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# Laser-induced fabrication of highly branched Au@TiO<sub>2</sub> nano-dendrites with excellent near-infrared absorption properties

Ziyu Wang, Hua Zhang, Linlin Xu, Ziwei Wang, Dameng Wang, Xiangdong Liu and Ming Chen\*

*School of Physics, Shandong University, Jinan 250100, China*

*\*chenming@sdu.edu.cn*

## **Abstract:**

In this report, highly branched Au@TiO<sub>2</sub> nano-dendrites with tailored surface topography have been conveniently fabricated via a novel and effective laser-induced strategy. The TiO<sub>2</sub> nano-spheres fabricated by laser ablation of Ti target in H<sub>2</sub>O<sub>2</sub> solution are characterized by abundant oxygen vacancies (OVs) on the (110) surface. Then, the hydroxyl radicals (OH<sup>•</sup>) groups will be easily formed on the OVs in the terms of water dissociation by UV laser irradiation of TiO<sub>2</sub> nano-spheres at liquid interface. With the aid of OH<sup>•</sup> groups, the formation of Au@TiO<sub>2</sub> nano-dendrites is based on overgrowth of gold on TiO<sub>2</sub> nano-spheres through the reduction of HAuCl<sub>4</sub>. The absorption spectra of Au@TiO<sub>2</sub> nano-dendrites show that localized surface plasmon resonance (LSPR) peaks can be effectively modulated from the visible region (~545nm) to the near-infrared region (NIR~1090nm). The as-prepared Au@TiO<sub>2</sub> nano-dendrites with excellent NIR absorption properties have promising potentials for developing important novel sensors and super photo-catalysts.

Electronic Supplementary Information (ESI) available: The PH value of the TiO<sub>2</sub> solution versus the UV-laser irradiation time. The typical TEM images and corresponding elemental mapping images of the Au@TiO<sub>2</sub> nano-dendrites obtained by UV-laser irradiation for 120min and using 100μL HAuCl<sub>4</sub>. The structure-evolutions of Au@TiO<sub>2</sub> nano-dendrites obtained from a same amount (100μL) of Au source in each experiment versus UV-laser irradiation time.

## Introduction

Hybrid nano-composites constructed by noble metal elements (Au, Ag, Pt, Pd, *etc*) supported on TiO<sub>2</sub> semiconductors are emerging as attractive multifunctional materials that integrate the unique optical and electronic properties of metal with the super photochemical/physical-activity of TiO<sub>2</sub> nano-structure.<sup>1-6</sup> Among these noble metals, Au nano-crystal is the most promising material owing to its high electro-catalytic activity and tailored localized surface plasmon resonance (LSPR) property, which can separate efficiently photo-excited electron-hole pairs of TiO<sub>2</sub> semiconductor. In particular, because of the synergistic effects between the TiO<sub>2</sub> and Au metal structures, the Au@TiO<sub>2</sub> nano-composites with tailored surface topography can also show strong LSPR absorption in the near-infrared (NIR) region. The fascinating Au@TiO<sub>2</sub> hybrid structures with enhanced reaction kinetics have attracted tremendous attention, owing to their intriguing applications for super-active catalysts, biomedical sensors, novel solar cells, photo-degradation, *etc*. For example, Razzari and Claverie group illustrated that an enhanced local electric field can be established at the Au-TiO<sub>2</sub> interface, and the plasmonic absorption can also be extended over the visible range.<sup>7</sup> Most recently, other researchers demonstrated that the novel nano-composites of TiO<sub>2</sub>@TiO<sub>2</sub>-Au incorporated copolymer show a higher rate of adsorption of toxic cationic methyl violet (MV)/anionic acid orange

dyes.<sup>8</sup> Increasing evidence has shown that the excellent properties of Au@TiO<sub>2</sub> nano-composites are highly dependent on their compositions and hybrid nano-structures.

Most recently, noble metal bimetallic nano-dendrite/hyper-branch structures with controllable branch lengths, such as Au@Pd,<sup>9-11</sup> Au@Au,<sup>12</sup> Au@Pt,<sup>13</sup> *etc*, exhibited good plasmonic properties, high-performance H<sub>2</sub>O<sub>2</sub> sensing and excellent catalytic activities, because their LSPR peaks can be modulated from the visible to the NIR region. It is noted that previous reports mainly focused on the synthesis of isolated Au island-like structures on the TiO<sub>2</sub> precursors.<sup>5-8</sup> If the Au nano-branches can be linked on the TiO<sub>2</sub> nano-structures, the novel hybrid nano-composites should possess superior catalytic performances than the Au island-structure, due to the longitudinal plasmonic properties. Up to now, there are very few reports on the controllable synthesis of Au@TiO<sub>2</sub> nano-dendrites. The main reason is related to the fact that the inevitable large mismatch of crystal lattices between Au and TiO<sub>2</sub> composites, which will limit the overgrowth of Au branch on the TiO<sub>2</sub> surface.<sup>2-4</sup>

It is well known that the oxygen vacancy (OV) will be easily generated on the TiO<sub>2</sub>(110) surface by UV light irradiation, resulting in abundant hydroxyl radical (OH<sup>•</sup>) groups formed and embedded on the surface (110).<sup>14-20</sup> Taking advantage of the enough OH<sup>•</sup> groups embedded

on the  $\text{TiO}_2(110)$  nano-structures, we deduce that the oriented crystal growth of Au composite on  $\text{TiO}_2$  surface will occur by the reduction of  $\text{HAuCl}_4$  with surface  $\text{OH}^-$  groups. Herein, for the first time, we demonstrate an innovative synthetic approach for the formation of novel  $\text{Au}@ \text{TiO}_2$  nano-dendrites with controllable surface structures. The adopted strategy is based on laser-induced fabrication of  $\text{TiO}_2(110)$  nano-spheres in  $\text{H}_2\text{O}_2$  solution, and then the UV-laser irradiation of  $\text{TiO}_2$ . The  $\text{H}_2\text{O}_2$  provides the oxygen sources, which is environmentally friendly and has negligible toxicity. Laser fabrication in liquid is a new green technology for the synthesis of novel metal stable phase of materials, which is characterized by unique high non-equilibrium processing with high temperature and pressure.<sup>21-27</sup> This is a breakthrough in the toxicity problems that arise from standard chemical fabrication. In this way, the  $\text{TiO}_2(110)$  nano-spheres are helpful for the generation of abundant  $\text{OH}^-$  groups *via* UV-laser irradiation in liquid. It is therefore possible to tailor the morphology of the  $\text{Au}@ \text{TiO}_2$  branches over a broad range by changing irradiation time. Moreover, the LSPR peaks of the as-prepared  $\text{Au}@ \text{TiO}_2$  nano-dendrites can be modulated from the visible ( $\sim 545$  nm) to the near-infrared region (NIR $\sim 1090$  nm). There is no doubt that the present results in this paper will be a breakthrough in the fabrication of noble metal-metal oxide semiconductor with hyper-branched structures.

### **Experimental section**

In a typical experiment of fabrication TiO<sub>2</sub> nano-spheres, a well-polished Ti metal (99.99%) has been used as a target placed on the bottom of a rotating glass dish (X-Y stage) with speed of ~1000 rpm filled with 3 mm depth of H<sub>2</sub>O<sub>2</sub> (30%) water solution (100mL). A Q-switched Nd-YAG( yttrium aluminum garnet) laser ( Quanta Ray, Spectra Physics) beam operating at a wavelength of 1064 nm with a pulse duration of about 6 ns and 10 Hz repetition was focused onto the Ti target by a quartz lens with 60 mm focal length. The power density of laser beam was about 3.2 GW/cm<sup>2</sup>, and the average spot size of the laser beam at the target surface was measured to be 300μm. The ablation time lasted about 40 minutes. After laser fragmentation of Ti metal, the colloidal suspensions were divided into ten beakers. The series of TiO<sub>2</sub> colloidal suspensions were separately irradiated under different time region (0~120 min) by a 365 nm cw semiconductor laser with power of 10 mW. Then, the Au@TiO<sub>2</sub> nano-dendrites were synthesized by co-reduction of HAuCl<sub>4</sub> with the OH<sup>-</sup> groups on the surface of TiO<sub>2</sub> nano-particles. Typically, 20~100 μL of aqueous solution containing about 3.5μmol of HAuCl<sub>4</sub> were added into 10mL TiO<sub>2</sub> solution. The mixture solutions were sonicated for 1 min. Then the products were separated by centrifugation at 18000 rpm for 10 min in an ultracentrifuge, and the precipitates were carefully washed in distilled water three times. The sediments were dropped on a copper mesh and dried in an oven at 60<sup>0</sup>C for observation

by transmission electron microscopy (JEOL-JEM-2100F). Morphological investigations and chemical composition measurements were performed by field emission scanning electron microscope (SEM, Hitachi S-4800) equipped with energy-dispersive x-ray spectroscopy (EDS). And the crystallographic investigation of the TiO<sub>2</sub> fabricated by laser ablation was analyzed by x-ray diffraction (XRD) patterns (Rigaku, RINT-2500HF) using Cu K $\alpha$  radiation ( $\lambda=0.15406\text{nm}$ ). The Fourier transforms infrared spectra (FTIR) of the TiO<sub>2</sub>-OH groups dried in vacuum at 60°C were measured by a UV-vis-NIR spectrometer (Shimadzu, UV-1700). Finally, the UV-visible-NIR absorption spectra of Au@TiO<sub>2</sub> nano-dendrites were measured with UV-vis-IR spectrometer (Shimadzu, UV-1800).

## Results and discussion

After pulse laser ablation of pure Ti target in H<sub>2</sub>O<sub>2</sub> solution, the low-magnification TEM image of the TiO<sub>2</sub> nano-structures is shown in Fig.1(a). The morphology of the products clearly shows numerous liquid-dispersed nano-particles with mean diameter of about 110 nm are well-defined spherical-like structures. The nano-spheres with solid interiors and smooth surfaces are not hinge joined, but are dispersed individually. In addition, the crystallographic investigation of the product was carried out by XRD in Fig.1(b). The XRD (20-60°) pattern reveals that a series of (110), (101), (111) and (211) TiO<sub>2</sub> diffraction peaks centered at 27.4°, 36.1°, 41.2° and 54.3° were detected, which proves to

be the rutile phase of  $\text{TiO}_2$ . The relatively strong peak centered at  $36.1^\circ$  also implies that the  $\text{TiO}_2$  (110) should be preferentially formed in the nano-spheres. After UV-laser irradiation for 120 min, the SEM image in Fig.1(c) illustrates that the smooth surfaces of the  $\text{TiO}_2$  changed to slightly rough-like structures. Moreover, the inset result shows that the ratio of O to Ti is about 4:1 according to the EDS result, which is obviously different from a common  $\text{TiO}_2$  material. Because some light elements, such as hydrogen, cannot be detected in EDS pattern, the existence of extra oxygen element originated from  $\text{OH}^-$  groups was evidenced by the FTIR spectra. FTIR spectrum of the same product in Fig.1(d) shows that this spectrum ( $1000\sim 4000\text{cm}^{-1}$ ) is dominated by the broad band with peak at  $3436\text{ cm}^{-1}$  of the strongly adsorbing OH stretching vibrations and relatively sharp peaks at  $1636$  and  $1437\text{ cm}^{-1}$  of OH bending mode. In addition to the  $\text{TiO}_2$  lattice vibrations at about  $670\text{ cm}^{-1}$ , the several improved FTIR spectra from  $\text{OH}^-$  groups combined with the obvious higher O element in the products confirm that abundant  $\text{OH}^-$  groups can be indeed embedded on the  $\text{TiO}_2$  nano-spheres by UV-light irradiation. Increasing the irradiation time should result in more  $\text{OH}^-$  groups formed on the  $\text{TiO}_2$  structures, which can be confirmed by measuring the PH value of the  $\text{TiO}_2$  water solution. It is well known that the hydroxyl radicals can be weakly ionized in the water solution, resulting in some hydrogen ions formed in the liquid. As shown in Fig.S1

†, the PH value of the TiO<sub>2</sub> solution linearly decreases from about 6.76 to 5.38 with an increase of irradiation time(0~120 min), implying more hydrogen ions formed in the solution. In this way, it is therefore to deduce that a longer irradiation time can lead to more OH<sup>-</sup> groups formed on the TiO<sub>2</sub> structures.

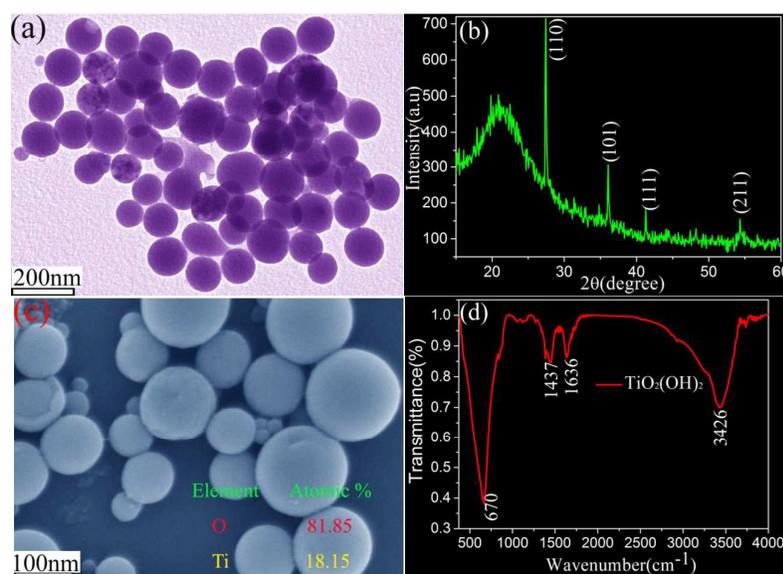


Fig. 1 (a) The typical low-magnification TEM image of the TiO<sub>2</sub> nano-spheres by laser ablation of Ti target in H<sub>2</sub>O<sub>2</sub> liquid. (b) XRD pattern of the products (c) The representative SEM image of the TiO<sub>2</sub> nano-spheres after UV-laser irradiation for 120 min. (d) FTIR spectrum of the products.

The evolution and modification of the TiO<sub>2</sub> nano-structures by using UV-laser irradiation are illustrated by the high-resolution transmission electron microscopy (HRTEM) of the products before and after irradiation for 120 min. The HRTEM images in Fig.2(a-b) clearly reveal that the well crystalline of the TiO<sub>2</sub> (110) structure with a periodicity corresponding to a *d*-spacing of 0.325nm can be de-crystallized after

UV-laser irradiation, resulting in some amorphous or distortion structures. The distortion structures should be attributed to the formation of OH<sup>-</sup> groups on the TiO<sub>2</sub> nano-spheres. The possible TiO<sub>2</sub>-OH structure growth processes have been proposed in a schematic growth diagram, as shown in Fig.2(c). At the moment of pulse laser arriving at Ti target, rapid boiling and vaporization of Ti element will occur, resulting in the nucleation of explosive Ti plasma with O element in H<sub>2</sub>O<sub>2</sub> solution. After laser ablation (~6ns), the rapid quenching process enables the disorder degrees of Ti and O species to become more and more intensive, which makes O species at a highly excited state. Under the UV-laser irradiation of the as-prepared TiO<sub>2</sub> (110) nano-spheres, oxygen vacancy (OV) sites can thus be expected to occur on the rutile surface owing to the photo-induced hole-electron pairs, which is a ubiquitous feature in nature.<sup>12-17</sup> Compared with commercial TiO<sub>2</sub> nano-particles, the degree of OV sites will be significantly enhanced due to the unique active O species generated in TiO<sub>2</sub> nano-spheres during laser ablation, leading abundant/enough OV sites formed on the surface. The abundant OVs will then act as adsorption sites for surrounding H<sub>2</sub>O molecules, and then the hydrophilic nature of the TiO<sub>2</sub> surface increases remarkably.<sup>12-20</sup> Meanwhile, the photo-induced holes enable the water dissociation to dominate the following process. The longer UV-irradiation time can lead to an increase in the number of surface OH<sup>-</sup> groups. The inset in Fig.2(c)

shows that the UV-laser irradiation for 120 min leads to an obvious change in the colloidal suspension color from light yellow to dark yellow, which is a reasonable evidence for the formation of abundant OH<sup>-</sup> groups embedded on the TiO<sub>2</sub> nano-spheres. The unique TiO<sub>2</sub> nano-sphere with enough OH<sup>-</sup> groups embedded on the surface is highly dependent on the enhanced active O species and subsequent UV-laser irradiation. Finally, interesting chemistry can thus be expected to occur at the abundant surface OH<sup>-</sup> groups on the TiO<sub>2</sub> nano-spheres.

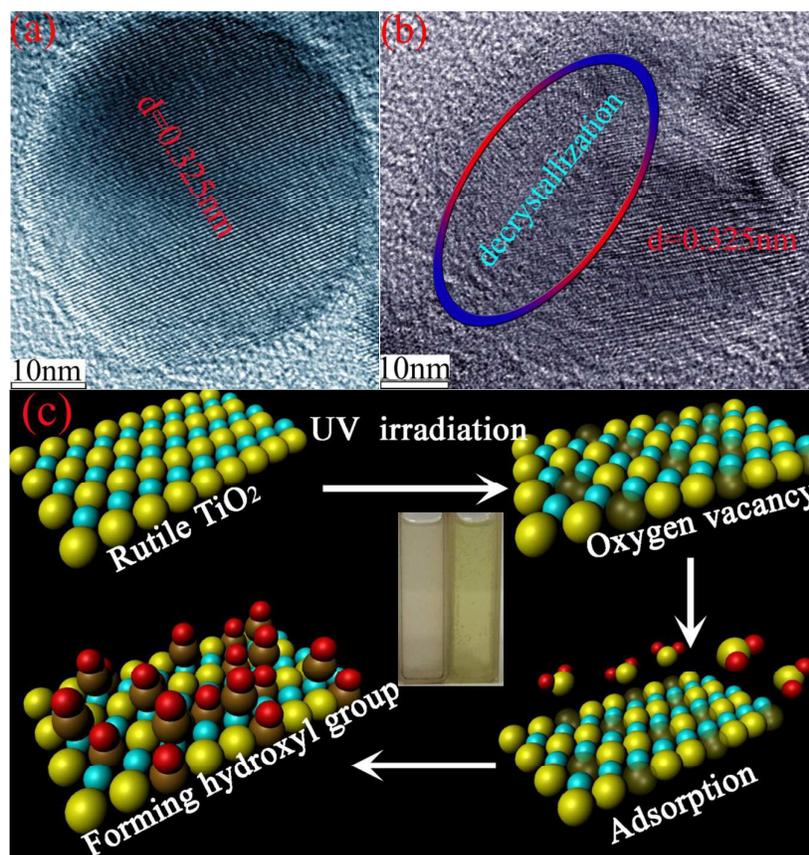


Fig.2 (a-b) The HRTEM images of the TiO<sub>2</sub> nano-spheres before and after UV-laser irradiation for 120 min, respectively. (c) The schematic growth of OH<sup>-</sup> groups on the TiO<sub>2</sub> nano-spheres by using UV-laser irradiation.

The abundant/enough OH<sup>-</sup> groups formed on the surface of TiO<sub>2</sub>

nano-spheres play a crucial role in the production of Au@TiO<sub>2</sub> nano-dendrites. To verify it, the as-prepared TiO<sub>2</sub> nano-spheres without any UV-laser irradiation were selected as the precursor for the fabrication of Au@TiO<sub>2</sub> nano-composites through the reduction of HAuCl<sub>4</sub>. As shown in Fig.3(a-b), isolated island-shaped Au nano-structures were formed on the TiO<sub>2</sub> nano-spheres, which is similar to the previous reports.<sup>1-7</sup> The typical region in Fig.3(c) with a *d*-spacing of 0.235nm could be indexed as the Au(111) plane structure. The large mismatch of crystal lattices between Au and TiO<sub>2</sub> is considered to be the main reason for the formation of island-shaped Au structures. The LSPR spectra of the TiO<sub>2</sub>, two Au@TiO<sub>2</sub> nano-composites by using 20 and 70μL HAuCl<sub>4</sub> are shown in Fig.3(c). The increasing HAuCl<sub>4</sub> concentration improved the peak intensity of Au particle-structure at about 530nm. There are no red-shifted spectra in the different nano-composites. The Au@TiO<sub>2</sub> nano-dendrites with obvious hierarchical branches cannot be generated owing to the inadequate OH<sup>-</sup> groups in the precursors.

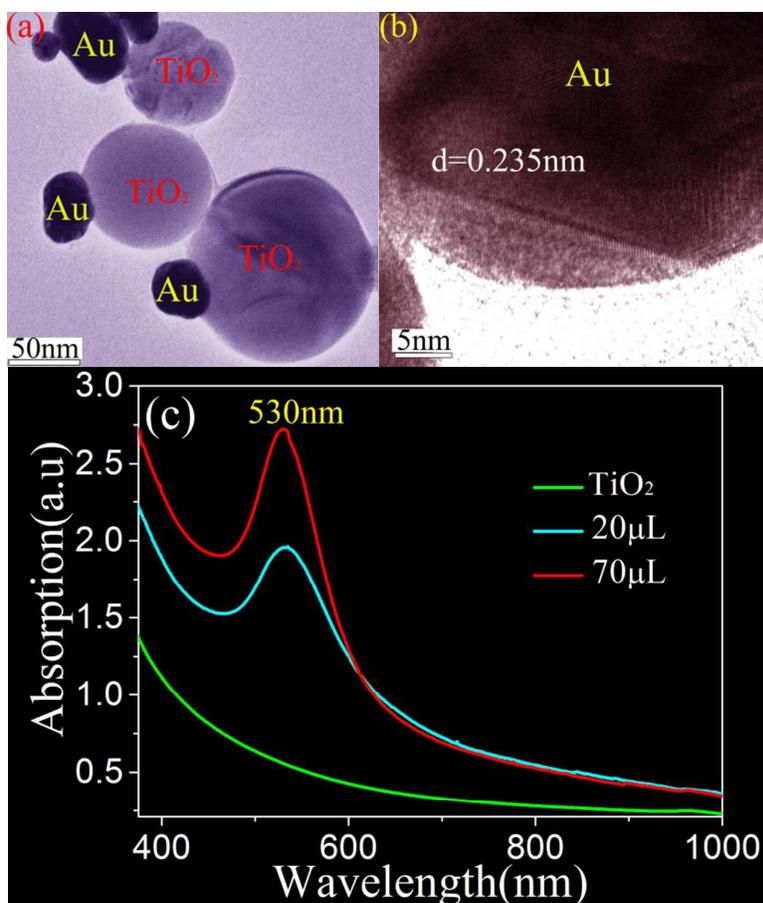


Fig.3 (a and b) The representative low-magnification and enlarged TEM images of the Au@TiO<sub>2</sub> hetero-structures fabricated by overgrowth of Au on the TiO<sub>2</sub> nano-spheres in the presence of 20µL HAuCl<sub>4</sub>. (c) The UV-visible absorption spectra of the as-prepared TiO<sub>2</sub> nano-spheres and Au@TiO<sub>2</sub> hetero-structures generated by 20 and 70µL HAuCl<sub>4</sub>.

Then, based on UV-laser irradiation for 60 min, the TiO<sub>2</sub> nano-spheres with OH<sup>-</sup> groups embedded on the surfaces were adopted as the precursors for the fabrication of Au@TiO<sub>2</sub> hybrid nano-materials. The obtained novel nano-structures by using 20µL and 100µL HAuCl<sub>4</sub> are shown in Fig.4(a) and (b). The low-magnification TEM image in Fig.4(a) displays that the hybrid nano-materials appeared to be complex nano-structures with dense core and hierarchical branches. The inset

shows that the typical small branch with a  $d$ -spacing of 0.235nm can be indexed to be the (111) plane of the Au structure. Moreover, enlarged and high-magnification TEM images in Fig.4(b-c) illustrate that the higher H<sub>2</sub>AuCl<sub>4</sub> concentration (100 $\mu$ L) enables the Au@TiO<sub>2</sub> nano-dendrites to possess more clearly hyper-branched surface structures. Compared with the nano-dendrites in Fig.4(a), the branch length significantly increases from about 35nm to approximately 75nm by measuring the size of more than 200 particles in sight of the TEM images. The Au(111) structure is also illustrated in Fig.4(d). The unique optical properties of the as-prepared Au@TiO<sub>2</sub> nano-dendrites with controllable branch lengths are illustrated by the UV-visible absorption spectra in Fig.4(e). The direct photographs of the TiO<sub>2</sub> nano-spheres and the Au@TiO<sub>2</sub> nano-dendrites (inset in Fig.4(e)) show that Au branch-structures lead to a significant change in the colloidal solution color from dark yellow to grey brown. The absorption spectra of the Au@TiO<sub>2</sub> nano-dendrites illustrate that the LSPR peaks distinctly red shifted from the visible  $\sim$ 545nm to about 806 nm with an increase of H<sub>2</sub>AuCl<sub>4</sub> content during the reduction process.

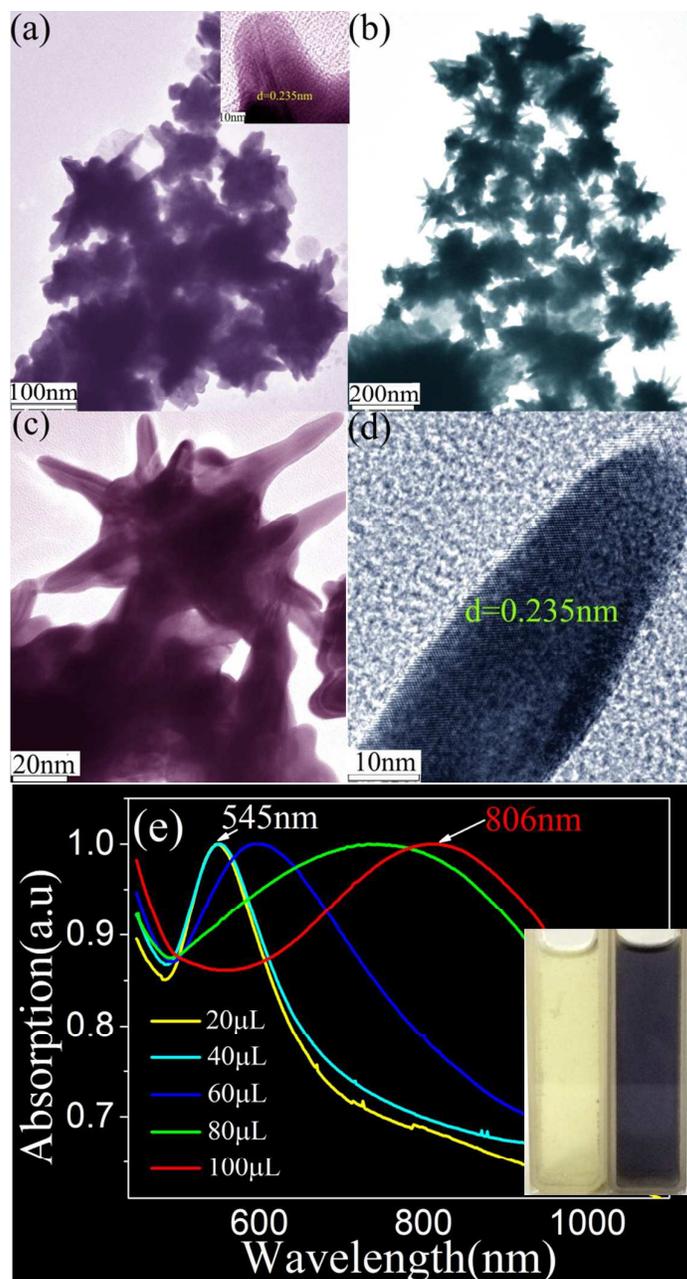


Fig. 4 (a and b) The typical low-magnification TEM images of the Au@TiO<sub>2</sub> nano-dendrites by using 20 μL and 100 μL HAuCl<sub>4</sub>, respectively. (c and d) The corresponding enlarged and high-magnification TEM images of Au@TiO<sub>2</sub> nano-dendrites by using 100 μL HAuCl<sub>4</sub>, respectively. The precursors were modified by UV-laser irradiation for 60 min. (e) The UV-visible absorption spectra of the as-prepared Au@TiO<sub>2</sub> nano-dendrites by using different amounts of HAuCl<sub>4</sub>.

Finally, we further increase the UV-laser irradiation time to 120 min in order to get the TiO<sub>2</sub> nano-spheres with abundant/enough OH<sup>-</sup> groups. By

using 100 $\mu$ L HAuCl<sub>4</sub> in the overgrowth process, the low- and high-magnification TEM images in Fig.5(a-d) clearly show that highly branched Au@TiO<sub>2</sub> nano-dendrites can be obtained by using TiO<sub>2</sub> nano-spheres with abundant OH<sup>-</sup> groups. Compared with the nano-dendrites in Fig.4, the branch is highly elongated by using the co-reduction of HAuCl<sub>4</sub> with enough surface OH<sup>-</sup> groups in the precursors, as shown in Fig.5 (b and c). Meanwhile, Fig.5 (d) reveals that the Au (111) structures can also be formed on the Au branches. Moreover, the elemental mapping images of the typical Au@TiO<sub>2</sub> nano-branched structure in Fig.S2<sup>†</sup> show that the hybrid nano-dendrite is indeed composed of Au, Ti and O elements, and the corresponding relative ratio is about 75:8:17, respectively. Then, the Au content in the Au@TiO<sub>2</sub> nano-branched structure is about 75%. The elemental mapping images can also provide detailed information of the elements distributions in the branched nano-structures. We found that the Ti and O elements can be detected in core region, and Au element was formed on the outside. The detailed structure-evolutions of Au@TiO<sub>2</sub> nano-dendrites obtained from a same amount (100 $\mu$ L) of HAuCl<sub>4</sub> in each experiment but different UV-laser irradiation times(0~120min) were shown in Fig.S3<sup>†</sup>. The experimental results are obtained by measuring the Au contents and the Au branch lengths of more than 200 particles in sight on the elemental mapping images and TEM images, respectively. As illustrated in Fig.S3(a

and b)†, the results clearly reveal that both the average Au content and Au branch length in the hybrid Au@TiO<sub>2</sub> nano-structures obtained from a some amount Au source increase linearly with an increase of irradiation time. Increasing irradiation time (0~120 min) result in the more OH<sup>-</sup> groups formed on the surface of TiO<sub>2</sub> structures. Therefore, the results in Fig.S3(a and b)† show that the mean Au content and Au branch length separately increases from about 11% and 24 nm to 75% and 167nm with an increase of irradiation time (0~120 min), respectively. The above results show that the amount of OH<sup>-</sup> groups plays an important role in the formation of higher branched Au@TiO<sub>2</sub> nano-dendrites. Then, the UV-visible absorption spectra of the hyper-branched Au@TiO<sub>2</sub> nano-dendrites are illustrated in Fig. 5(e). It is interesting to note that the LSPR peaks can be modulated from the visible~545nm to the NIR region ~1090nm with the increase of the HAuCl<sub>4</sub> content (20~100μL) during the overgrowth process. The enhanced NIR absorption property should be attributed to longitudinal plasmon wavelength of the Au elongated branches on the TiO<sub>2</sub> nano-dendrites. It is reasonable to deduce that the highly branched Au@ TiO<sub>2</sub> nano-dendrites with excellent NIR absorption properties will be very suitable for developing super-active photo-catalysts, novel solar cells, and biomedical sensor, *etc.*

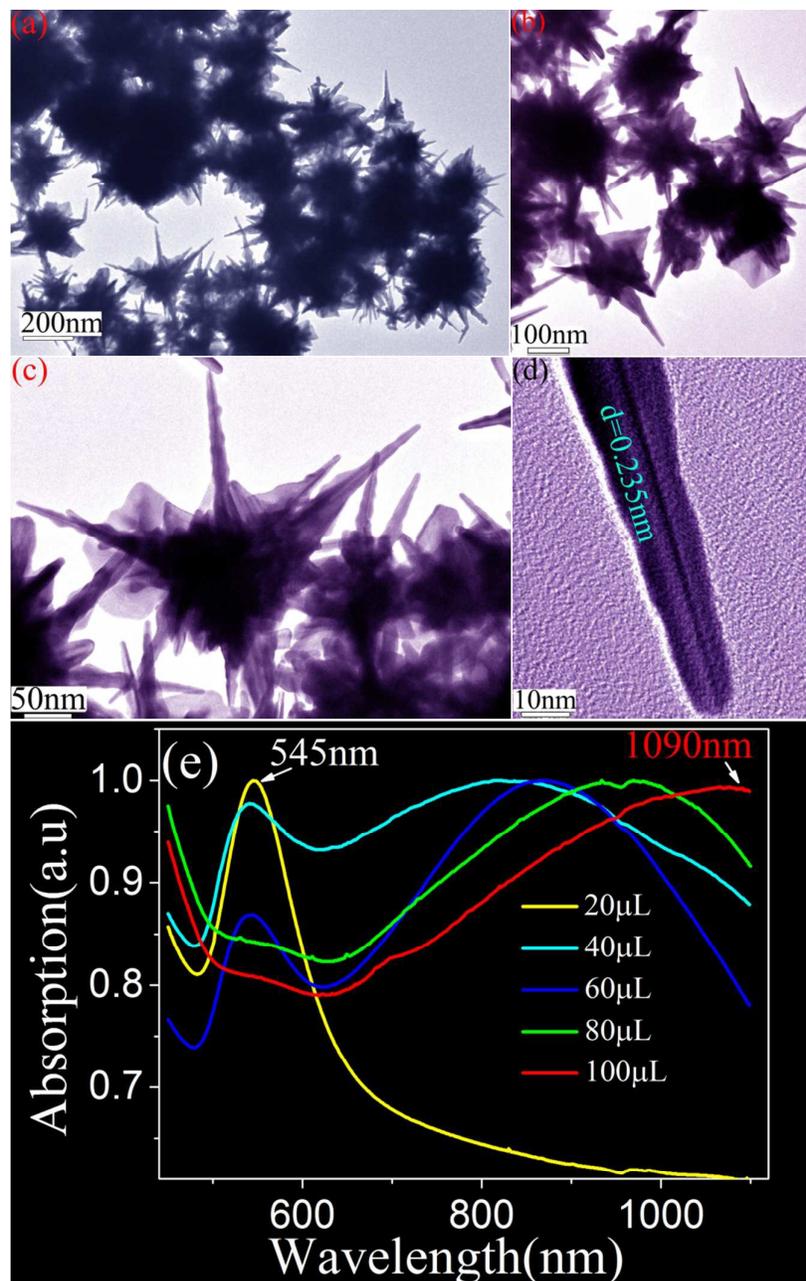


Fig.5 (a-d) The typical low- and high-magnification TEM images of the Au@TiO<sub>2</sub> nano-dendrites by using 100 μL HAuCl<sub>4</sub>, respectively. The precursors were modified by UV-laser irradiation for 120 min. (e) The UV-visible absorption spectra of the as-prepared Au@TiO<sub>2</sub> nano-dendrites by using different amount HAuCl<sub>4</sub>.

## Conclusions

In summary, hybrid Au@TiO<sub>2</sub> nano-dendrites with tailored branched

structures have been carefully devised by using the reduction of  $\text{HAuCl}_4$  with abundant  $\text{OH}^-$  groups embedded on the  $\text{TiO}_2$  nano-spheres. To reveal the formation mechanism of abundant  $\text{OH}^-$  groups on the  $\text{TiO}_2$  surfaces, the unique active O species generated in  $\text{TiO}_2$  nano-spheres during pulse laser fabrication and subsequent UV-laser irradiation have been proposed. The absorption spectra of the as-prepared  $\text{Au@TiO}_2$  nano-dendrites demonstrate that the LSPR peaks can be effectively modulated from the visible~545nm to NIR~1090nm. The obtained results in this paper will be a breakthrough in the fabrication of noble metal@metal oxide semiconductor hyper-branched nano-structures. The obtained materials may have significant applications in super-active photo-catalysts, novel solar cells, and biomedical sensors, *etc.*

### **Acknowledgments**

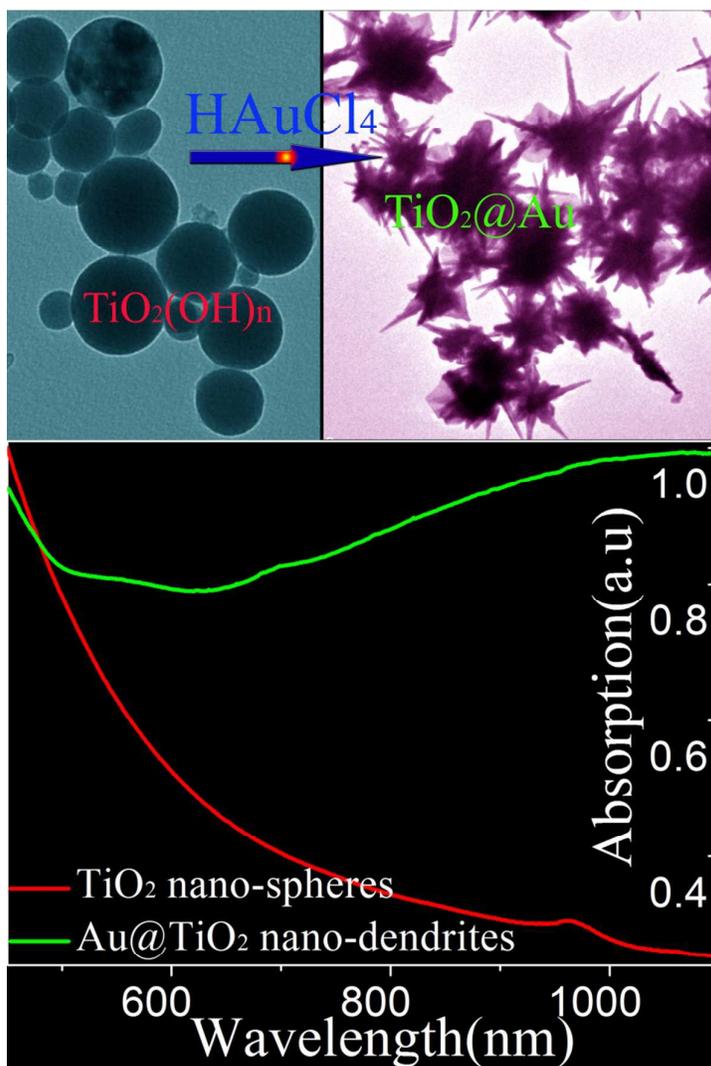
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TEXT : The highly branched  $\text{Au}@TiO_2$  nano-dendrites with excellent near-infrared absorption properties have been conveniently fabricated via a novel and effective laser-induced strategy.