification.

2.2. Synthesis of $\alpha$–Fe$_2$O$_3$–Au NPs with smell ring-like, large ring-like, and cannular-like morphologies

The small ring-like, large ring-like and cannular-like of $\alpha$–Fe$_2$O$_3$ NPs was carried out following a modified hydrothermal procedure [15]. 1.3 ml FeCl$_3$ solution (0.3 M) was added into 38 ml deionized water, and 0.4 ml K$_2$HPO$_4$ (18 mM), 0.4 ml Na$_2$SO$_4$ (55 mM) was added in order under vigorous stirring. After 10 min, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and heat at 220 °C for 48 h. After the synthesis, the autoclave was cooled to room temperature, the precipitate was separated by centrifugation, and washed with distilled water and absolute ethanol. Next, the final product was dispersed and stored in deionized water for further use. Noted that, for large ring-like $\alpha$–Fe$_2$O$_3$ NPs, the amount of FeCl$_3$ solution (0.3 M) was 2 ml based on other parameters being hold, for cannular-like of $\alpha$–Fe$_2$O$_3$ NPs, the amount of FeCl$_3$ solution (0.3 M) and K$_2$HPO$_4$ (18 mM) solution was 2 ml and 0.89 ml respectively, while other parameters remain unchanged. The $\alpha$–Fe$_2$O$_3$–Au heterogeneous structure nanocomposite was produced by seed growth method. In a typical synthesis process of $\alpha$–Fe$_2$O$_3$–Au NPs, 2 ml of a colloidal solution of $\alpha$–Fe$_2$O$_3$ NPs (1 mg mL$^{-1}$) was mixed with 13 ml deionized water in a 25 ml glass vial under vigorous stirring at a speed of 500 rpm and the room temperature. Then, 0.6 ml lysine solution (10 mM) was added dropwise, after continue stirring for 24 h, Then 2.17 ml HAuCl$_4$ solution (1 mM), the value of pH was adjusted to 10.7 by 50 μL KOH solution (2 M), was quickly added into $\alpha$–Fe$_2$O$_3$/lysine suspension solution. Next, 13 μL sodium citrate solution (0.1 mM) was added under dark condition and stirring for 24 h. The mixed solution was transferred into a new glass vial and 0.3 ml L-AA solution (0.1 M) was added dropwise. After 30 min, the product was separated by centrifugation, washed with deionized water and anhydrous ethanol, respectively. The final product was dispersed into deionized water.

2.3. Characterization

The morphology of the samples was characterized by field emission scanning electron microscope (FESEM, FEI Quanta 250) at an acceleration voltage of 20 kV and transmission electron microscopy (TEM, JEOL-2100) operated at an acceleration voltage of 200 kV. The structural characterization was further investigated by x-ray diffraction (XRD), which was performed on a Bruker-AXS D8 Advance diffractometer operated at 40 kV voltage and 30 mA current using Cu Kα radiation (λ = 1.5418 Å) in the range of 15° to 90°. The UV–vis spectrum of the samples was recorded on a Hitachi UV–vis spectroscope (UV–4100). The surface structure of the samples was investigated through the x-ray photoelectron spectroscopy (XPS, Kratos Axis UL equipped with monochromatic Al Ka radiation, 150 W, 5 kV at 1486.6 eV) by referencing the spectra use the C 1s peak at a binding energy of 284.8 eV.
2.4. Performance measurements
We also investigate the photothermal properties, SERS properties, and Finite Difference Time Domain (FDTD) simulation, as well as electrochemical catalysis properties of H₂O₂. The details as shown in the supporting information.

3. Result and discussion

3.1. Microstructures and characterization
The morphology of α-Fe₂O₃ NPs was well-controlled in the presence of PO₄³⁻/SO₄²⁻ ion. Observed in detail, panels a, d and g of figure 1 show the SEM images of the α-Fe₂O₃ NPs. Panels b, e and h of figure 1 show the TEM images of the α-Fe₂O₃–Au NPs, and the hollow structure and size distribution has been marked by the corresponding geometrical models. The average radius \( r \) of small ring-like α-Fe₂O₃–Au NPs (Fe₂O₃–Au–r₁) is around 38.3 nm, and the average ring thickness \( d \) and the height \( L \) is about 19.6 nm and 56.8 nm (figure S1 is available online at stacks.iop.org/MRX/6/1250b5/mmedia), respectively. It is worthwhile to note that the Au NPs is covered and anchored onto the surface of α-Fe₂O₃ NPs, thus the stability of Au NPs is largely enhanced, so as to improve the catalysis stability of the α-Fe₂O₃–Au NPs [16]. When the concentration of Fe³⁺ ion was increasing, as shown in figures 1(d) and (e), the value of average radius, ring thickness and the height was increased to 47.5 nm, 22.8 nm and 62.7 nm (figure S2), indicating that the large ring-like α-Fe₂O₃–Au NPs (Fe₂O₃–Au–r₂) was formed. Figures 1(g) and (h) shows that the cannular-like α-Fe₂O₃–Au NPs (Fe₂O₃–Au–c), synthesized by increasing the ratio of PO₄³⁻/SO₄²⁻ ion, present an average radius, ring thickness and the height of around 41.0 nm, 17.6 nm and 118.2 nm (figure S3), respectively. Au NPs have been controllable growth on the surface of α-Fe₂O₃ NPs and have an uniform morphology, it shows the lattice match problem between metal and metal oxides has been solved by modifying surfactant to bind AuCl₄⁻ ion and through strong reductant L-AA to make Au NPs induced growth on the surface of α-Fe₂O₃ NPs.

Figure 2(a) is the x-ray powder diffraction patterns of the α-Fe₂O₃–Au NPs. The diffraction peaks can be ascribed to the rhombohedral structure α–Fe₂O₃ (JCPDS No. 33-0664) and the face-centered cubic structure of Au NPs (JCPDS No. 04-0784). The appearance of the sharp and narrow peaks suggests that the as-synthesized α–Fe₂O₃ NPs and α–Fe₂O₃–Au NPs have good crystallinity [17, 18]. The UV/Vis spectra of the as synthesis NPs revealed their ultraviolet absorption difference under 600 nm wavelength (figure 2(b)). There is obvious

Figure 1. Wide-field low-magnification SEM images of the α–Fe₂O₃ NP samples: (a) small ring-like, (d) large ring-like, (g) cannular-like of α–Fe₂O₃ NPs. The scale bar in the images is 500 nm. The TEM images and corresponding ideal geometrical models of the α–Fe₂O₃–Au heterogeneous structure: (b), (c) Fe₂O₃–Au–r₁, (e), (f) Fe₂O₃–Au–r₂, (b), (i) Fe₂O₃–Au–c. The scale bar in the images is 100 nm.
absorption peak in 550 nm when Au NPs load on the surface of α–Fe₂O₃ NPs, which attributed to Localized Surface Plasmon Resonance (LSPR) of the Au NPs \[19, 20\]. Simultaneously, the red shift of the absorption peak of α–Fe₂O₃ NPs indicates the present of α–Fe₂O₃–Au heterojunction structure, which is consistent with the TEM result.

Further evidence for the composition and purity of these products was also performed by XPS spectra, to investigate the atom valence state and the synergistic effect between Au NPs and α–Fe₂O₃ NPs. All spectra have corrected by C 1s \((284.8 \text{ eV})\). As shown in figure 3(a), compared with the XPS spectra obtained from the pure α–Fe₂O₃ NPs, a new peak of Au 4f and Au 4d can be observed from the sample after anchoring Au NPs, and Au 4f\(_{7/2}\) \((83.8 \text{ eV})\) and Au 4f\(_{5/2}\) \((87.5 \text{ eV})\) diffraction peak can be used to prove Au\(^0\) state \[21–23\]. The representative high-resolution spectra of the Au 4f regions are shown in figures 3(b)–(d), the diffraction peak in 85.0 eV (Au\(^+\)) and 86.0 eV (Au\(^++\)) cannot find demonstrate that the Au atom valence state is Au\(^0\) in α–Fe₂O₃–Au NPs rather than oxidation state Au ion. The binding energy of Au 4f\(_{7/2}\) is shift to the left (the direction of the negative axis, figure S4), which shows that there are the strong interaction between Au NPs and α–Fe₂O₃ substrate \[18, 24, 25\].
3.2. Photothermal properties measurements of $\alpha$–Fe$_2$O$_3$–Au NPs

Light absorption in nanoparticles is readily dissipated as heat. In this study, we used 808 nm wavelength laser irradiation 10 min (energy density 0.4 W cm$^{-2}$). For all solutions containing nanoparticles, a significant temperature rise in the bulk solution is observed after the laser is turned on at time, $t = 150$ s. As shown in figure 4(a), the $\alpha$–Fe$_2$O$_3$–Au NPs heat the surrounding bulk aqueous solution to maximum temperatures, $T_{\text{max}} \approx 42$ °C, while the pure $\alpha$–Fe$_2$O$_3$ NPs, $T_{\text{max}} \approx 37.2$ °C, the DI water used as controls show very small temperature increase. The Fe$_2$O$_3$–Au–r1 heat the bulk solution to slightly higher temperatures than that of the large rings-like and cannular-like NPs (figure 4(b)). The rise of temperature of $\alpha$–Fe$_2$O$_3$ NPs is about 8 °C at a irradiation cycle and it is about 15 °C for the $\alpha$–Fe$_2$O$_3$–Au NPs at the same condition, while the temperature change of H$_2$O solution is very slow, which will be a prospect applied to actual photothermal therapy [26]. The energy absorption rate and heat dissipation rate of the nanocomposites is shown in figure 4(c). The energy absorption rate and the energy transfer efficiency of heterogeneously structured $\alpha$–Fe$_2$O$_3$–Au NPs is obviously more than that of $\alpha$–Fe$_2$O$_3$ hollow structure (figure 4(d)), which prove that the loaded Au NPs improve the absorption efficiency of light and photoelectron energy absorption rate of the heterogeneously structured $\alpha$–Fe$_2$O$_3$–Au NPs. This consequence is consistent with the UV–vis result. Furthermore, the heat dissipation rate of each kind material is relatively low indicates the absorption photon energy is mainly used to rise the system temperature [27]. This suggest that heterogeneously structured $\alpha$–Fe$_2$O$_3$–Au NPs can be used for optics catalysis and light degradation process.

3.3. FDTD simulation testing of $\alpha$–Fe$_2$O$_3$–Au NPs

In order to explain the photothermal property and find the diversity between $\alpha$–Fe$_2$O$_3$–Au and $\alpha$–Fe$_2$O$_3$ NPs, we used FDTD simulation to display the difference of the $\alpha$–Fe$_2$O$_3$–Au and $\alpha$–Fe$_2$O$_3$ NPs under irradiation. FDTD simulation with 400–1000 nm wavelength transverse–electric light source and vertical irradiation on the surface of nanoparticle (figure 5(a)). The small amplitude of the local electric field in the polarization direction of Au and $\alpha$–Fe$_2$O$_3$ NPs, which indicates that the effect of surface plasma enhancement is weak (figures 5(b)–(e)). The amplitude of the local electric field of Au NPs is more than that of the $\alpha$–Fe$_2$O$_3$ NPs, and the effect of the surface plasma enhancement is obviously improved when loaded Au NPs to form heterogeneously structured $\alpha$–Fe$_2$O$_3$–Au NPs (figures 5(f)–(h)) [28]. As the dimensional changed, the amplitude of the local electric field of $\alpha$–Fe$_2$O$_3$–Au NPs is rise from 2.2 to 7.3. Simultaneously, the contacting area between Au NPs and substrate ($\alpha$–Fe$_2$O$_3$ NPs) is an important factor for the heterogeneous structure which have excellent absorption light property and surface Raman effect than single materials [6].

![Image](https://example.com/image.png)

Figure 4. (a) Temperature traces of the solutions containing the $\alpha$–Fe$_2$O$_3$ and $\alpha$–Fe$_2$O$_3$–Au NPs under laser irradiation, (b) heating curve of the solutions, (c) the energy absorption rate and energy dissipation rate, and (d) energy transfer efficiency of the $\alpha$–Fe$_2$O$_3$ and $\alpha$–Fe$_2$O$_3$–Au NPs.
3.4. SERS measurements of $\alpha$–Fe$_2$O$_3$–Au NPs

In order to further prove the synergistic effect between Au NPs and substrate ($\alpha$–Fe$_2$O$_3$ NPs) and expand the application field of $\alpha$–Fe$_2$O$_3$–Au heterogeneous structure, we used R6G ($10^{-6}$ M) as probe molecular to test the SERS property of $\alpha$–Fe$_2$O$_3$–Au NPs (Figure 6). The $\alpha$–Fe$_2$O$_3$ NPs made no response to R6G molecular and the vibration peak was not shown in the SERS process. However, the vibration peak of $\alpha$–Fe$_2$O$_3$–Au NPs is obviously enhanced and show SERS enhancement effect for R6G molecular. We have choice Raman peak in 614 cm$^{-1}$ as the research object, the obtained AEF of Au NPs, $\alpha$–Fe$_2$O$_3$–Au–r1, $\alpha$–Fe$_2$O$_3$–Au–r2 and

![Figure 5. FDTD simulation of the distribution of the local electric fields: (a) the schematic plot of vertical irradiation, (b) Au NPs, (c)–(e) the corresponding $\alpha$–Fe$_2$O$_3$ NPs, (f) Fe$_2$O$_3$–Au–r1 NPs, (g) Fe$_2$O$_3$–Au–r2 NPs, (h) Fe$_2$O$_3$–Au–c NPs.](image)

![Figure 6. SERS spectra of $\alpha$–Fe$_2$O$_3$–Au and $\alpha$–Fe$_2$O$_3$ NPs, excitation wavelength: 633 nm, later power: 17 mW, objective: 100 times, data collection time: 10 s.](image)
α–Fe₂O₃–Au cis × 10⁴, 5 × 10⁴, 2 × 10⁴ and 2 × 10⁴, respectively. It showing that heterogeneously structured α–Fe₂O₃–Au NPs can be used as SERS-active substrate materials.

3.5. Electrochemistry measurements of H₂O₂:
We have used α–Fe₂O₃–Au NPs as electrode materials to test the electrochemical catalytic ability of H₂O₂ in physiology system (PBS, pH = 7.4). Cyclic voltammetry (CV) curve is shown in figure 7(a). The current response of α–Fe₂O₃–Au heterogeneous structure was obvious higher than that of Au NPs and α–Fe₂O₃ NPs when system containing 200 μM H₂O₂ at a scan rate of 50 mV s⁻¹. The α–Fe₂O₃–Au electrode presents the most significant enhancement in cathode peak current among the as-used electrodes, indicating a quite sensitive nature of the α–Fe₂O₃–Au electrode toward H₂O₂ [29–32]. The best response from α–Fe₂O₃–Au–c NPs due to Au NPs is uniform loaded on the surface of NPs, and the smaller thickness bring the higher size effect and large contact area. Figure 7(b) shows the amperometric responses of α–Fe₂O₃–Au electrode with increasing the H₂O₂ concentrations from 0.1 mM to 10 mM in PBS solution, the Fe₂O₃–Au–c electrode exhibits a fast and linear response to the variation of the concentration of H₂O₂ increasing from 0.1 mM to 4 mM (figure 7(c)). The related current response equation is I(μA) = −8.284 x–8.706 (R² = 0.9731). As shown in table 1, under the same applied potential, the sensitivity and detection limit of the Fe₂O₃–Au–c electrode are estimate to be 42.265 μA mM⁻¹ cm⁻² and 1.166 μM (signal-to-noise ratio (S/N) = 3), respectively. Fe₂O₃–Au–c NPs has a most low detection liner and fast and step-like response for H₂O₂, the sensitivity of the Fe₂O₃–Au–c NPs is 2.16 and 1.15 times as high as that of Fe₂O₃–Au–r1 and Fe₂O₃–Au–r2, respectively.

Electrochemical impedance spectroscopy (EIS) was used to investigate the interface properties of different electrode materials in the presence of 5 mM K₃[Fe(CN)]₆ with 0.1 M KCl as the supporting electrolyte (figure 7(d)). The resistance of α–Fe₂O₃–Au NPs is obvious decreasing when the Au NPs loaded on the surface of

| Simple | Slope [μA mM⁻¹] | Adj.R² | Sensitivity [μA mM⁻¹ cm⁻²] | Detection limit [μM] |
|--------|----------------|--------|-----------------------------|---------------------|
| Fe₂O₃–Au–r1 | -3.831 | 0.9935 | 19.546 | 2.522 |
| Fe₂O₃–Au–r2 | -7.206 | 0.9733 | 36.765 | 1.314 |
| Fe₂O₃–Au–c | -8.284 | 0.9731 | 42.265 | 1.166 |

α–Fe₂O₃–Au–c is 3 × 10⁴, 5 × 10⁴, 2 × 10⁴ and 2 × 10⁴, respectively. It showing that heterogeneously structured α–Fe₂O₃–Au NPs can be used as SERS-active substrate materials.
α–Fe$_2$O$_3$ NPs, indicating α–Fe$_2$O$_3$–Au heterogeneous structure can improve the electron conduction ability of α–Fe$_2$O$_3$ NPs. The resistance of Fe$_2$O$_3$–Au–c heterogeneous structure is minimum, which is consistent with the CV and amperometric responses result.

4. Conclusions

In conclusion, we reported a facile and efficient approach to achieve morphology control of heterogeneously structured α–Fe$_2$O$_3$–Au NPs. SEM, TEM, XRD, UV–vis, and XPS characterization was used to prove the existence of heterogeneous structure. The lattice mismatches between metal and metal oxide materials is well solved, and the anchoring Au nanoparticles on the small ring, large-ring, and cannulars–like α–Fe$_2$O$_3$ NPs are all similar morphologically. In addition, we extend the research to investigate the photothermal property, FDTD simulation, SERS and electrochemistry measurements for H$_2$O$_2$ of heterogeneously structured α–Fe$_2$O$_3$–Au NPs. The heterogeneous structure obviously improves the energy absorption rate and efficient energy transfer of the photothermal property. As the SERS-active substrate, the AEF is 5 × 10$^4$. The heterogeneously structured α–Fe$_2$O$_3$–Au NPs display excellent response capacity due to the improved electronic transmission ability from Au NPs is uniform loaded on the surface of α–Fe$_2$O$_3$ NPs and the large contact area. The synthetic route in this article shows the innovative in the preparation technique of new heterogeneous structures. In general, the α–Fe$_2$O$_3$–Au heterogeneous structure are multifunctional, and these multifunctional properties have been exploited to create structures that are more economical and active than pure Au nanoparticle catalysts and will also find real world applications.

Acknowledgments

This work was supported by the Middle-aged and Young Teacher’s Training Program of Yunnan University (No. C1762210200, WX069051), the Research Fund of Yunnan Education Bureau, China (Grant No. 2018JS012), the Science and Engineering Fund of Yunnan University (Grant No. 2017YDQN10), and the Open Fund of Yunnan Key Laboratory of Opto-electronic Information Technology (Grant No. YNOE-2018-02).

ORCID iDs

Jin Zhang @ https://orcid.org/0000-0002-4127-0184

References

[1] Araújo J E, Lodeiro C, Capelo J L, Rodríguez–González B, dos Santos A A, Santos H M and Fernández–Lodeiro J 2014 Novel nanocomposites based on a strawberry–like gold–coated magnetite (Fe$_3$O$_4$/Au) for protein separation in multiple myeloma serum samples Nano Res. 8 1189–98
[2] Huang J et al 2015 Rational design and synthesis of gammaFe$_2$O$_3$@Au magnetic gold nanoflowers for efficient cancer theranostics Adv. Mater. 27 5049–56
[3] Liu M, Liu R and Chen W 2013 Graphene wrapped Cu$_x$O nanocubes: non-enzymatic electrochemical sensors for the detection of glucose and hydrogen peroxide with enhanced stability Biosens. Bioelectron. 45 206–12
[4] Xu G, Li L, Shen Z, Tao Z, Zhang Y, Tian H, Wei X, Shen G and Han G 2015 Magnetite Fe$_3$O$_4$ nanoparticles and hematite α–Fe$_2$O$_3$ uniform oblique hexagonal microdisks, drum–like particles and spindles and their magnetic properties J. Alloy Compd. 629 36–42
[5] Kang X, Wang I, Wu H, Akay I A, Liu J and Lin Y 2009 Glucose oxidase–graphene–chitosan modified electrode for direct electrochemistry and glucose sensing Biosens. Bioelectron. 25 901–5
[6] Li X, Zhang X, Ma H, Wu D, Zhang Y, Du B and Wei Q 2014 Cathodic electrochemiluminescence immunosensor based on nanocomposites of semiconductor carboxylated g-C$_3$N$_4$ and graphene for the ultrasensitive detection of squamous cell carcinoma antigen Biosens. Bioelectron. 55 330–6
[7] Zhang Y, Li Y, Wu W, Jiang Y and Hu B 2014 Chitosan coated on the layers’ glucose oxidase immobilized on cysteamine/Au electrode for use as glucose biosensor Biosens. Bioelectron. 60 271–6
[8] Zhang X, Sun S, Lv J, Tang L, Kong C, Song X and Yang Z 2014 Nanoparticle–aggregated CuO nanoellipsoids for high-performance non-enzymatic glucose detection J. Mater Chem. A 2 10073–80
[9] Xu F, Cui K, Sun Y, Guo C, Liu Z, Zhang Y, Shi Y and Li Z 2010 Facile synthesis of urchin-like gold submicrostructures for nonenzymatic glucose sensing Talanta 82 1845–52
[10] Xu F, Deng M, Li G, Chen S and Wang L 2013 Electrochemical behavior of cuprous oxide–reduced graphene oxide nanocomposites and their application in nonenzymatic hydrogen peroxide sensing Electrochim. Acta 88 59–65
[11] Lang Q, Yin L, Shi J, Li L, Xia L and Liu A 2014 Co-immobilization of glycoamylase and glucose oxidase for electrochemical sequential enzyme electrode for starch biosensor and biofuel cell Biosens. Bioelectron. 51 158–63
[12] Yang A, Bi J, Yang S, Zhang J, Chen A and Liang S 2014 Highly surface–roughened catapperillar–like Au/Ag nanotubes for sensitive and reproducible substrates for surface enhanced Raman spectroscopy RSC Adv. 4 45836–61
[13] Chen K J, Lee C F, Rick J, Wang S H, Liu C C and Hwang B J 2012 Fabrication and application of amperometric glucose biosensor based on a novel PtPd bimetallic nanoparticle decorated multi-walled carbon nanotube catalyst Biosens. Bioelectron. 33 75–81
14. Hsu C W and Wang G J 2014 Highly sensitive glucose biosensor based on Au-Ni coaxial nanorod array having high aspect ratio Biosens. Bioelectron. 56 204–9
15. Jia C J et al 2008 Large-scale synthesis of single-crystalline iron oxide magnetic nanorings J Am Chem Soc. 130 16968–77
16. Anran C, Yu D, Zhimao Y and Shengchun Y 2015 Constructing heterostructure on highly roughened caterpillar-like gold nanotubes with cuprous oxide grains for ultrasensitive and stable nonenzymatic glucose sensor Biosens. Bioelectron. 74 967–73
17. Li Z, Chen H, Bao H B and Gao M Y 2004 One-pot reaction to synthesize water-soluble magnetite nanocrystals Chem. Mater. 16 1391–3
18. Zhao K, Tang H, Li L and Wang J 2015 High activity of Au/γ-Fe2O3 for CO oxidation: effect of support crystal phase in catalyst design Acscatal. 5 3526–39
19. Tilocca A 2015 Realistic models of bioactive glass radioisotope vectors in practical conditions: structural effects of ion exchange The Journal of Physical Chemistry C 119 27442–8
20. Liu Y, Xu Z, Yin M, Fan H, Cheng W, Lu L, Song Y, Ma J and Zhu X 2015 Enhanced photoelectrocatalytic performance of alpha-Fe2O3 thin films by surface plasmon resonance of Au nanoparticles coupled with surface passivation by atom layer deposition of Al2O3 Nanoscale Res. Lett. 10 374
21. Fang B, Zhang C, Wang G, Wang M and Ji Y 2011 A glucose oxidase immobilization platform for glucose biosensor using ZnO hollow nanospheres Sensors Actuators B 155 504–10
22. Hwa K Y and Subramani B 2014 Synthesis of zinc oxide nanoparticles on graphene–carbon nanotube hybrid for glucose biosensor applications Biosens. Bioelectron. 62 127–33
23. Karuppiah C, Palanisamy S, Chen S-M, Veeramani V and Periakaruppan P 2014 A novel enzymatic glucose biosensor and sensitive non-enzymatic hydrogen peroxide sensor based on graphene and cobalt oxide nanoparticles composite modified glassy carbon electrode Sensors Actuators B 196 650–6
24. Hernández J A, Gómez JA, Zepeda TA, Fierro-González JC and Fuentes GA 2015 Insight into the deactivation of Au/Co3O4 catalysts studied by in situ spectroscopy during the CO-PROX reaction Acscatal. 5 4003–12
25. Jia C, Zhong W, Deng M and Jiang J 2016 Microscopic Insight into the Activation of O2 by Au Nanoparticles on ZnO(101) Support The Journal of Physical Chemistry C 120 4322–8
26. Liu S and Ju H 2003 Reagentless glucose biosensor based on direct electron transfer of glucose oxidase immobilized on colloidal gold modified carbon paste electrode Biosens. Bioelectron. 19 177–83
27. Murph SE, Larsen GK and Lascola RJ 2016 Multifunctional hybrid Fe2O3-Au nanoparticles for efficient plasmonic heating J. Vis. Exp. 108 53598
28. Nguyen MT, Farnesi Carnellone M and Gebauer R 2015 On the electronic, structural, and thermodynamic properties of Au supported on alpha-Fe2O3 surfaces and their interaction with CO J. Chem. Phys. 143 034704
29. Kumar DR, Manoj D and Santhanakrishmi J 2014 Au-ZnO bullet-like heterodimer nanoparticles: synthesis and use for enhanced nonenzymatic electrochemical determination of glucose RSC Adv. 4 8946–8952
30. Si P, Kauan P, Guo L, Son H and Kim DH 2011 Highly stable and sensitive glucose biosensor based on covalently assembled high density Au nanostructures Biosens. Bioelectron. 26 3845–51
31. Zheng Y, Cheng Y, Wang Y, Bao F, Zhou L, Wei X, Zhang Y and Zheng Q 2006 Quasicubic alpha-Fe2O3 nanoparticles with excellent catalytic performance J. Phys. Chem. B 110 3093–100
32. Wang J, Gao H, Sun F, Hao Q and Xu C 2013 Highly sensitive detection of hydrogen peroxide based on nanoporous Fe3O4/CoO composites Biosens. Bioelectron. 42 550–5