In situ growth of Au nanoparticles on Fe₂O₃ nanocrystals for catalytic applications

Cao, Shao-Wen; Fang, Jun; Mohammad Mehdi Shahjamali; Wang, Zheng; Yin, Zhen; Yang, Yanhui; Barber, James; Loo, Say Chye Joachim; Xue, Can; Boey, Freddy Yin Chiang

2012

Cao, S., Fang, J., Mohammad, M. S., Wang, Z., Yin, Z., Yang, Y., et al. (2012). In situ growth of Au nanoparticles on Fe₂O₃ nanocrystals for catalytic applications. *CrystEngComm*, 14(21), 7229–7235.

<https://hdl.handle.net/10356/96941>

<https://doi.org/10.1039/c2ce25746g>

© 2012 The Royal Society of Chemistry. This is the author created version of a work that has been peer reviewed and accepted for publication by CrystEngComm, The Royal Society of Chemistry. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1039/c2ce25746g>].

Downloaded on 26 Apr 2023 23:26:05 SGT

In-situ Growth of Au Nanoparticles on Fe₂O₃ Nanocrystals for Catalytic Applications

Shao-Wen Cao,^a Jun Fang,^a Mohammad Mehdi Shahjamali,^a Zhen Yin,^a Zheng Wang,^a Freddy Y. C. Boey,^a James Barber,^{a,b} Say Chye Joachim Loo^{*a} and Can Xue^{*a}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Gold nanoparticles are successfully grown in-situ on α -Fe₂O₃ nanocrystals through a cysteine-linked seed-planting approach followed by photo-assisted growth. The size of the gold particles on α -Fe₂O₃ nanocrystals can be further tuned from 2 to 20 nm by using photoinduced seed-mediation strategy. The formed Au- α -Fe₂O₃ hetero-nanoparticles are highly dispersible in aqueous and alcohol solvents, and capable of efficient catalysis for 4-NP reduction. In addition, they also show promoted photocatalytic efficiencies for visible-light-driven dye degradation and water oxidation due to the enhancement by surface plasmon resonance of the attached gold nanoparticles. The present strategy gives a promising way to prepare hetero-nanostructures composed by metal oxide nanocrystals and metal nanoparticles with tailorable sizes for broad applications in catalysis and photocatalysis.

Introduction

In the past a few years hybrid nanomaterials composed of multi-functional components have attracted tremendous research interest in the fields of optics,¹ magnetics,² catalysts,³ chemical sensors,⁴ biomedical applications,⁵ and so on. The prosperous applications of these hybrid nanomaterials are owing to their tailorable composition, versatile structure, and improved stability and dispersity.⁶ Among them, gold-iron oxide nanocomposites are particularly attractive recently due to their combined optical, catalytic and magnetic properties.⁷⁻¹² For instance, the Au-Fe₃O₄ composites have been extensively used as magnetic probes in various biotechnologies,^{5,8,9,13} while Au- α -Fe₂O₃ composites have been pursued for catalysis.^{11,14,15} Significant progress has been made in the synthesis of gold-metal oxide composites such as Au-TiO₂,¹⁶⁻²¹ Au-ZnO,^{22,23} Au-Fe₃O₄,^{8,24} Au- γ -Fe₂O₃,^{25,26} and Au- α -Fe₂O₃.²⁷⁻²⁹ However, the controlled synthesis of gold-metal oxide hetero-nanoparticles over gold particle sizes still faces tremendous challenges. In comparison to the gold-loaded bulk composites, hetero-nanoparticles would be more desirable as they have larger metal-semiconductor interface area, which allows for more efficient electronic interaction between metal and semiconductor.

Herein we present a novel strategy for in-situ growth of gold nanoparticles on α -Fe₂O₃ nanocrystals, which leads to the formation of hetero-nanoparticles with gold unit size tailorable from 2 to 20 nm via a photo-assisted process. Comparing to the previously reported methods, such as using gold seed nanocrystals to grow iron oxide domains for synthesizing Au-Fe₃O₄ heterostructures,²⁴ and the layer-by-layer method to assemble gold particles on Fe₂O₃ surfaces,³⁰ the photo-assisted approach presented here allows us to in-situ grow individual Au nanoparticles of different sizes on small metal oxide nanocrystals. Notably, the prepared Au- α -Fe₂O₃ hetero-nanoparticles can not only be used for efficient catalysis of 4-nitrophenol (4-NP) reduction, but also show high photocatalytic efficiency for visible-light-driven dye degradation and water oxidation.

Experimental section

Synthesis of α -Fe₂O₃ nanocrystals

In a typical experiment, Fe(NO₃)₃•9H₂O (202 mg) and CO(NH₂)₂ (80 mg) were dissolved in ultrapure water (25 mL) under magnetic stirring. The resultant solution was sealed in a 40 mL teflonlined stainless-steel autoclave, heated, and maintained at 160 °C for 6 h. After cooled to room temperature, the red products were washed several times with water.

In-situ growth of 2-nm Au nanoparticles on α -Fe₂O₃ nanocrystals

In a typical procedure, the as-obtained α -Fe₂O₃ nanocrystals (20 mg) was dispersed in 20 mL ultrapure water to form a suspension, followed by the addition of L-cysteine aqueous solution (5 mL, 0.01M). The mixture was then sonicated for 30 minutes, followed by the addition of HAuCl₄ aqueous solution (10 mL, 3 mM). After vigorous stirring for another 30 minutes, an aqueous solution of L-ascorbic acid (20 mL, 0.05M) was quickly added into the solution. The reaction was allowed for 3 h under

rapid stirring. The products were separated via centrifugation and washed with water and ethanol repeatedly. The product is referred as 2-nm Au- α -Fe₂O₃ hetero-nanoparticles.

Growth of larger Au nanoparticles (7, 11, 20-nm) on α -Fe₂O₃ nanocrystals

The as-obtained 2-nm Au- α -Fe₂O₃ hetero-nanoparticles (5 mg) and sodium dodecyl sulfate (SDS) (14.4 mg) were dispersed in a mixed solvent of 5 mL ultrapure water and 5 mL isopropanol. Then 5 mL aqueous solution of HAuCl₄ with different concentrations (0.3 mM for 7-nm, 0.6 mM for 11-nm, 1.2 mM for 20-nm Au- α -Fe₂O₃ hetero-nanoparticles) was dropwise added into the suspension, respectively, under irradiation with a 150-W halogen lamp (Fiber-Lite MI-150, Dolan-Jenner Industries, USA). The halogen lamp was immediately turned off after the addition of HAuCl₄ solution. The products were separated and washed with water and ethanol repeatedly.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer (Cu K α source) at a scan rate of 1 °/min with the 2 θ range from 20 to 60°. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. The energy dispersive X-ray (EDX) spectra were taken on a JEOL JSM-7600F scanning electron microscope equipped with energy dispersive X-ray analysis system. UV-vis spectra were recorded on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA).

Catalytic reduction of 4-nitrophenol (4-NP)

Before catalytic measurements, the powders were treated by UV/ozone cleaning to remove cysteine bound and other organic species on the product surface. The aqueous suspension of as-prepared Au- α -Fe₂O₃ hetero-nanoparticles (1 mg/mL) was added into 5 mL aqueous solution of 4-NP (20 mg/L) with the molar ratio of Au to 4-NP fixed at about 1:4. Subsequently, the above solution was mixed with 2.5 mL fresh solution of NaBH₄ (25 mM). The reaction was carried out at room temperature and UV-vis absorption spectra were recorded at different intervals.

Photocatalytic degradation of rhodamine B (RhB)

Before photocatalytic measurements, the powders were treated by UV/ozone cleaning to remove cysteine bound and other organic species on the product surface. The reaction suspension was prepared by dispersing the prepared Au- α -Fe₂O₃ hetero-nanoparticles (containing 5 mg α -Fe₂O₃) into RhB aqueous solution (10 mL, 4 mg/L). The suspension was sonicated for 15 min and then stirred overnight in the dark to ensure an adsorption/desorption equilibrium. Then the suspension was irradiated under continuous stirring by using a 150-W Xe lamp (MAX-150, Asahi Spectra, USA) with a UV cut-off filter ($\lambda > 420$ nm). Analytical samples were taken out from the reaction suspension after various reaction time and centrifuged at 10,000 rpm for 5 min to remove the particles. The RhB concentration was analyzed according to the absorption intensity at 554 nm in the measured UV-vis spectra.

Photocatalytic oxidation of water for O₂ generation

Before photocatalytic measurements, the powders were treated by UV/ozone cleaning to remove cysteine bound and other organic species on the product surface. In a typical experiment, Au- α -Fe₂O₃ hetero-nanoparticles (containing 5 mg α -Fe₂O₃) were dispersed in an aqueous solution of Na₂S₂O₈ (15 mL, 5.33 mM). The suspension was sealed in the reaction flask and purged with argon for 3 h to drive away the residual oxygen. The photocatalytic water oxidation was carried out by irradiating the suspension with a 300-W Xe lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420$ nm). The gas product composition was analyzed every 30 min by gas chromatograph (Agilent 7890A GC with TCD detector).

Scheme 1. Schematic illustration of the synthetic route for the Au- α -Fe₂O₃ hetero-nanoparticles.

Results and discussion

Fig. 1 TEM micrographs of α -Fe₂O₃ nanoparticles.

Fig. 2 XRD patterns of different samples: (a) α -Fe₂O₃; (b) 2-nm Au- α -Fe₂O₃; (c) 7-nm Au- α -Fe₂O₃; (d) 11-nm Au- α -Fe₂O₃; (e) 20-nm Au- α -Fe₂O₃.

The synthetic route of Au- α -Fe₂O₃ hetero-nanoparticles is illustrated in Scheme 1. Firstly, hydrophilic α -Fe₂O₃ nanocrystals (~25 nm, Fig. 1) as the base unit were prepared by an adapted hydrothermal method using Fe(NO₃)₃•9H₂O and urea.³¹ XRD analysis (Fig. 2a) confirms the product as α -Fe₂O₃ phase. Gold nanoparticles of ~2 nm were grown on the α -Fe₂O₃ nanocrystal surfaces by reducing HAuCl₄ with ascorbic acid in the presence of L-cysteine.³² In this process, the L-cysteine plays two important roles. First, the existence of -SH group in cysteine allows for the growth of gold nanoparticles with very small sizes (< 3 nm).³³ Second, cysteine binds with α -Fe₂O₃ through the carboxylate group and captures gold atoms through Au-S bonding onto α -Fe₂O₃ surface. These gold atoms serve as nucleating sites for further growth on the α -Fe₂O₃ nanocrystal surface. The product was subsequently washed repeatedly with water so as to remove excessive reagents and other free floating gold nanoparticles. Fig. 3 confirms the successful growth of 2-nm gold on α -Fe₂O₃ nanocrystals, and the product is referred as 2-nm Au- α -Fe₂O₃ hetero-nanoparticles. These hetero-nanoparticles are very stable so that the gold nanoparticles do not dislodge from the α -Fe₂O₃ surface even after repeated washing with sonication. The gold nanoparticles with size around 2 nm usually show very weak visible-light absorption, which is contributed by both the 5d → 6sp interband transitions^{34,35} and weak surface plasmon resonance (SPR).³⁶⁻³⁸ Therefore, the UV-Vis spectrum (Fig. 4) does not show distinguishable absorption features from 2-nm gold nanoparticles which may be overlapped by the absorption of α -Fe₂O₃ nanocrystals. Note that XRD analysis (Fig. 2b) does not show the characteristic peak of Au due to the low crystallinity of the 2-nm gold nanoparticles. In comparison, when pure α -Fe₂O₃ nanoparticles without L-cysteine modification were used, large and irregular gold nanoparticles formed and very few of them were grown on the α -Fe₂O₃ surface, as shown in Fig. S1 marked as compared sample i.

Fig. 3 TEM images (a, b) and histogram of gold size distribution (c) of 2-nm Au- α -Fe₂O₃ hetero-nanoparticles.

Fig. 4 UV-vis absorption spectra of colloidal solution of α -Fe₂O₃ and different Au- α -Fe₂O₃ hetero-nanoparticles with normalized absorbance.

The growth of larger gold nanoparticles on the α -Fe₂O₃ nanocrystals were carried out through photo-induced reduction of HAuCl₄ by isopropanol. The photoreduction of HAuCl₄ preferentially occurs on the surface of gold nanoparticle seeds that have been grown on the α -Fe₂O₃ nanocrystals, which is attributed to several reasons. First, it is well known in catalysis that the small metal nanoparticle (<5 nm) surface can significantly reduce the activation energy of chemical reactions.³⁹ As such these 2-nm gold nanoparticles can serve as catalytic sites to grow up from the HAuCl₄-isopropanol redox reaction. Second, the excitation of 2-nm gold nanoparticles through both interband transition and SPR absorption can induce photocatalytic reaction of HAuCl₄ with isopropanol.^{40,41} Third, although α -Fe₂O₃ also can function as a photocatalyst, the photoexcited electrons would likely be transferred very quickly to the 2-nm gold nanoparticles and thereby reduce HAuCl₄ on the gold surfaces for further gold particle growth rather than directly reducing HAuCl₄ on α -Fe₂O₃ surface. Indeed, when pure α -Fe₂O₃ nanoparticles without 2-nm Au

seeds attached were used for photocatalytic reaction of HAuCl_4 and isopropanol, gold nanoparticles did appear but very few of them were grown on the $\alpha\text{-Fe}_2\text{O}_3$ surface no matter it is modified with cysteine or not (Fig. S2a-d as compared sample ii and iii), and the gold nanoparticle size was difficult to control. This observation confirms that the pre-existence of the 2-nm Au seeds on the $\alpha\text{-Fe}_2\text{O}_3$ surface is indispensable in order to achieve in-situ growth of larger Au nanoparticles with controllable size. A fact is that the addition of HAuCl_4 is important for the growth of larger gold nanoparticles, since without adding additional HAuCl_4 , only 2-nm Au seeds could not further grow to larger gold particles under the short-time photo-irradiation (Fig. S2e and f as compared sample iv).

The final gold nanoparticle size in $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles can be tailored by varying the initial HAuCl_4 concentration. Fig. 5 shows the hetero-nanoparticle product with average gold size of ~ 7 nm, ~ 11 nm and ~ 20 nm, respectively. It indicates that the gold nanoparticles are directly attached on the surface of the $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals with clear interfaces between each other. Due to the Ostwald ripening effect and inhomogeneous light excitation, it is difficult to achieve simultaneous uniform growth of all 2-nm gold seeds. As a result, some small gold nanoparticles with sizes less than 5 nm coexist on the $\alpha\text{-Fe}_2\text{O}_3$ surface along with larger gold nanoparticles. With increasing size, the gold crystal features start to emerge in XRD patterns (Fig. 2c-e). The EDX analysis (Fig. 6a-d) further confirms the presence of gold on these hetero-nanoparticles with an estimated gold content of 19.8, 24.6, 30.2, and 36.5 wt % for 2-nm, 7-nm, 11-nm, and 20-nm $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles, respectively. Note that the gold units still remain dispersed on the $\alpha\text{-Fe}_2\text{O}_3$ crystal surface though the loading amount is relatively high. And these hetero-nanoparticles can still be easily suspended in aqueous solution. In addition, this cysteine-linked seed planting strategy combining with photoinduced seed-mediation growth method is superior for preparing $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles as compared with simply mixing pre-synthesized gold nanoparticles (Fig. S3a and S3b) with cysteine-modified $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals. The latter did not result in the formation of heterogeneous $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ nanoparticles as shown in Fig. S3c and S3d (compared sample V).

Fig. 5 TEM images and histograms of gold size distribution of different samples: (a, b) 7-nm $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles; (c, d) 11-nm $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles; (e, f) 20-nm $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles.

The 7-nm, 11-nm, and 20-nm $\text{Au-}\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles exhibit increasing plasmon absorption at around 535 nm, 540 nm, and 550 nm, respectively (Fig. 4), which is relatively red-shifted comparing to normal free colloidal gold nanoparticles of similar sizes.³⁶ This might be due to the attached $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles that increase the local dielectric constant near the gold nanoparticles and delocalize the gold surface electrons upon plasmon excitation, which causes electron deficiency and shifts the absorption band to longer wavelength. Similar phenomena have also been reported on $\text{Au-Fe}_3\text{O}_4$ hetero-nanoparticles,⁴²

suggesting strong electronic interaction between gold and iron oxide at their interface. In comparison, the spectrum of a simple mixture of α -Fe₂O₃ nanocrystals with free gold nanoparticles (Fig. S4) shows only the overlapped result of their absorption with no indication of red-shift of Au SPR. These results indirectly confirm that in the prepared Au- α -Fe₂O₃ hetero-nanoparticles samples, the larger gold nanoparticles are indeed generated on the α -Fe₂O₃ surface rather than in free standing formats.

Fig. 6 EDX spectra of hetero-nanoparticles of (a) 2-nm Au- α -Fe₂O₃; (b) 7-nm Au- α -Fe₂O₃; (c) 11-nm Au- α -Fe₂O₃; (d) 20-nm Au- α -Fe₂O₃. The Si peak comes from the silicon substrate.

In order to evaluate the catalytic activity of the prepared Au- α -Fe₂O₃ hetero-nanoparticles, we used the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by NaBH₄ as a model reaction. This reaction has been widely used for the analysis of the catalytic activity of metal nanoparticles.⁴³⁻⁴⁵ The 4-NP reduction processes were monitored by time-resolved UV-vis absorption spectra as shown in Fig. 7. After NaBH₄ was introduced into the 4-NP solution in the presence of Au- α -Fe₂O₃ hetero-nanoparticles, the solution color diminished and the characteristic absorption peak of 4-nitrophenolate ion at 400 nm decreased gradually, while a new peak at 298 nm ascribed to the appeared 4-AP. Note that the Au- α -Fe₂O₃ hetero-nanoparticles remained highly dispersed throughout the 4-NP reduction reaction even though the gold nanoparticles on α -Fe₂O₃ surfaces are small. The catalytic reaction completed within 60 sec for the 2-nm Au- α -Fe₂O₃ hetero-nanoparticles (Fig. 7a), while the hetero-nanoparticles with larger gold units show much slower catalytic process. It took 240 sec and 7 min for 7-nm and 11-nm Au- α -Fe₂O₃ hetero-nanoparticles, respectively (Fig. 7c and e). This observation indicates that the gold nanoparticles grown on the α -

Fe₂O₃ nanocrystals are quite active for catalysis and smaller gold nanoparticles exhibit higher catalytic activities.

Fig. 7 UV-vis adsorption spectra taken after adding NaBH₄ into 4-NP solution in the presence of various catalysts and the corresponding curves of $\ln(A_t/A_0)$ versus reaction time: (a, b) 2-nm Au- α -Fe₂O₃ hetero-nanoparticles; (c, d) 7-nm Au- α -Fe₂O₃ hetero-nanoparticles; (e, f) 11-nm Au- α -Fe₂O₃ hetero-nanoparticles.

Since the amount of NaBH₄ is in large excess, the reduction of 4-NP may be estimated as a pseudo-first-order reaction.⁴⁴ The reaction kinetics can be described as $-\ln(C_t/C_0) = kt$, where k is the rate constant and t is the reaction time. C_0 and C_t are the concentration of 4-NP at beginning and at time t , respectively. A correlation of $\ln(A_t/A_0)$ (corresponding to $\ln(C_t/C_0)$) versus reaction time t was obtained (shown in Fig. 7b, d, and f) for 2-nm, 7-nm and 11-nm Au- α -Fe₂O₃ hetero-nanoparticles, respectively. The corresponding kinetic rate constant k was estimated to be $4.9 \times 10^{-2} \text{ sec}^{-1}$, $1.3 \times 10^{-2} \text{ sec}^{-1}$, and $5.9 \times 10^{-3} \text{ sec}^{-1}$, respectively. Note that the kinetic rate constant k for 2-nm Au- α -Fe₂O₃ hetero-nanoparticles is much higher than that in the recent report for oxide-supported Au nanocatalysts ($10.64 \times 10^{-3} \text{ sec}^{-1}$)⁴⁶ and Ag-Pd nanocatalysts ($33 \times 10^{-3} \text{ sec}^{-1}$)⁴⁷ with similar ratio of catalysts versus nitrophenol. The high catalytic activity may be attributed to highly dispersed α -Fe₂O₃ nanocrystals with well distributed small gold nanoparticles on their surfaces, allowing effective interactions between the reactants and metal catalysts.

Fig. 8 (a) Photocatalytic degradation ratio of RhB versus irradiation time by using various photocatalysts based on equal amounts of $\alpha\text{-Fe}_2\text{O}_3$; (b) The amount of oxygen evolution versus irradiation time through photocatalytic water oxidation by using various photocatalysts based on equal amounts of $\alpha\text{-Fe}_2\text{O}_3$; (c) The three-run test of photocatalytic water oxidation by using the 11-nm Au- $\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles.

We also evaluated the photocatalytic activities of the Au- $\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles through Rhodamine B (RhB) degradation under visible-light ($\lambda > 420$ nm) irradiation. Fig. 8a shows the comparison of photocatalytic degradation rates of RhB by using different Au- $\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles containing equal amounts of $\alpha\text{-Fe}_2\text{O}_3$. It indicates that the 11-nm Au- $\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles exhibit the highest photocatalytic activity with nearly 82% RhB degraded within 8 hours. While in comparison the degradation percentage of RhB on pure $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals is only 35%. Both 7-nm and 20-nm Au- $\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles also show better activities than pure $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals.

The improved photocatalytic efficiency for Au- $\alpha\text{-Fe}_2\text{O}_3$ hetero-nanoparticles is attributed to two major factors. First, the gold nanoparticles grown on the $\alpha\text{-Fe}_2\text{O}_3$ nanocrystal surface may act as electron sinks to retard the recombination of the photogenerated electrons and holes in $\alpha\text{-Fe}_2\text{O}_3$ so as to improve the charge separation on its surfaces. Second, the SPR of the gold nanoparticles may also contribute to the photocatalytic efficiency. It is known that the SPR-excitation of metal nanostructures can generate strongly enhanced localized electric fields with magnitudes up to 10^5 times of the incident energy.⁴⁸ By this way, the metal nanostructures act like optical antenna to concentrate the light energy at the near surfaces. Therefore the $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals near the Au- $\alpha\text{-Fe}_2\text{O}_3$ interfaces would encounter much more intense band gap excitation by this SPR-enhanced electric field, which can generate more photo-excited electrons for the photocatalytic reaction. Moreover, the wide overlap between Au-plasmon band and $\alpha\text{-Fe}_2\text{O}_3$ absorption in the visible light range enables intensive plasmon-exciton coupling that significantly increases the electron-hole separation efficiency,⁴⁹⁻⁵³ and thereby promote the photocatalytic efficiency. It

should be noted that the 2-nm Au- α -Fe₂O₃ hetero-nanoparticles show lower photocatalytic efficiency than pure α -Fe₂O₃ probably because the active sites on α -Fe₂O₃ surfaces are excessively covered by the small 2-nm gold nanoparticles, which reduces the chance of RhB adsorption and oxidation by the photogenerated holes on α -Fe₂O₃ surfaces and lower down the overall photocatalytic efficiency. While the weak excitation of these 2-nm gold nanoparticles could not provide sufficient photocatalytic driving force to remedy efficiency loss from reduced active sites on α -Fe₂O₃ surfaces. Overall the results suggest that the photocatalytic efficiencies of Au- α -Fe₂O₃ nanocrystals are influenced by both photogenerated charge carriers and active surface sites.

In addition, the RhB degradation process may also involve the dye-sensitization process as previously reported,⁵⁴ which should play similar roles and equal effect between the pure α -Fe₂O₃ nanocrystals and the α -Fe₂O₃ samples with gold nanoparticles grown there as the comparison was based on equal α -Fe₂O₃ amount. As for the dye-sensitization on gold nanoparticles, we have tested the 13-nm gold nanoparticles with similar gold amount with that in 11-nm Au- α -Fe₂O₃ hetero-nanoparticles for RhB degradation. The result (Fig. 8a) indicates that the pure gold nanoparticles show even much weaker dye degradation capability than pure α -Fe₂O₃ nanocrystals. Therefore, we believe that the in-situ grown gold nanoparticles do improve the visible-light photocatalytic efficiency of α -Fe₂O₃ nanocrystals. We also compared the photocatalytic activities for different Au- α -Fe₂O₃ hetero-nanoparticles containing of equal amounts of gold. The results (Fig. S5) still indicate that the 11-nm Au- α -Fe₂O₃ hetero-nanoparticles exhibit the highest photocatalytic activity. This further confirms the important effect of gold nanoparticles to improve the visible-light photocatalytic efficiency.

Consistently, a similar trend was observed when employing the Au- α -Fe₂O₃ hetero-nanoparticles for photocatalytic water oxidation under visible light irradiation ($\lambda > 420$ nm). Here S₂O₈²⁻ was used as the sacrificial electron acceptor. As shown in Fig. 8b, the O₂ evolution rate from the 11-nm Au- α -Fe₂O₃ hetero-nanoparticles (10.81 $\mu\text{mol}\cdot\text{h}^{-1}$) is obviously larger than that from pure α -Fe₂O₃ nanoparticles (5.15 $\mu\text{mol}\cdot\text{h}^{-1}$), while the 2-nm Au- α -Fe₂O₃ hetero-nanoparticles exhibit less oxygen evolution efficiency (4.41 $\mu\text{mol}\cdot\text{h}^{-1}$). To verify the recycling capability of the Au- α -Fe₂O₃ hetero-nanoparticles, a three-run test of photocatalytic water oxidation was carried out by using the 11-nm Au- α -Fe₂O₃ hetero-nanoparticles. Fig. 8c reveals only slight decrease in the oxygen evolution after the three-run test, indicating very good stability of the Au- α -Fe₂O₃ hetero-nanoparticles in photocatalytic reactions.

Conclusions

In summary, gold nanoparticles have been successfully grown in-situ on α -Fe₂O₃ nanoparticles through a cysteine-linked seed planting strategy combining with photo-assisted growth. The size of the gold particles on α -Fe₂O₃ nanocrystals can be further tuned from 2 to 20 nm by using photoinduced seed-mediation strategy. These Au- α -Fe₂O₃ hetero-nanoparticles are capable of efficient catalysis for 4-NP reduction, and show enhanced efficiency for visible-light-driven photocatalytic dye degradation and water oxidation. The work reported here is significant for the following reasons. First, it is the first report on the size tunable preparation of Au- α -Fe₂O₃ hetero-nanoparticles. The cysteine-assisted approach enables direct growth of gold seeds on α -Fe₂O₃ surfaces with solid adherence. It thereby provides a potential universal way for the growth of highly dispersed noble metal nanoparticles on the surfaces of metal oxide nanocrystals. Second, the hetero-structure formation with larger gold nanoparticles is achieved by growing gold nanoparticles of controllable sizes on α -Fe₂O₃ surfaces through a simple photochemical seeding protocol. Importantly, the process does not require any precipitation and high temperature annealing process, while still ensures preferential Au growth on α -Fe₂O₃ surfaces with firm contact. Third, this work provide a decent strategy to prepare hetero-nanostructures composed of size-tunable gold nanoparticles and metal oxide nanocrystals, which are highly dispersible in aqueous and alcohol solvents and capable for various catalytic and photocatalytic applications.

Acknowledgements

The authors acknowledge financial support from NTU Start-Up Grant (SUG), NTU seed funding for Solar Fuels Laboratory, MOE AcRF-Tier1 RG 44/11, and CRP (NRF-CRP5-2009-04) from NRF Singapore.

Notes and references

^a Solar Fuels Laboratory, School of Materials Science and Engineering Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore. E-mail: cxue@ntu.edu.sg, joachimloo@ntu.edu.sg

^b Division of Molecular Biosciences, Imperial College London, South Kensington Campus London SW7 2AZ, U.K.

† Electronic Supplementary Information (ESI) available: Detailed experimental procedure for compared samples and additional characterization data.. See DOI: 10.1039/b000000x/

1 J. Gao, B. Zhang, Y. Gao, Y. Pan, X. Zhang and B. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 1428.

2 E. V. Shevchenko, M. I. Bodnarchuk, M. V. Kovalenko, D. V. Talapin, R. K. Smith, S. Aloni, W. Heiss and A. P. Alivisatos, *Adv. Mater.*, 2008, **20**, 4323.

3 F. Maillard, G. Q. Lu, A. Wieckowski. and U. Stimming, *J. Phys. Chem. B*, 2005, **109**, 16230.

- 4 X. H. Liu, J. Zhang, X. Z. Guo, S. H. Wu and S. R. Wang, *Nanotechnology*, 2010, **21**, 095501.
- 5 J. Bao, W. Chen, T. T. Liu, Y. L. Zhu, P. Y. Jin, L. Y. Wang, J. F. Liu, Y. G. Wei and Y. D. Li, *ACS Nano*, 2007, **1**, 293.
- 6 K. C. F. Leung, S. H. Xuan, X. M. Zhu, D. W. Wang, C. P. Chak, S. F. Lee, W. K. W. Ho and B. C. T. Chung, *Chem. Soc. Rev.*, 2012, **41**, 1911.
- 7 X. L. Zhao, Y. Q. Cai, T. Wang, Y. L. Shi and G. B. Jiang, *Anal. Chem.*, 2008, **80**, 9091.
- 8 C. J. Xu, J. Xie, D. Ho, C. Wang, N. Kohler, E. G. Walsh, J. R. Morgan, Y. E. Chin and S. H. Sun, *Angew. Chem. Int. Ed.*, 2008, **47**, 173.
- 9 C. J. Xu, B. D. Wang and S. H. Sun, *J. Am. Chem. Soc.*, 2009, **131**, 4216.
- 10 H. Y. Xie, R. Zhen, B. Wang, Y. Feng, P. Chen and J. Hao, *J. Phys. Chem. C*, 2010, **114**, 4825.
- 11 Y. Liu, C. J. Jia, J. Yamasaki, O. Terasaki and F. Schüth, *Angew. Chem. Int. Ed.*, 2010, **49**, 5771.
- 12 C. S. Levin, C. Hofmann, T. A. Ali, A. T. Kelly, E. Morosan, P. Nordlander, K. H. Whitmire and N. J. Halas, *ACS Nano*, 2009, **3**, 1379.
- 13 Z. C. Xu, Y. L. Hou and S. H. Sun, *J. Am. Chem. Soc.*, 2007, **129**, 8698.
- 14 Z. Y. Zhong, J. Highfield, M. Lin, J. Teo and Y. F. Han, *Langmuir*, 2008, **24**, 8576.
- 15 J. Zhang, X. H. Liu, L. W. Wang, T. L. Yang, X. Z. Guo, S. H. Wu, S. R. Wang and S. M. Zhang, *J. Phys. Chem. C*, 2011, **115**, 5352.
- 16 S. Pradhan, D. Ghosh and S. W. Chen, *ACS Appl. Mater. Inter.*, 2009, **1**, 2060.
- 17 Z. W. Seh, S. H. Liu, S. Y. Zhang, M. S. Bharathi, H. Ramanarayan, M. Low, K. W. Shah, Y. W. Zhang and M. Y. Han, *Angew. Chem. Int. Ed.*, 2011, **50**, 10140.
- 18 X. N. Fu, J. Liu, H. Yang, J. C. Sun, X. Li, X. K. Zhang and Y. X. Jia, *Mater. Chem. Phys.*, 2011, **130**, 334.
- 19 S. C. Chan and M. A. Barteau, *Langmuir*, 2005, **21**, 5588.
- 20 T. Kiyonaga, Q. L. Jin, H. Kobayashi and H. Tada, *ChemPhysChem*, 2009, **10**, 2935.
- 21 Z. W. Seh, S. H. Liu, S. Y. Zhang, K. W. Shaha and M. Y. Han, *Chem. Comm.*, 2011, **47**, 6689.
- 22 P. Li, Z. Wei, T. Wu, Q. Peng and Y. D. Li, *J. Am. Chem. Soc.*, 2011, **133**, 5660.
- 23 S. Sarkar, A. Makhali, T. Bora, S. Baruah, J. Dutta and S. K. Palz, *Phys. Chem. Chem. Phys.*, 2011, **13**, 12488.
- 24 Y. M. Lee, M. A. Garcia, N. A. F. Huls and S. H. Sun, *Angew. Chem. Int. Ed.*, 2010, **49**, 1271.
- 25 C. George, A. Genovese, F. Qiao, K. Korobchevskaya, A. Comin, A. Falqui, S. Marras, A. Roig, Y. Zhang, R. Krahne and L. Manna, *Nanoscale*, 2011, **3**, 4647.
- 26 A. Comin, K. Korobchevskaya, C. George, A. Diaspro and L. Manna, *Nano Lett.*, 2012, **12**, 921.
- 27 J. Zhang, X. H. Liu, X. Z. Guo, S. H. Wu and S. R. Wang, *Chem. Eur. J.*, 2010, **16**, 8108.
- 28 Z. F. Ma, H. L. Han, S. J. Tu and J. G. Xue, *Colloid. Surf. A*, 2009, **334**, 142.
- 29 Z. Y. Zhong, J. Ho, J. Teo, S. Shen and A. Gedanken, *Chem. Mater.*, 2010, **19**, 4776.
- 30 M. Spuch-Calvar, J. Pérez-Juste and L. M. Liz-Marzán, *J. Colloid Interf. Sci.*, 2007, **310**, 297.
- 31 S. W. Cao and Y. J. Zhu, *Acta Mater.*, 2009, **57**, 2154.
- 32 Y. Wang, Y. H. Shen, A. J. Xie, S. K. Li, X. F. Wang and Y. Cai, *J. Phys. Chem. C*, 2010, **114**, 4297.
- 33 R. C. Jin, *Nanoscale*, 2010, **2**, 343.
- 34 S. Link, A. Beeby, S. FitzGerald, M. A. El-Sayed, T. G. Schaaff and R. L. Whetten, *J. Phys. Chem. B*, 2002, **106**, 3410.
- 35 J. Zheng, C. W. Zhang and R. M. Dickson, *Phys. Rev. Lett.*, 2004, **93**, 077402.
- 36 J. P. Wilcoxon, R. L. Williamson and R. Baughman, *J. Chem. Phys.*, 1993, **98**, 9933.
- 37 M. M. Alvarez, J. T. Khoury, T. G. Schaaff, M. N. Shafgullin, I. Vezmar and R. L. Whetten, *J. Phys. Chem. B*, 1997, **101**, 3706.
- 38 G. C. Lica, B. S. Zelakiewicz, M. Constantinescu and Y. Y. Tong, *J. Phys. Chem. B*, 2004, **108**, 19896.
- 39 C. Xue, G. S. Métraux, J. E. Millstone and Mirkin, C. A. *J. Am. Chem. Soc.*, 2008, **130**, 8337.
- 40 H. Y. Zhu, X. B. Ke, X. Z. Yang, S. Sarina and H. W. Liu, *Angew. Chem. Int. Ed.*, 2010, **49**, 9657.
- 41 H. Y. Zhu, X. Chen, Z. F. Zheng, X. B. Ke, E. Jaatinen, J. C. Zhao, C. Guo, T. F. Xie and D. J. Wang, *Chem. Comm.*, 2009, 7524.
- 42 H. Yu, M. Chen, P. M. Rice, S. X. Wang, R. L. White and S. H. Sun, *Nano Lett.*, 2005, **5**, 379.
- 43 S. Wunder, F. Polzer, Y. Lu, Y. Mei and M. Ballauff, *J. Phys. Chem. C*, 2010, **114**, 8814.
- 44 S. Panigrahi, S. Basu, S. Praharaj, S. Pande, S. Jana, A. Pal, S. K. Ghosh and T. Pal, *J. Phys. Chem. C*, 2007, **111**, 4596.
- 45 M. Schrunner, M. Ballauff, Y. Talmon, Y. Kauffmann, J. Thun, M. Moller and J. Breu, *Science*, 2009, **323**, 617.
- 46 Z. Y. Zhang, C. L. Shao, P. Zou, P. Zhang, M. Y. Zhang, J. B. Mu, Z. C. Guo, X. H. Li, C. H. Wang and Y. C. Liu, *Chem. Comm.*, 2011, **47**, 3906.
- 47 K. Jiang, H. X. Zhang, Y. Y. Yang, R. Mothes, H. Lang and W. B. Cai, *Chem. Comm.*, 2011, **47**, 11924.
- 48 S. Y. Gao, K. Ueno and H. Misawa, *Acc. Chem. Res.*, 2011, **44**, 251.
- 49 J. L. Wu, F. C. Chen, Y. S. Hsiao, F. C. Chien, P. L. Chen, C. H. Kuo, M. H. Huang and C. S. Hsu, *ACS Nano*, 2011, **5**, 959.
- 50 E. Thimsen, F. L. Formal, M. Grätzel and S. C. Warren, *Nano Lett.*, 2011, **11**, 35.
- 51 I. Thomann, B. A. Pinaud, Z. B. Chen, B. M. Clemens, T. F. Jaramillo and M. L. Brongersma, *Nano Lett.*, 2011, **11**, 3440.
- 52 S. W. Cao, Z. Yin, J. Barber, F. Y. C. Boey, S. C. Loo and C. Xue, *ACS Appl. Mater. Interf.*, 2012, **4**, 418.
- 53 H. W. Gao, C. Liu, H. E. Jeong and P. Yang, *ACS Nano*, 2012, **6**, 234.
- 54 M. C. Yin, Z. S. Li, J. H. Kou and Z. G. Zou, *Environ. Sci. Technol.*, 2009, **43**, 8361.