Stabilizing ultrasmall Au clusters for enhanced photoredox catalysis

Bo Weng\textsuperscript{1,2}, Kang-Qiang Lu\textsuperscript{1,2}, Zichao Tang\textsuperscript{3}, Hao Ming Chen\textsuperscript{4} & Yi-Jun Xu\textsuperscript{1,2}

Recently, loading ligand-protected gold (Au) clusters as visible light photosensitizers onto various supports for photoredox catalysis has attracted considerable attention. However, the efficient control of long-term photostability of Au clusters on the metal-support interface remains challenging. Herein, we report a simple and efficient method for enhancing the photostability of glutathione-protected Au clusters (Au GSH clusters) loaded on the surface of SiO\textsubscript{2} sphere by utilizing multifunctional branched poly-ethylenimine (BPEI) as a surface charge modifying, reducing and stabilizing agent. The sequential coating of thickness controlled TiO\textsubscript{2} shells can further significantly improve the photocatalytic efficiency, while such structurally designed core-shell SiO\textsubscript{2}-Au GSH clusters-BPEI@TiO\textsubscript{2} composites maintain high photostability during longtime light illumination conditions. This joint strategy via interfacial modification and composition engineering provides a facile guideline for stabilizing ultrasmall Au clusters and rational design of Au clusters-based composites with improved activity toward targeting applications in photoredox catalysis.

\textsuperscript{1}State Key Laboratory of Photocatalysis on Energy and Environment College of Chemistry, Fuzhou University, 350116 Fuzhou, People’s Republic of China. \textsuperscript{2}College of Chemistry, New Campus, Fuzhou University, 350116 Fuzhou, People’s Republic of China. \textsuperscript{3}State Key Laboratory of for Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, 361005 Xiamen, People’s Republic of China. \textsuperscript{4}Department of Chemistry, National Taiwan University, 106 Taipei, Taiwan. Correspondence and requests for materials should be addressed to H.M.C. (email: haomingchen@ntu.edu.tw) or to Y.-J.X. (email: yjxu@fzu.edu.cn)
Noble metal nanoparticles (MNPs) are uniquely suited for heterogeneous catalysis because of their relatively high specific surface areas and abundant active centers. The size of MNPs has been shown to be one of the most important factors that dictates the performance of a catalyst. However, the catalytically active nano-sized MNPs are at a thermodynamic unstable state, which are inclined to sinter—they form fewer, larger particles—under thermal and/or light irradiation conditions. For instance, it has been demonstrated that nano-sized gold nanoparticles irradiated by a femtosecond laser-induced white-light supercontinuum can initiate a growth of larger nanoparticles. Additionally, the shape of silver nanospheres can be converted into triangular nanoprisms under the illumination of light at wavelengths between 350 and 700 nm. Thus, a variety of solid support strategies have been utilized in practical catalytic systems for stabilization of the small MNPs in heterogeneous catalysis since the size and shape of MNPs provide important control over the catalytic efficiency.

Recently, the ultrasmall MNPs with size regime of 1–3 nm in diameter (often called metal clusters, e.g., gold (Au) clusters) that are composed of a specific number of metal atoms and of ligands have received considerable attention due to their distinctive physicochemical properties, which are different from their plasmonic counterpart owing to the quantum size effect, surface geometric effect (e.g., surface atom arrangement and low-coordinated atoms), and high surface-to-volume ratio. These ultrasmall ligands (typically thiolate)-protected Au clusters exhibit discrete electronic structure, which have been regarded as one of the prototypes of highly tunable molecular-sized materials for catalysis and solar energy conversion. In particular, the thiolate-protected Au clusters, typically glutathione-protected Au clusters (Au GSH clusters), are able to serve as both photosensitizer and catalytic center for multifunctional use in photocatalytic redox systems, such as water splitting, selective organic synthesis, and pollutants degradation. However, such ultrasmall Au GSH clusters suffer from serious instability under light irradiation due to its extremely high surface energy and large surface. The loading of ultrasmall Au GSH clusters onto different supports is often inefficient to avoid coalescence and agglomeration of these Au GSH clusters, which thereby results in either the difficulty of unambiguous photocatalytic mechanism assignment or a loss of photocatalytic activity.

Regarding the Au clusters-based photocatalysts, seminal works have been reported for understanding the observed aggregation of Au GSH clusters at the semiconductor/metal interface. For instance, the irradiation of high-energy electron beams can lead to the aggregation of Au GSH clusters into larger Au NPs (~5 nm diameter) after 2 h continuous visible light illumination (λ > 420 nm) over Au GSH-sensitized Pt/TiO2 photocatalysts. It has also been reported that the photogenerated electrons from Au GSH clusters and/or TiO2 can be captured by Au (I) component on the outer layer of Au GSH clusters (i.e., Au(0)/Au(1)-GSH) to produce Au NPs and the photocatalytic decomposition of GSH ligands tethered on the Au clusters surface can also lead to formation of metallic Au NPs. Recently, a diffusion/aggregation mechanism has been proposed to elucidate the photoinduced coalescence of Au GSH clusters to larger metallic Au NPs at the Au/TiO2 interface under light illumination. Despite various studies on disclosing underlying mechanism of transformation of ultrasmall molecular-like Au GSH clusters to Au NPs, the effective control of Au GSH clusters with long-term stability on the substrates under in situ photo-irradiation conditions still remains a challenge, which becomes the main bottleneck for the development of Au clusters-based catalysts systems for photocatalytic applications.

Herein, we report a simple, combinatorial approach to stabilize ultrasmall Au GSH clusters on the SiO2 sphere support and improve their photocatalytic efficiency by using multifunctional branched poly-ethylenimine (BPEI) for surface modification and coating thickness controlled semiconductor TiO2 shell for interfacial composition engineering. The BPEI is shown to behave as a surface charge modifying, reducing and stabilizing agent for interfacial modification of SiO2–Au GSH clusters composites. Specifically, the size and structure of Au GSH clusters can be well retained over 10 h under continuous visible light irradiation (λ > 420 nm) because of the high reductive ability of BPEI to inhibit the organic ligand oxidation process over Au GSH clusters. In addition, while simultaneously maintaining the photostability of Au GSH clusters, the sequential coating of TiO2 shells for constructing core-shell SiO2–Au GSH clusters–BPEI@TiO2 (SABT) nanostructures has been demonstrated to significantly ameliorate the photoactivity by regulating the photoelectrochemical and adsorption properties of SABT composites synergistically. Therefore, the strategy via interfacial modification and composition manipulation by coating semiconductor shell provides an efficient way for stabilizing Au GSH clusters with improved photocatalytic activity, which is anticipated to enable the broad development of Au clusters-based composite system for photocatalysis applications in solar energy conversion.

Results

Structural characterizations of Au GSH clusters. The successful fabrication of Au GSH clusters has been proved by transmission electron microscopy (TEM) analysis and the characteristic emissive properties of Au GSH clusters. As apparently shown in Supplementary Fig. 1a, TEM image shows the uniform dispersed ultrasmall Au GSH clusters with mean diameter around 1.4 nm (Supplementary Fig. 1b). The Au GSH clusters solution exhibits yellow emissive properties under the blacklight illumination (Supplementary Fig. 1d and e), which is different from that of plasmonic Au counterparts. UV–vis absorption spectrum of Au GSH clusters in Supplementary Fig. 1c suggests that the Au GSH clusters show an absorption onset at ~520 nm with a distinct shoulder around 400 nm, which is attributed to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) transition originated from the ligand-to-metal charge transfer, indicating that Au GSH clusters could be used as visible light photosensitizers. The photoluminescence (PL) excitation spectrum exhibits a maximum at 400 nm, which coincides well with the absorption shoulder observed in the absorption spectrum. The PL emissive spectra of Au GSH clusters with different excitation wavelengths in Supplementary Fig. 1f show a low energy emission band with the peak maximum at 605 nm, which is ascribed to the triplet metal-centered state, and the shape of the PL spectra is independent of the excitation wavelength. The large Stokes shift in the emission, where the absorption band shoulder appears at around 400 nm and the emission maximum is seen at 605 nm, is consistent with the excited state being a ligand-metal charge transfer state.

Enhancing the photostability of Au GSH clusters. The insulative SiO2 spheres with rather low optical absorption

ARTICLE NATURE COMMUNICATIONS | DOI: 10.1038/s41467-018-04020-2 | www.nature.com/naturecommunications

2 NATURE COMMUNICATIONS | (2018) 9:1543 | www.nature.com/naturecommunications
(Supplementary Fig. 3) have been chosen as inert supports to predominantly focus on investigating the photosensitizer role of Au GSH clusters in photocatalytic applications. The schematic synthesis procedure for SiO$_2$-Au GSH clusters composites via interfacial modification process has been displayed in Fig. 1a. The SiO$_2$ spheres become positively charged (Supplementary Fig. 4a) after surface modification with BPEI$^{36}$, a conjugated reducible dendrimer, which leads to a substantial electrostatic attraction with negatively charged Au GSH clusters (Supplementary Fig. 4c) by Coulombic forces, thereby forming SiO$_2$-Au GSH clusters-BPEI composites (SAB) with strong interfacial interaction between Au GSH clusters and SiO$_2$ supports. In contrast, the common protocol used for loading Au GSH clusters onto the supports involves a pH value adjusted process under acidic conditions.

**Fig. 1** Photostability test and characterizations. **a** Schematic illustration of synthesis procedure for SiO$_2$-Au GSH clusters-BPEI composites (SAB) and photostability testing of as-prepared SAB; transmission electron microscopy (TEM) images of SAB **b** before and **e** after visible light irradiation ($\lambda > 420$ nm) for 10 h and SiO$_2$-Au GSH clusters-pH (SAP) **c** before and **f** after visible light irradiation for 10 h; the corresponding models of **d** SAB and **g** SAP after visible light irradiation for 10 h; high-resolution X-ray photoelectron spectroscopy (XPS) spectra of **h** S 2p and **i** Au 4f for SAB before/after visible light irradiation; **j** UV-vis diffuse reflectance spectrum (DRS) spectrum of SAP after 10 h visible light irradiation. Insets in **b** and **e** are the corresponding models of SAB and SAP before visible light irradiation. The histograms in **c** and **f** correspond to the particle size distributions of Au GSH clusters in the SAB and SAP after visible light irradiation for 10 h, respectively. The yellow spheres in **d** represent Au GSH clusters and the purple spheres in **g** represent Au nanoparticles. Scale bar, 5 nm.
conditions. As illustrated in Supplementary Fig. 5, SiO2 dispersion is firstly adjusted to acidity (pH value at about 2) by adding dilute hydrochloric acid solution and then the Au GSH clusters solution is added into the above dispersion for fabricating SiO2:Au GSH clusters-pH composites (SAP). Notably, due to the protonation of carboxylic groups in the glutathione ligands under acidic conditions and the relatively weak electropositivity of SiO2 spheres (Supplementary Fig. 4b), the as-prepared sample of SAP generally exhibits a weak Au–oxide interaction. The difference in the interaction between SiO2 and Au GSH clusters over SAB and SAP samples may lead to the different loading amounts of Au GSH clusters on SiO2 surface, which has been investigated by the inductively coupled plasma optical emission spectroscopy. As revealed in Supplementary Table 1, the addition amount of Au GSH clusters in SAP (0.86%) is higher than that of SAP with 0.28% Au GSH clusters, which could be attributed to the strong coulombic force between positively charged BPEI-SiO2 spheres and the negatively charged Au GSH clusters. The XRD patterns of SAB and SAP samples in Supplementary Fig. 6 suggest the similar crystalline structure of the composites and the diffraction peaks of Au GSH clusters are hardly observed for both of SiO2:Au GSH clusters composites, which may be due to the low loading amount and poor crystallinity of Au GSH clusters.

To initially investigate the photostability of Au GSH clusters, the composites of SAB and SAP have been exposed to continuous visible light irradiation (λ > 420 nm) for 10 h under ambient conditions. TEM analysis suggests that Au GSH clusters maintain almost the same size on the surface of SiO2 spheres for SAB composites before and after photo-irradiation (Fig. 1b–d), while ~1.4 nm Au GSH clusters aggregate to around 6 nm Au nanoparticles (NPs) for SAP samples after photo-irradiation (Fig. 1e–g), indicating that the aggregation of Au GSH clusters in the SAB samples has been effectively inhibited by BPEI interfacial modification, which is significantly different from that of SAP. The UV–vis diffuse reflectance spectrum (DRS) of SAP after light illumination in Fig. 1j shows a pronounced surface plasmon resonance (SPR) peak located at around 540 nm belonging to the metallic Au NPs, which consists with the TEM image of SAP sample after 10 h irradiation of visible light in Supplementary Fig. 7, further suggesting the seriously photoinduced aggregation of Au GSH clusters into Au NPs on the surface of SiO2 spheres over SAP. Additionally, the TEM images in Supplementary Fig. 8 suggest that the size of Au GSH clusters over SAB after 24 h visible light irradiation (λ > 420 nm) is 1.4 nm, which is nearly unchanged as compared to that before light illumination (Fig. 1b), indicating that the interfacial modification of BPEI layer over SAB can provide a long-time protection (24 h) with regard to the stabilization of Au GSH clusters. When the irradiation time over SAB is further prolonged to 36 and 48 h, the size of Au GSH clusters will increase to 2.0 and 2.1 nm, respectively, as illustrated in Supplementary Fig. 9, which indicates the slight aggregation of Au GSH clusters. Such increase in the size of Au GSH clusters may be attributed to the partial depleetion of BPEI, since the BPEI layer that serves as a reducing agent would undergo oxidation and/or decomposition in the way to stabilize the Au GSH clusters. To further investigate the role of BPEI in inhibiting the growth of Au GSH clusters, the SAP sample is modified by BPEI (BPEI-SAP) and the obtained BPEI-SAP composite is irradiated under visible light (λ > 420 nm) for 10 h. The HRTEM image of BPEI-SAP after light illumination in Supplementary Fig. 10a suggests that, as compared with SAP samples (Fig. 1e–g), the serious aggregation of Au GSH clusters can be prevented to some extent and the size of Au GSH clusters is calculated to be 2.0 nm (Supplementary Fig. 10b).

To ensure whether the stability enhancement of Au GSH clusters due to the modification of BPEI is universal, we have performed a series of control experiments including the effects of various metal oxide supports and the structure of Au GSH clusters. The surfaces of different metal oxide supports, including rutile TiO2, ZnO, and ZrO2, have been positively charged by the BPEI modification (Supplementary Fig. 11), which can subsequently interact with the negatively charged Au GSH clusters (Supplementary Fig. 4c) via an electrostatic self-assembly method to produce metal oxide-Au GSH clusters-BPEI composites (MABs) and the photostability of MABs has been investigated under the same conditions as that for SAB and SAP. As illustrated in Supplementary Fig. 12, the mean diameter of Au GSH clusters on the surfaces of various metal oxide supports after continuous visible light (λ > 420 nm) for 10 h is determined to be 1.4 nm, indicating the critical role of BPEI in inhibiting the aggregation of Au GSH clusters and excluding the supports effect on the photostability enhancement of Au GSH clusters. Additionally, Supplementary Note 1 elucidates that, even though the Au GSH clusters suffer from serious aggregation on the surface of anatase TiO2 due to the presence of abundance surface hydroxyl group, the presence of BPEI layer can protect ultrasmall Au GSH clusters from being fusion to some extent under visible light illumination, suggesting the universality of the interfacial modification strategy on stabilizing Au GSH clusters. To further confirm our inference and achieve a generally valid conclusion, the Au25-glutathione clusters (Au25(SG)18), which are well known as the most stable one among the thiolated clusters of this class, have been decorated on the surface of BPEI modified SiO2 spheres to produce SiO2:Au25(SG)18 clusters-BPEI composites (SASB). The photostability test in Supplementary Fig. 13 suggests that the size of Au25(SG)18 clusters can be well maintained, thereby demonstrating that the introduction of BPEI layer for interfacial modification over SASB is an effective strategy to impede the photoinduced coalescence of Au25(SG)18 clusters to larger metallic Au NPs upon visible light illumination (λ > 420 nm). To understand the role of BPEI in improving the stability of Au GSH clusters in SAB, X-ray photoelectron spectroscopy (XPS) analysis has been conducted. Survey XPS spectra in Supplementary Fig. 14d evidence the presence of Au, S, N, C, O and Si elements in the SAB composites before/after visible light irradiation. As mirrored in Fig. 1i, the two doublet 4f peaks in the high-resolution spectrum of Au 4f suggest that the there are two different elemental chemical states of Au species. The Au 4f7/2 and Au 4f5/2 peaks with binding energies of 86.9 and 83.1 eV are ascribed to metallic Au (Au0), and the other doublet at 87.75 and 84.05 eV for Au 4f7/2 and Au 4f5/2 are assigned to Au+ ion. The Au0 content determined by XPS is found to constitute ~90% of all Au atoms. The samples of SAB before/after photo-irradiation exhibit similar Au 4f spectra, demonstrating the well reserved structural properties of Au GSH clusters during the visible light irradiation (λ > 420 nm). Additionally, previous work has verified that the Au GSH clusters aggregation procedure is accompanied with a ligand oxidation process of Au GSH clusters, which results in a new S 2p peak matching the binding energy of R–SO2 species (169.2 eV)45. As for the SAB composites after photo-irradiation of 10 h, only one S 2p3/2 peak located at 161.5 eV (Fig. 1h), corresponding to the ligand features (RS–Au) in various monothiolate Au GSH clusters, is observed, which is similar with that of SAB sample before light irradiation, demonstrating that the organic ligand oxidation process over the Au GSH clusters in SAB has been efficiently inhibited during visible light irradiation. The enhanced photostability of Au GSH clusters in the SAB composites can be attributed to the introduction of BPEI with high reductive ability, which could serve as effective reductive agents to hamper the ligand oxidation process over Au GSH clusters during photo-irradiation process. As illustrated in Supplementary Fig. 14a–c, the slight
The photoactivity can be ignored. After coupling with Au GSH clusters, the incorporation of Au GSH clusters, which can generate the occupied molecular orbital (HOMO) to the lowest unoccupied charge carriers. Notably, it has been demonstrated that the CB of SiO2 spheres exhibit negligible photoactivity toward RhB irradiation (λ > 420 nm), indicating the low photosensitization efficiency of Au GSH clusters. Accordingly, based on the above control experiments, we can deduce that it is the high reductive ability and branched structure of BPEI that play a critical role in hampering the ligand oxidation process over Au GSH clusters, thereby stabilizing Au GSH clusters against aggregation under continuous light illumination condition.

The photocatalytic performances of bare SiO2 spheres and SiO2-Au GSH clusters-BPEI (SAB) composites have been tested by degradation of organic dye rhodamine B (RhB), a typical nonselective photocatalytic processes, under visible light irradiation (λ > 420 nm). As shown in Supplementary Fig. 17, SiO2 spheres exhibit negligible photoactivity toward RhB degradation during 10 h visible light irradiation, which suggests that SiO2 spheres are not photocatalytically active under visible light irradiation and the dye photosensitization effect of RhB on the photoactivity can be ignored. After coupling with Au GSH clusters as visible light photosensitizers, the SAB sample shows obvious activity toward photocatalytic RhB degradation (Supplementary Fig. 17). The observed photoactivity can be attributed to the incorporation of Au GSH clusters, which can generate electron–hole pairs by electron transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) under visible light irradiation, thereby driving RhB degradation. However, it should be noted that only 38% of RhB has been degraded after 10 h irradiation of visible light over SAB, indicating the low photosensitization efficiency of Au GSH clusters.

Such observed low photoactivity could be attributed to large band gap of SiO2 support, by which the photogenerated electrons in the LUMO of Au GSH clusters cannot transfer to the conduction band (CB) of SiO2 efficiently, thereby leading to simultaneously serious recombination of charge carriers. Notably, it has been demonstrated that the CB edge potential of metal oxides (e.g., ZnO and rutile TiO2) is more positive than the LUMO potential of Au GSH clusters, which enables the transformation of photoexcited electrons from Au GSH clusters to the metal oxide supports. The photoactivities of BPEI modified metal oxides-Au GSH clusters composites (denoted as MAB) have been evaluated toward RhB degradation under visible light irradiation (λ > 420 nm). As shown in Supplementary Fig. 18, the samples of MAB exhibit moderate photocatalytic activity and stability of SABT composites. The photocatalytic performances of SABT composites have been characterized by XRD and DRS analysis, respectively. As reflected in Supplementary Fig. 20, all of the samples possess analogous XRD patterns with a broad peak located at ca. 23°, corresponding to amorphous silica and the intensities of SiO2 diffraction peaks become weak with increasing the thickness of TiO2 shells. However, no typical diffraction peaks of TiO2 have been observed in XRD spectra because TiO2 is amorphous by TIP hydrolysis. Due to the relatively low content of Ti and O elements over SABT-0.05 composites. Additionally, the elemental mapping analysis identifies the spatial distribution of these elements in SABT-0.05. As displayed in Fig. 2b, c, d, e, f, the distribution ranges of Ti and O elements are slightly larger than that of Au, which is itself slightly larger than that of Si. These corroborate the intelligently designed core-shell SABT structure, among which the thin TiO2 layer is located at the most surface, while the SiO2 spheres serve as the core and the Au GSH clusters are located between the SiO2 core and TiO2 shell.

The phase composition and optical properties of the SABT composites have been characterized by XRD and DRS analysis, respectively. As reflected in Supplementary Fig. 20, all of the samples possess analogous XRD patterns with a broad peak located at ca. 23°, corresponding to amorphous silica and the intensities of SiO2 diffraction peaks become weak with increasing the thickness of TiO2 shells. However, no typical diffraction peaks of TiO2 have been observed in XRD spectra because TiO2 is amorphous by TIP hydrolysis. Due to the relatively low content and weak diffraction intensity of Au GSH clusters, the diffraction peaks of Au GSH clusters in the SABT composites have been illustrated in Fig. 2a. In brief, the SAB composites are firstly dispersed in ethanol, followed by adding hexadecylamine (HDA) surfactants and ammonia under vigorously stirring at room temperature. The HDA surfactants could segregate the surface of SAB. Then, different amounts of titanium isopropoxide (TIP) have been introduced into the dispersion under stirring. During this process, TIP hydrolysis products (i.e., TiO2) participate in hydrogen-bonding interactions with the amino groups of HDA molecules to form inorganic–organic composites that coat the SAB spheres to produce SABT. Scanning electron microscopy (SEM) images of SABT composites in Supplementary Fig. 19 show the uniform spherical morphology of these SABT composites. TEM analysis in Fig. 2 shows that the core-shell structures of SABT composites are well defined, and the thickness of TiO2 shell can be well-tuned from few to dozens nanometer by adjusting the addition amounts of TIP from 0.05 to 0.2 mL (marked as SABT-x, where x represents the volume of added TIP). In particular, the Au GSH clusters embedded into TiO2 shell are distinguishable, especially for the samples of SABT-0.05 (Fig. 2c) and SABT-0.1 (Fig. 2d) with thin TiO2 shell. Noteworthily, the Au GSH clusters in core-shell SABT composites maintain their original sizes, suggesting the stability of Au GSH clusters during such a mild TiO2 coating process at room temperature. The energy-dispersive X-ray (EDX) spectrum in Fig. 2h evidences the presence of Au, O, Si, and Ti elements over SABT-0.05 composites. Additionally, the elemental mapping analysis identifies the spatial distribution of these elements in SABT-0.05. As displayed in Fig. 2b, c, d, e, f, the distribution ranges of Ti and O elements are slightly larger than that of Au, which is itself slightly larger than that of Si. These corroborate the intelligently designed core-shell SABT structure, among which the thin TiO2 layer is located at the most surface, while the SiO2 spheres serve as the core and the Au GSH clusters are located between the SiO2 core and TiO2 shell.

Photocatalytic activity and stability of SABT composites. The photocatalytic performances of SABT composites have been
evaluated toward rhodamine B (RhB) photodegradation under visible light illumination (λ > 420 nm). As delineated in Fig. 3a, the photoactivity over SAB sample can be significantly enhanced by coating TiO₂ shell and the dependence of RhB degradation efficiency on the thickness of the TiO₂ shell shows a clear volcano behavior. The photocatalytic degradation of RhB firstly increases with increasing thickness of TiO₂ layer, and the maximum RhB degradation efficiency has been achieved over SABT-0.15 and then decreases. Specifically, 99.1% conversion of RhB is achieved over SABT-0.15 after visible light irradiation for 0.5 h, and the photocatalytic efficiency of SABT-0.15 is about 19 times higher than that of SAB with only 4.9% conversion of RhB under identical reaction conditions. Furthermore, the sample of TiO₂-Au GSH cluster-BPEI (TAB) exhibits worse catalytic activity than the SABT composites, which indicates that the intelligently designed core-shell structure of SABT is favorable for enhancing the photocatalytic performance of Au GSH clusters-semiconductor composites. The pseudo-first order kinetic of the degradation of RhB based on the above data is shown in Supplementary Table 2. It is clear that all of the SABT samples show higher reaction rate than the SAB and TAB samples, among which SABT-0.15 exhibits the highest reaction rate of 0.119 min⁻¹ among these SABT composites. Additionally, the photocatalytic degradation of RhB over SiO₂-Au GSH clusters-pH@TiO₂ composites (SAPT) with different TiO₂ shell thickness has also been investigated. Due to the addition amount of Au GSH clusters in SAP is different from that of SAB (Supplementary Table 1), the photocatalytic activities of RhB degradation over various SAPT composites with different TiO₂ shell thickness have been normalized with respect to the loading amount of Au GSH clusters in SAB for a fair comparison. As displayed in Supplementary Fig. 22, the coating of TiO₂ shell greatly improves the photocatalytic efficiency of SAP sample and the SAPT-0.15 composites exhibit the best photoactivity among these samples. However, the RhB degradation efficiency over SAPT-0.15 composites is worse than that of SABT-0.15 (Fig. 3a) under identical reaction conditions, which suggests that the presence of BPEI layer is beneficial for the photoactivity enhancement since the photostability of Au GSH clusters in the SABT-0.15 is significantly ameliorated.

To investigate the effect of surface coating of TiO₂ shell on the photocatalytic performance and exclude the possible dye photosensitization effect of RhB on the activity46, the visible light photoactivities of SiO₂ spheres, TAB, SAB, and SAPT composites toward photocatalytic reduction of p-methoxy nitrobenzene to p-methoxy aniline have been evaluated, which is a typical six-electron reduction reaction (Supplementary Fig. 23).24,27,47,57 As presented in Fig. 3b, the higher photocatalytic activity of SABT composites than that of SiO₂ spheres and SAB sample verifies the positive role of TiO₂ shell in improving the photoactivity of SiO₂-
Fig. 3 Photocatalytic activity and the underlying mechanism. Photocatalytic degradation of a RhB over blank SiO2 spheres, TiO2, SAB, TAB, and SABT composites with different TiO2 shell thickness under visible light irradiation (λ > 420 nm) for 0.5 h; b photocatalytic reduction of p-methoxy nitrobenzene to p-methoxy aniline over blank SiO2 spheres, TiO2, SAB, TAB, and SABT composites with different TiO2 shell thickness under visible light irradiation for 5 h; c recycling photocatalytic degradation of RhB over optimal SABT-0.15 composite under visible light irradiation (λ > 420 nm); d transient photocurrent densities of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness under visible light irradiation (λ > 420 nm); e scheme illustrating the photogenerated electron transport pathways between Au GSH clusters and TiO2 shell (the blue arrow represents the photoexcitation process of electron-hole pairs; the orange dash line means the recombination of electron-hole pairs; e and h in the blue cycles correspond to the photogenerated electron and hole, respectively); f cyclic voltammograms of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness; g bar plots showing the remaining RhB in reaction solutions after being kept in dark for 3 h to achieve the adsorption-desorption equilibrium over SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness; h nitrogen adsorption-desorption isotherms of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness; i surface area of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness. Note that the error bars represent the photoactivity s.d. values calculated from triplicate experiments.

Au GSH clusters composites. And the SABT-0.15 shows the best photocatalytic degradation of HvB over blank SiO2 spheres, TiO2, SAB, TAB, and SABT composites with different TiO2 shell thickness under visible light irradiation (λ > 420 nm) for 0.5 h. Photocatalytic reduction of p-methoxy nitrobenzene to p-methoxy aniline over blank SiO2 spheres, TiO2, SAB, TAB, and SABT composites with different TiO2 shell thickness under visible light irradiation for 5 h. Recycle photocatalytic degradation of RhB over optimal SABT-0.15 composite under visible light irradiation (λ > 420 nm). Transient photocurrent densities of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness under visible light irradiation (λ > 420 nm). Schematic diagram illustrating the photogenerated electron transport pathways between Au GSH clusters and TiO2 shell (the blue arrow represents the photoexcitation process of electron-hole pairs; the orange dash line means the recombination of electron-hole pairs; e and h in the blue cycles correspond to the photogenerated electron and hole, respectively). Cyclic voltammograms of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness. Bar plots showing the remaining RhB in reaction solutions after being kept in dark for 3 h to achieve the adsorption-desorption equilibrium over SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness. Nitrogen adsorption-desorption isotherms of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness. Surface area of SiO2 spheres, SAB and SABT composites with different TiO2 shell thickness. The error bars represent the photoactivity s.d. values calculated from triplicate experiments.

One even though the crystallization of TiO2 can be improved by calcination and hydrothermal treatment, the Au GSH clusters in SABT-0.15 suffer from serious instability under high temperature and aggregate into metallic Au nanoparticles with large size, as displayed in Supplementary Fig. 24, 25, thereby deteriorating the photocatalytic performance of SABT-0.15 sample toward various photocatalytic reactions under visible light illumination (λ > 420 nm) (Supplementary Fig. 26).

The photostability of the optimal SABT-0.15 has been evaluated via recycling experiments, as shown in Fig. 3c. The apparent activity loss has not been observed for Hvb photo-degradation during ten successive recycle runs, indicating that SABT-0.15 is able to serve as a stable visible light photocatalyst. Unfortunately, the size information of Au GSH clusters in SABT-0.15 after visible light illumination cannot be directly obtained.
due to the thick TiO$_2$ shell. Alternatively, the SABT-0.05 composite with a thin layer of TiO$_2$ has been selected as a representative sample for observing the size of Au GSH clusters after photocatalytic reactions. The TEM image (Supplementary Fig. 27) and EDX spectrum (Supplementary Fig. 28) of SABT-0.05 irradiated in RhB solution under visible light for 4 h suggest that the Au GSH clusters maintain their particle size, verifying the excellent photostability of Au GSH clusters in SABT-0.05.

**Mechanism of the photoactivity improvement.** To understand the origin of photoactivity enhancement of SABT compared to SAB sample and the effects of TiO$_2$ shell thickness on photoactivities of SABT composites, we have investigated the structure-photocatalytic activity relationship in terms of joint analysis on the charge separation efficiency and surface area. The photoelectrochemical (PEC) analysis has been performed to investigate the charge carrier transfer process over SiO$_2$ spheres, SAB and SABT with different TiO$_2$ shell thickness. Figure 3d shows the periodic on/off transient photocurrent response of these samples under the intermittent visible light photo-irradiation. Bare SiO$_2$ spheres show no photocurrent response under visible light irradiation ($\lambda>420$ nm), which is consistent with its large band gap$^{47}$. After coupling with Au GSH Clusters, the obvious photocurrent density over SAB verifies the substantial photosensitization effect of Au GSH clusters on the PEC performance of SAB in the range of visible light$^{15,63,64}$. With the coating of TiO$_2$ thin layer, the SABT-0.05 sample exhibits higher photocurrent density than SAB, which suggests that the separation of photoinduced charge carriers over SABT-0.05 has been efficiently facilitated as compared to that of SAB. However, a thicker TiO$_2$ shell leads to the decreased photocurrent densities of SABT composites, which may be attributed to the fact that the thicker layer of TiO$_2$ will block the transport of photogenerated electrons from Au GSH clusters to the back contact, thus reducing the overall photocurrent response. The cyclic voltammograms (CV) curves of bare SiO$_2$ spheres, SAB and SABT composites in Fig. 3f reveal that the introduction of thin TiO$_2$ layer can enhance the current densities of SABT composites as compared to that of SAB, while the thick TiO$_2$ layer results in decreased current densities, which is consistent with the transient photocurrent results in Fig. 3d. Electrochemical impedance spectroscopy (EIS), as a method to monitor charge transfer process on the electrode and at the contact interface between electrode and electrolyte$^{64}$, has further confirmed that the SABT with thin shell of TiO$_2$ layer improves the charge carrier migration of SABT composites efficiently as compared to that with thick one (Supplementary Fig. 29). The above PEC experiments together confirm that the coating of thin TiO$_2$ layer is beneficial for efficiently separating and transferring the photogenerated electrons from Au GSH clusters (Fig. 3e), hampering the recombination of charge carriers, and thereby resulting in the higher photocatalytic efficiency of SABT composites than that of SiO$_2$ spheres and SAB under visible light illumination ($\lambda>420$ nm).

The nitrogen (N$_2$) adsorption–desorption isotherms have been performed to investigate the surface area of blank SiO$_2$ spheres, SAB and SABT composites. As illustrated in Fig. 3h, i and Supplementary Table 3, the loading of Au GSH clusters leads to little variation of surface area of bare SiO$_2$ spheres, while the surface area of the SABT is gradually improved by increasing the thickness of TiO$_2$ shell. Adsorption experiments toward RhB (Fig. 3g) and p-methoxy nitrobenzene (Supplementary Fig. 30) in the dark suggest that the SABT composites exhibit improved adsorption capacity as compared to SiO$_2$ spheres and SAB sample. In addition, with the increased thickness of TiO$_2$ shell, the adsorption capacity of SABT composites increases, which is consistent with the surface area of SABT composites (Fig. 3i). The above characterizations suggest that the primary role of coating TiO$_2$ semiconductor layer onto SAB for ameliorating the photocatalytic efficiency of SABT composites is two-fold. One is to improve the separation and migration efficiency of photo-induced charge carriers from excited Au GSH clusters to the reactants. The other is to enhance the adsorption capacity of the catalysts toward the reactants. By adjusting the thickness of TiO$_2$ shells, the photoactivity of SABT can be tuned due to cooperative adsorption and PEC properties. Therefore, the optimal SABT-0.15 composites exhibit the highest activity toward photocatalytic degradation of RhB among these SABT samples.

Control experiments using different radical scavengers help us to further understand the underlying reaction mechanism of the degradation of RhB over SABT-0.15. As shown in Supplementary Fig. 31, the addition of benzoquinone (BQ) scavenger for superoxide radicals$^{55}$ almost terminates the photocatalytic reaction of RhB degradation. A similar and obvious phenomenon for photocatalytic reaction is also observed, when tert-butyl alcohol (TBA) scavenger for hydroxyl radicals$^{66}$, ammonium formate (AF) scavenger for holes$^{67}$, and potassium persulfate (K$_2$S$_2$O$_8$) scavenger for electrons$^{68}$ are added, indicating that the hydroxyl radicals, holes, electrons, and superoxide radicals all show a significant impact on the degradation of RhB. Nevertheless, the inhibition degree of photocatalytic induced by the addition of TBA, AF, and K$_2$S$_2$O$_8$ is smaller than the case of BQ, suggesting that the superoxide radicals play a more important role than other reactive species toward photodegradation of RhB over SABT-0.15. Taking K$_2$S$_2$O$_8$ as scavenger for photogenerated electrons$^{55}$, the control experiments for photoreduction of p-methoxy nitrobenzene under visible light illumination ($\lambda>420$ nm) have been performed (Supplementary Fig. 32). The addition of K$_2$S$_2$O$_8$ greatly inhibits the reduction of p-methoxy nitrobenzene, which confirms that the reduction reactions are driven by the photoexcited electrons. Supplementary Fig. 33 shows the electron spin resonance (ESR) spectra of superoxide radicals detected over the samples, which suggests that the coating of thin TiO$_2$ shells contributes to improving the amounts of such reactive oxidative species (ROSs) generated over SABT. This is consistent with the more efficient separation and transfer of charge carriers over SABT than that over SiO$_2$ spheres and SAB. Although the onslaught of ROSs on organic ligands of Au GSH clusters can lead to the instability of Au GSH clusters and their aggregation into large Au nanoparticles$^{15}$, the following factors are considered to be the decisive role for achieving high photostability of Au GSH clusters in SABT composites. On one hand, as discussed above, BPEI has high reductive capability$^{44,45}$, which can primitively protect the organic ligands of Au GSH clusters from being oxidized during the photo-irradiation process. On the other hand, the intelligent design of core-shell SABT composites by coating TiO$_2$ shell can enhance the adsorption capacity of catalysts toward reactants, which would consume the ROSs timely and effectively reduce the possibility of the reactions between ROSs with the organic ligands of Au GSH clusters, thus leading to the improvement of the photostability of Au GSH clusters in SABT composites.

**Discussion**

Although prior literatures have already elucidated the coalescence and agglomeration mechanism of ultrasmall Au GSH clusters, it still remains a challenging task to achieve highly stable Au GSH clusters on the substrates under in situ photo-irradiation conditions, which significantly impedes the practical implementations of Au clusters-based catalysts systems. In this work, the utilization of multifunctional BPEI as a surface charge modifying, reducing
and stabilizing agent for interfacial modification of SiO2–Au GSH clusters composites has demonstrated to be an efficient and universal strategy for protecting the Au GSH clusters from being fusion during longtime light illumination. Such photostability enhancement is ascribed to the high reductive ability of BPEI, by which the organic ligand oxidation process over Au GSH clusters can be inhibited, and this in turn results in the improvement of durability. Additionally, while simultaneously maintaining the photostability of Au GSH clusters, the sequential coating of nanoparticles (ZnO and ZrO2), metal oxide nanoparticles (ZnO and ZrO2)-Au nanospheres were separated by centrifugation, washed with ethanol and DI water repeatedly, and centri-

**Methods**

**Materials.** Gold(III) chloride trihydrate (HaAuCl3·3H2O), acetonitrile (C3H5N, HPLC grade), sodium hydroxide (NaOH), hydrochloric acid (HCl), tetraethyl orthosilicate (C4H8O4Si, TEOS), isopropanol (C3H8O), ethanol (C2H5OH), ammonium (NH4OH), p-methyl nitrobenzene (C6H4NO2), rhodamine B (C23H26ClN2O3, Rhb); ammonium formate (CH2NO2), potassium persulphate (K2S2O8), tert-butyl alcohol (C4H9OH), P-benzozocinone (C12H9O2) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1-g-thionated lithium (C7H4LiNO2), hexaammonium (C6H24N6H2), Hbranched poly-ethyleneimine (Mn~35,000, BPEI) and titanium isopropoxide (C4H9O3Ti, TIP), 5,5-dimethyl-1-pyrroline-N-oxide (C5H6NO, DMPO) were obtained from Sigma-Aldrich. All materials were analytical grade and used as received without further purification. Deionized (DI) water used in the synthesis was from local sources.

**Catalyst preparation.** Synthesis of Au GSH clusters: Au GSH clusters were fab-

ricated by procedures reported previously with modification31. Typically, 0.24 g of gold(III) chloride trihydrate were first dissolved in 200 mL DI water. Then, 100 mL DI water contained 0.276 g of Na2S2O4 were added into above solution under stirring. A colorless solution was obtained after 2 h stirring and the mixture was heated at 333 K for 24 h. After removing the heat source, the Au GSH clusters were recrystallized in acetonitrile and then washed with water and acetonitrile (1: 3 in volume) for three times by centrifuging at 10,500g for 5 min. A desired concentration of Au GSH clusters solution was obtained by redispersing the purified Au GSH clusters in DI water with assistance of few drops of 0.5 M NaOH and stored at 277 K for further use.

Synthesis of SiO2 spheres: In a typical reaction, a mixture containing 13 ml of ammonium (25~28%), 63.3 mL of isopropanol and 23.5 mL of DI water was heated to 308 K in an oil bath. A volume of 0.6 mL of TEOS (99%) was introduced into this solution dropwise and the mixture was kept at 308 K for 30 min. Then, 5 mL of TEOS were added dropwise into the reaction system. After 2 h reaction, the SiO2 spheres were separated by centrifugation, washed with ethanol and DI water repeatedly, and finally dried in air.

Synthesis of BPEI-modified SiO2 spheres: A volume of 4 mL BPEI solution (86 mg mL−1) was added into 200 mL ethanol with SiO2 spheres concentration of 2 mg mL−1. The mixtures were refluxed at 333 K in an oil bath for 4 h. The BPEI-modified SiO2 spheres were washed with ethanol and DI water repeatedly, and finally dried in air.

Synthesis of SiO2–Au GSH clusters-BPEI composite (SAB): 0.1 g positively charged BPEI-modified SiO2 spheres were dispersed in 30 mL DI water by ultrasonication. Then, 2 mL of NH4OH and 0.2 mL of Na2S2O4 were added dropwise into this dispersion. After stirring for 1 h, SAB were isolated by centrifugation, washed with ethanol and DI water repeatedly, and finally dried in air.

Synthesis of core-shell SiO2–Au GSH clusters-BPEI@TiO2 nanostructures: 0.08 g of as-prepared SAB composite and 0.08 g of HDA (90%) were ultrasonically dispersed in 9.74 mL of ethanol. Then, 0.2 mL of ammonium formate was introduced into above solution. After reaction for 10 min, the core-shell SiO2–Au GSH clusters-BPEI@TiO2 composites were collected by centrifugation, washed with ethanol and DI water repeatedly, and centrifugally dried in air.

**Characterization.** Zeta sizer 3000HS A was employed to determine the Zeta potentials (ξ) values of the samples at room temperature. The optical properties of the samples were measured by UV–vis spectrophotometer (Perkin Elmer Lambda 950, UV–Vis-NIR). The XRD patterns of different samples were collected by a Bruker Advance X-ray diffractometer (40 kV, 40 mA) with Cu Kα radiation. The SEM images were taken on FEI Nova Nano-SEM 230 spectrophotometer. TEM, EDX, and elemental mapping results were obtained by a JEOL model JEM 2010 EX instrument. PL spectra of the samples were recorded on an Edinburgh FL/FS920 spectrophotometer. XPS measurement was performed on a Thermo Scientific ESCA Lab 250 spectrometer with monochromatic Al Kα X-ray source. The CLs peak at 284.6 eV was used to calibrate binding energies. The loading amounts of Au GSH clusters in the SAP and SAB samples were quantified by an inductively coupled plasma optical emission spectroscopy instrument (ICP- OES, PerkinElmer Optima 2000DV). The surface areas of various samples were obtained by the Micrometrics ASAP 3020 equipment. Mass spectra were recorded on an Agilent Technologies ESI-TOF-MS. EIS signal was recorded using a Bruker EPR A300 spectrometer.

**Photoelectrochemical measurements.** Degradation of organic dye: Ten milligrams of catalyst were suspended in 40 mL of 10 mg L−1 RhB solution. The mixture was stirred in dark for 3 h and then irradiated with a 300 W Xe arc lamp (λ > 420 nm) under ambient conditions. After photocatalytic reaction, 4 mL of sample solution were taken from reaction system and analyzed on a Varian UV–vis spectrophotometer (Cary 50, Varian Co.).

Reduction of aromatic nitro compound: Fifty milligrams of photocatalyst and 100 mg ammonium formate were dispersed in 30 mL of 5 mg L−1 p-methoxy nitrobenzene solution. After stirring in dark for 3 h, the mixture was irradiated by visible light (λ > 420 nm) using a 300 W Xe arc lamp. After photocatalytic reaction, 4 mL of sample solution were taken from reaction system and analyzed on a Varian UV–vis spectrophotometer (Cary 50, Varian Co.).

**Data availability.** The data that support the findings of this study are available from the figshare repository with DOI number 10.6084/m9.figshare.5938669.

Received: 25 October 2017 Accepted: 23 March 2018 Published online: 18 April 2018

**References**

1. Bell, A. T. The impact of nanoscience on heterogeneous catalysis. Science 299, 1688–1691 (2003).

2. Chen, T. & Rodionov, V. O. Controllable catalysis with nanoparticles: bimetallic alloy surfaces and synthetic adsorbates. ACS Catal. 6, 4025–4033 (2016).

3. Van Santen, R. A. Complementary structure sensitive and intensive catalytic relationships. Acc. Chem. Res. 42, 57–66 (2009).

4. Roucoux, A., Schulz, J. & Patin, H. Reduced transition metal colloids: a novel family of reusable catalysts? Chem. Rev. 102, 3757–3778 (2002).

5. Quan, B. et al. Single-atom catalysis of CO oxidation using Pt/Fe/Ox. Nat. Chem. 3, 634–641 (2011).

6. Corma, A. & Garcia, H. Supported gold nanoparticles as catalysts for organic reactions. Chem. Soc. Rev. 37, 2096–2126 (2008).

7. White, R. J., Luque, R., Budarin, V. L., Clark, J. H. & Macquarrie, D. J. Supported metal nanoparticles on porous materials. Methods and applications. Chem. Soc. Rev. 38, 481–494 (2009).

8. Cavicchi, R. E., Meier, D. C., Presser, C., Prabhoo, V. M. & Guha, S. Single laser pulse effects on suspended-Au nanoparticle size distributions and morphology. J. Phys. Chem. C 117, 10866–10875 (2013).

9. Besner, S., Kabashin, A. V., Winnik, F. M. & Meunier, M. Synthesis of size-tunable polymer protected gold nanoparticles by femtosecond laser-based ablation and seed growth. J. Phys. Chem. C 113, 9526–9531 (2009).

10. Jin, R. et al. Photoinduced conversion of silver nanostructures to nanoparticles. Science 294, 1901–1903 (2001).
21. Han, N. S. et al. Unexpected size effect observed in ZnO-Au composite nanoclusters: stable sites and optical properties. *Nanoscale* 7, 1549–1565 (2015).

22. Stamplecoskie, K. G., Chen, Y.-S. & Kamat, P. V. Excited-state behavior of metal-cluster-decorated TiO2 nanotube arrays: a composite semiconductor interface: implications for the complexity of gold clusters-based photocatalysis. *Sci. Rep.* 6, 22742 (2016).

23. Xiao, F.-X. et al. Metal-cluster-decorated TiO2 nanotube arrays: a composite semiconductor interface for enhanced visible light photocatalytic activity. *J. Phys. Chem. C* 118, 1370–1376 (2014).

24. Xiao, F.-X. et al. Metal-cluster-decorated TiO2 nanotube arrays: a composite semiconductor interface toward versatile photocatalytic and photoelectrochemical applications. *Small* 11, 554–567 (2015).

25. Negishi, Y. et al. Enhanced photocatalytic water splitting by BaLa2TiO3 loaded with ~1 nm gold nanoclusters using glutathione-protected Au125 clusters. *Nano Lett.* 5, 7188 (2013).

26. Stemplecoskie, K. G., Chen, Y.-S. & Kamat, P. V. Size-dependent state behavior of glutathione-protected gold clusters and their light-harvesting capacity. *J. Am. Chem. Soc.* 116, 1109–11099 (2014).

27. Xiao, F.-X. et al. Light-induced in situ transformation of metal clusters to metal nanocrystals for photocatalysis. *ACS Appl. Mater. Interfaces* 7, 28105–28109 (2015).

28. Chen, Y.-S. & Kamat, P. V. Glutathione-capped gold nanoclusters as photosensitizers. Visible light-induced hydrogen generation in neutral water. *J. Am. Chem. Soc.* 137, 10735–10744 (2015).

29. Kogo, A., Sakai, N. & Tatsuma, T. Photocatalysis of Au125-modified TiO2 under visible and near infrared light. *Electrochem. Commun.* 12, 996–999 (2010).

30. Ramasyamu, P. et al. Size tuning of Au nanospheres formed by electron beam irradiation of Au125 quantum clusters anchored within and outside of dopedidipentane tubes. *J. Mater. Chem.* 19, 8456–8462 (2009).

31. Luo, Z. et al. From aggregation-induced emission of Au(I)-thiolate complexes to ultrabright Au(0)/Au(I)-thiol core–shell nanoclusters. *J. Am. Chem. Soc.* 134, 16662–16670 (2012).

32. Cha, S.-H., Kim, J.-U., Kim, K.-H. & Lee, J.-C. Preparation and photoluminescence properties of gold(I)-alkanethiolate complexes having highly ordered supramolecular structures. *Chem. Mater.* 19, 6297–6303 (2007).

33. Wu, Z. & Jin, R. On the ligand’s role in the fluorescence of gold nanoclusters. *Nano Lett.* 10, 2568–2573 (2010).

34. Shibu, E. S., Muhammed, M. A. H., Tsukuda, T. & Pradeep, T. Ligand exchange of Au125 nanocluster leading to functionalized gold clusters: spectroscopy, kinetics, and luminescence. *J. Phys. Chem. C* 112, 12168–12176 (2008).

35. Negishi, Y., Nobusada, K. & Tsukuda, T. Glutathione-protected gold clusters revisited: bridging the gap between gold(I)-thiolate complexes and thiolate-protected gold nanoclusters. *J. Am. Chem. Soc.* 127, 5261–5270 (2005).

36. Sakai, N. & Tatsuma, T. Photovoltaic properties of glutathione-protected gold nanoclusters adsorbed on TiO2 electrodes. *Adv. Mater.* 22, 3185–3188 (2010).

37. Negishi, Y., Chaki, N. K., Shibu, Y., Whetten, R. L. & Tsukuda, T. Origin of the magic stability of Au125 gold clusters: a case study on Au125(S2C6H13)3. *J. Am. Chem. Soc.* 129, 11322–11323 (2007).

38. Li, H. et al. Mesoporous Au/TiO2 nanocomposites with enhanced photocatalytic activity. *J. Am. Chem. Soc.* 129, 4538–4539 (2007).
Zhang, Y., Zhang, N., Tang, Z.-R. & Xu, Y.-J. Graphene transforms wide band gap ZnS to a visible light photocatalyst. The new role of graphene as a macromolecular photosensitizer. *ACS Nano* **6**, 9777–9789 (2012).

67. Pan, X. & Xu, Y.-J. Efficient thermal- and photocatalyst of Pd nanoparticles on TiO$_2$ achieved by an oxygen vacancies promoted synthesis strategy. *ACS Appl. Mater. Interfaces* **6**, 1879–1886 (2014).

68. Yuan, L., Yang, M.-Q. & Xu, Y.-J. A low-temperature and one-step method for fabricating ZnIn$_2$S$_4$-GR nanocomposites with enhanced visible light photocatalytic activity. *J. Mater. Chem. A* **2**, 14401–14412 (2014).

Acknowledgements

Y.-J.X. acknowledges the support from the National Natural Science Foundation of China (U1463204, 21173045), the Award Program for Minjiang Scholar Professorship, the NSF of Fujian Province for Distinguished Young Investigator Rolling Grant (2017J07002), the Independent Research Project of State Key Laboratory of Photocatalysis on Energy and Environment (No. 2014A05), the 1st Program of Fujian Province for Top Creative Young Talents, and the Program for Returned High-Level Overseas Chinese Scholars of Fujian province. H.M.C. appreciates the support from the Ministry of Science and Technology, Taiwan (Contracts No. MOST 106-2119-M-002-031).

Author contributions

Y.-J.X. proposed the research direction and supervised the project. B.W. designed and performed the experiments. Z.C.T. performed MS measurement and H.M.C. provided helpful suggestions in conducting the study. K.Q.L. carried out TEM characterization and analysis. Y.-J.X. and B.W. wrote and revised the manuscript. All authors participated in discussion and reviewed the manuscript before submission.

Additional information

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-04020-2.

Competing interests: The authors declare no competing interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless otherwise indicated in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018