

NANO EXPRESS

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Bimetallic core/shell nanoparticle-decorated 3D urchin-like hierarchical TiO₂ nanostructures with magneto-responsive and decolorization characteristics

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Abstract

The semiconductors decorated with noble metals or magnetic metals have attracted increasing attention due to multifunctional properties. In this article, we prepare novel bimetallic core/shell nanoparticle (Co@Au and Co@Ag)-decorated 3D urchin-like hierarchical TiO₂ nanostructures through combining electroless plating and *in situ* replacement processes. The morphology and structure are characterized by scanning electron microscopy, transmission electron microscopy, energy-dispersive spectroscopy, and a surface area analyzer. It demonstrates that Co@Au and Co@Ag nanoparticles are uniformly decorated on urchin-like TiO₂ nanostructures. The composite nanostructures show not only surface plasmon absorption band from Au or Ag but also a magneto-responsive characteristic from Co. This allows composite nanostructures to exhibit advantages including enhanced decolorization efficiency compared to pure TiO₂ nanostructures and facile separation from a solution by magnetic field.

Keywords: Bimetallic nanoparticles; Urchin-like TiO₂; Magnetic response; Surface plasmon resonance; Decolorization

Background

The combinations of semiconductors with noble metals or magnet metals have been demonstrated to be interesting in fields ranging from catalysis and optics to biotechnology [1]. Besides doping noble metals or magnet metals into semiconductors, the assembly of noble metal or magnetic metal nanoparticles onto semiconductors with special morphology, such as nanospheres, tubes and wires, films, and even three-dimensional nanostructures, has raised great interest [2,3]. Different from doped systems, the composite nanostructures may combine the unique properties of semiconductors and noble metals or magnetic metals and show multifunctional behaviors [2,3].

Titania (TiO₂) is a high-performance functional material with a wide range of applications due to its semiconductive and biocompatible natures [4]. TiO₂ decorated with nanoparticles of noble metal has attracted enormous attention. However, the simultaneous and effective

control of the composition, morphology, structure, and distribution of decorated nanoparticles is still a challenge. In recent years, a lot of effort has been made on the study of TiO₂ microspheres decorated with monometallic nanoparticles. And even there are a few reports about 3D hierarchical TiO₂ microspheres decorated with noble metal nanoparticles. In the previous work, we have prepared a kind of Au or Ag nanoparticle-decorated 3D urchin-like TiO₂ nanostructures, which exhibit an enhanced photocatalytic activity compared with the pure urchin-like TiO₂ nanostructures and commercial P25 photocatalyst [5]. However, the percentages of methyl blue degraded by Ag-decorated TiO₂ and Au-decorated TiO₂ are only about 78% and 68% after 3 h of UV-vis light irradiation [5]. So, there is still a large space to improve on the degraded efficiency.

Bimetallic nanostructures often exhibit improved physical and chemical properties over their monometallic counterpart and hence are useful in many applications [6]. Especially, core/shell nanoparticles with a magnetic core and a noble-metallic shell have attracted a great deal of attention [7]. The magnetic core can provide magnetic

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functionality and delivery power and the noble-metallic shell can offer a well-developed function, such as surface for biomolecule attachment and plasmonically active components for optical imaging [8]. Core/shell nanoparticles, such as $\text{Fe}_3\text{O}_4/\text{Au}$, Co/Ag , and Co@Au , have attracted considerable attention [9–11]. These materials have great potential applications in the areas of electronics, photonics, catalysis, biotechnology, and so on.

Herein, we report novel 3D hierarchical TiO_2 nanostructures decorated with bimetallic nanoparticles that have a magnetic cobalt core and a silver or gold nanoshell. The samples are prepared through a two-step method involving electroless plating and *in situ* replacement processes. The resulting composite 3D nanostructures show a distinct surface plasmon absorption band in the visible region and a good magnetic response to an external magnetic field. Furthermore, the composite 3D nanostructures can quickly decolorize methyl blue solution at room temperature. The bimetallic nature and 3D hierarchical architecture have shown excellent properties in extensive application. The combination of such bimetallic nanoparticles and TiO_2 with a hierarchical nanostructure can not only combine multiple functionalities of dissimilar materials but also address the aggregation of nanoparticles. To the best of our knowledge, there is no report of the synthesis of the magnetically bimetallic core-shell nanospheres-decorated 3D hierarchical TiO_2 nanostructures. We present here the preparation, characterization, and the properties of two kinds of magnetically bimetallic core-shell nanoparticles (Co@Au and Co@Ag)-decorated 3D urchin-like hierarchical TiO_2 nanostructures in detail.

Methods

Synthesis of hierarchical TiO_2 nanostructures

Hierarchical TiO_2 nanostructures were obtained by a solvothermal method described in our previous article [12,13]. In a typical synthesis, tributyltin chloride (TBT) was dissolved in toluene in an ice-water bath, and subsequently, TiCl_4 aqueous solution was added dropwise into the TBT/toluene solution under stirring. The mixture was transferred into a stainless steel autoclave lined with Teflon and heated at 150°C for 24 h. The precipitates were filtered, washed with ethanol several times, and dried to obtain urchin-like 3D hierarchical TiO_2 nanostructures.

Pre-activation of hierarchical TiO_2 nanostructures

In order to decorate with metal nanoparticles, TiO_2 nanostructures were pre-activated by the method as described in Ref. [14]. Firstly, the TiO_2 particles were dispersed in a solution of 0.1 M $\text{SnCl}_2/0.1$ M HCl for 40 min. During this process, the ‘sensitizer’ (Sn^{2+}) was modified onto the surface of TiO_2 nanostructures.

Then, the particles were washed with water and centrifuged, and the supernatant was discarded. Subsequently, the Sn^{2+} -sensitized TiO_2 nanostructures were dispersed in an aqueous solution of 1.5×10^{-3} M $\text{PdCl}_2/0.25$ M HCl for another 40 min. During this process, the ‘catalyzer’ (Pd crystal seeds) was deposited onto the surface of TiO_2 nanostructures. Finally, the particles were washed with water again by centrifugation to get Pd-modified TiO_2 nanostructures.

Synthesis of Co nanoparticle-decorated hierarchical TiO_2 nanostructures

An amount of 0.5 g of activated TiO_2 particles was dispersed in an aqueous CoCl_2 solution (50 mL, 0.01 to 0.025 M) by mechanical stirring. Then, the suspension was protected by N_2 and placed in a water bath at 30°C . After stirring for 1 h, a freshly prepared and ice-cold NaBH_4 solution (80 mL, 0.005 to 0.015 M) was added dropwise with the rate of 2 mL/min. Within several minutes, the color of suspension changed from pink to dark gray, indicating the formation of Co nanoparticles. After further reaction for 40 min under stirring, the precipitate was separated by a magnet and washed with water three times to get Co nanoparticle-decorated TiO_2 nanostructures. They are named as Co/TiO_2 .

Synthesis of Co@Au or Co@Ag nanoparticle-decorated hierarchical TiO_2 nanostructures

Co@Au or Co@Ag nanoparticles are facilely prepared at room temperature by *in situ* replacement reaction, in which Co nanoparticles are partly replaced by a noble metal salt. The process is shown as follows: 0.2 g of Co nanoparticle-decorated TiO_2 nanostructures were dispersed into an aqueous HAuCl_4 solution (50 mL, 0.5×10^{-3} M) or AgNO_3 solution (50 mL, 1.5×10^{-3} M) by mechanical stirring. After stirring for 1 h, the precipitate was centrifuged and washed with water three times to get resulting Co@Au or Co@Ag nanoparticles-decorated hierarchical TiO_2 nanostructures. They are named as $\text{Co@Au}/\text{TiO}_2$ or $\text{Co@Ag}/\text{TiO}_2$.

Characterization

The morphology of samples was observed by scanning electron microscopy (SEM; JSM-6700 F, Electron Optics Laboratory Co., Ltd, Tokyo, Japan) and transmission electron microscopy (TEM; JEOL-3010, Electron Optics Laboratory Co., Ltd, Tokyo, Japan). The chemical composition of samples was analyzed by transmission electron microscopy equipped with energy-dispersive X-ray (TEM/EDX; JEOL-3010, Electron Optics Laboratory Co., Ltd, Tokyo, Japan) spectroscopy. The special surface areas were determined by a Quantachrome Nova2000e surface area and pore size analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Absorbance spectra

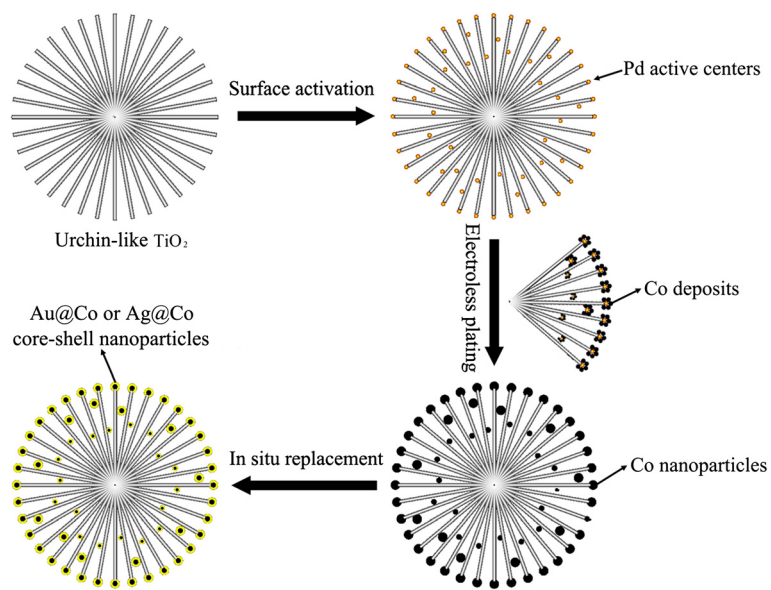


Figure 1 Synthesis process of the 3D urchin-like hierarchical TiO_2 nanostructures decorated with magnetically bimetallic core-shell nanostructures.

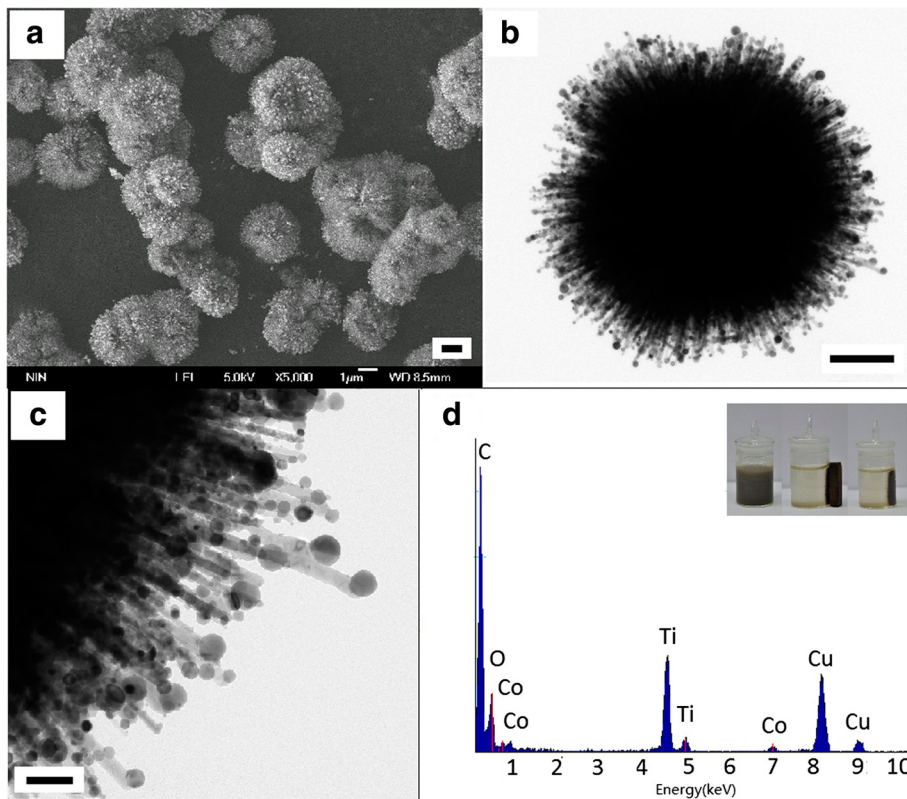


Figure 2 SEM image (a), TEM images (b, c), and EDX spectra (d) of the hierarchical Co/TiO_2 nanostructures. Inset in (d) shows the response of Co/TiO_2 to a magnet. (Scale bar = 1 μm for (a), scale bar = 500 nm for (b), scale bar = 100 nm for (c)).

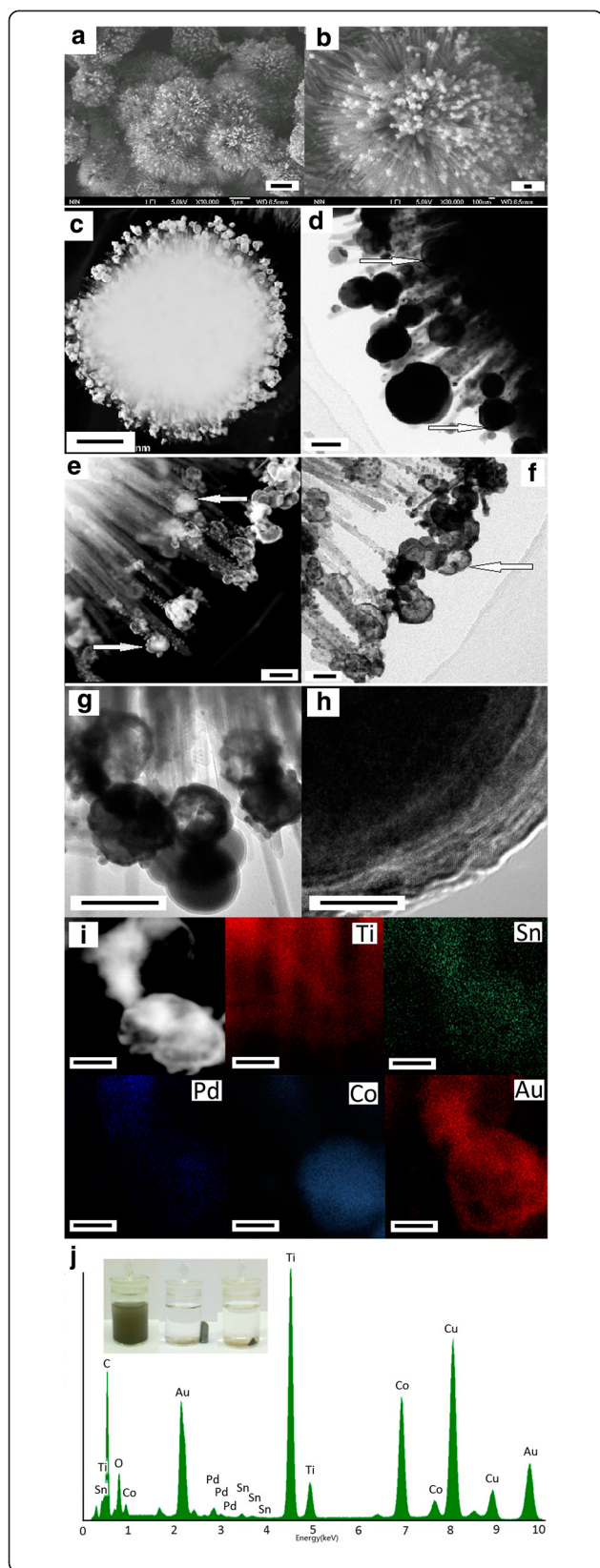


Figure 3 Typical morphology, structure, and composition of the hierarchical Co@Au/TiO_2 nanostructures. SEM images (a, b), dark-field and bright-field TEM images (c-f), high-resolution TEM images (g, h), the local elemental mapping (i), and corresponding EDX spectra of the nanoparticles on the tips of TiO_2 nanorods (j) for the 3D urchin-like hierarchical Au@Co/TiO_2 nanostructures. The inset in (j) shows the response of Au@Co/TiO_2 to a magnet. (Scale bar = 1 μm for (a), scale bar = 100 nm for (b), scale bar = 500 nm for (c), scale bar = 100 nm for (d-g), scale bar = 10 nm for (h), scale bar = 50 nm for (i)).

were measured using UV-vis spectrophotometer (HITACHI U-4100, HITACHI High-Technologies Corporation, Tokyo, Japan).

Decolorization procedures

Analytical-grade methyl blue (MB, molecular formula: $\text{C}_{37}\text{H}_{27}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3$, supplier: Tianjin Chemical Reagent Co. Ltd of China) was served as the target dye. Decolorization experiments are conducted at room temperature with a prepared solution of 40 mg/L MB dye in a 100-mL beaker. Typically, 10 mg of pure urchin-like TiO_2 , Co@Au/TiO_2 or Co@Ag/TiO_2 were respectively added into 30 mL of MB aqueous solution. After the suspension was stirred for about 15 min under daylight lamp of 40 W, the catalyst was separated by centrifugation and the reaction mixture was analyzed by UV-vis spectrophotometer (HITACHI U-4100).

Results and discussion

The synthesis process of the 3D urchin-like hierarchical Co@Au/TiO_2 or Co@Ag/TiO_2 nanostructures is shown schematically in Figure 1. Firstly, the urchin-like hierarchical TiO_2 nanostructures with diameters 1 to 4 μm are obtained by a solvothermal method [12,13]. Secondly, the surface of the urchin-like TiO_2 is implanted with Pd nanodots by activating treatment. The Pd nanodots will act as a catalyst for the next electroless plating of Co nanoparticles. Thirdly, Co nanoparticles are deposited around the Pd active centers in an electroless plating solution to obtain Co/TiO_2 . Finally, the Co/TiO_2 particles are dispersed into AgNO_3 solution or HAuCl_4 solution. Owing to the presence of seed Co nanodots, Ag^+ or Au^{3+} is reduced and Ag or Au shell is deposited outside the Co nanodots. Thus, 3D urchin-like hierarchical Co@Au/TiO_2 or Co@Ag/TiO_2 nanostructures are formed by *in situ* replacement.

The morphology and structure of the pure urchin-like hierarchical TiO_2 nanostructures have been characterized in detail in our previous article [12]. The diameters of TiO_2 nanostructures can be well controlled in the range of 1 to 4 μm . Figure 2 shows the typical SEM and TEM images of Co/TiO_2 nanostructures with the mole ratio of Co to TiO_2 of 0.15:1. It can be observed from

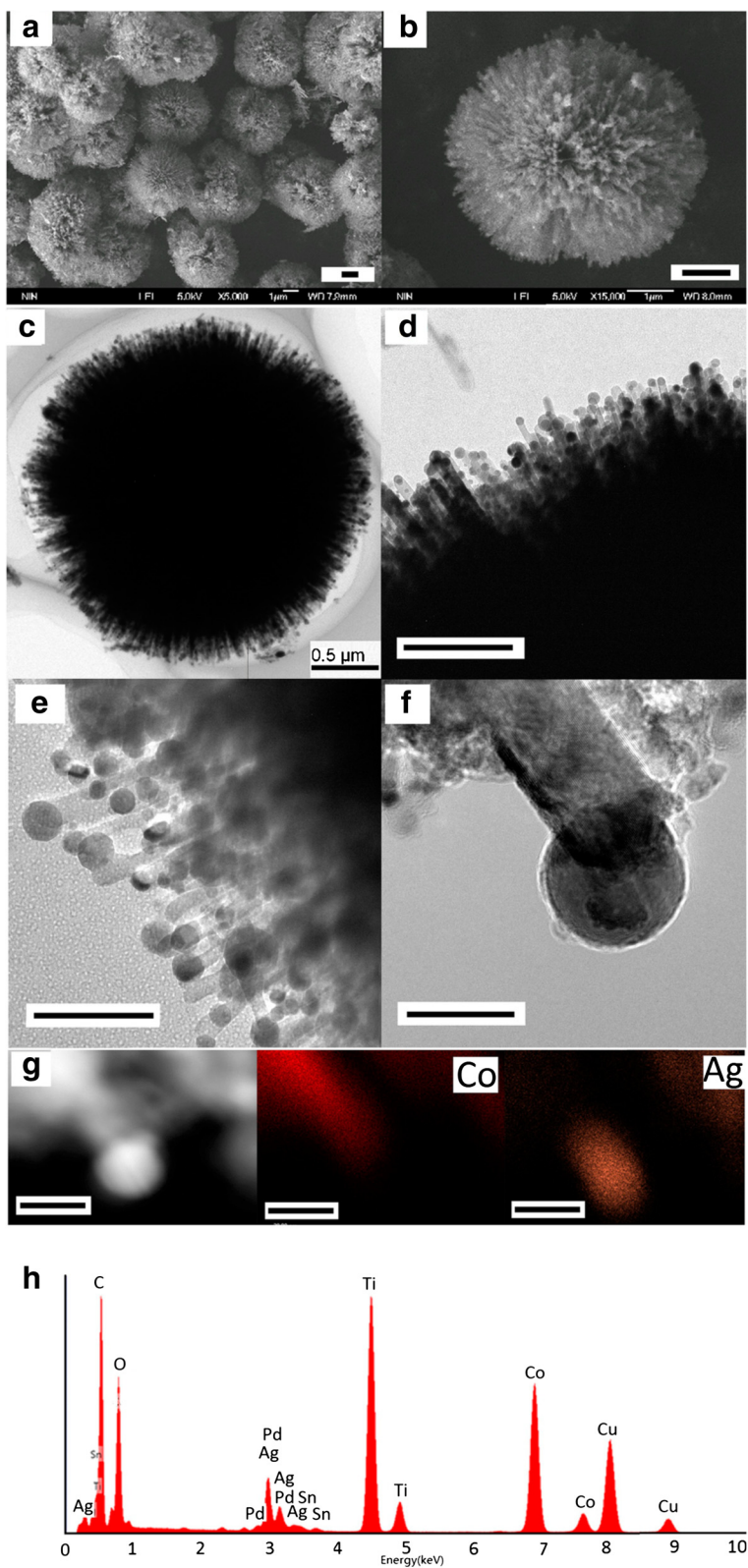


Figure 4 (See legend on next page.)

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Figure 4 Typical morphology, structure, and composition of the hierarchical Co@Ag/TiO₂. SEM images (a, b), TEM images (c, d), and high-resolution TEM images (e, f), the local elemental mapping (g), and corresponding EDX spectra of the nanoparticles on the tips of TiO₂ nanorods (h) for the 3D urchin-like hierarchical Ag@Co/TiO₂ nanostructures. (Scale bar = 1 μm for (a-b); scale bar = 500 nm for (c); scale bar = 200 nm for (d); scale bar = 100 nm for (e); scale bar = 20 nm for (f-g)).

Figure 2a that small spherical Co nanoparticles are assembled on the surface of 3D urchin-like TiO₂. According to the high-resolution TEM images as shown in Figure 2b, c, the Co nanoparticles are firmly attached on the surface of TiO₂ nanorods, and their diameters are in the range of 10 to 100 nm. Furthermore, the Co nanoparticles formed on the tip of TiO₂ nanorods are larger than that formed in the middle of nanorods. This can be ascribed to the space limitation. In addition, the size of Co nanoparticles, especially on the tip of TiO₂ nanorods, increases with the ratio of Co to TiO₂. The EDX analysis in Figure 2d shows that the Co/TiO₂ is composed of Ti, Co, and O elements. The signals of Cu and C are from the copper grid used. No Sn and Pd elements are detected by the EDX analysis, which may be due to their low content. However, small amounts of Sn and Pd elements can be determined by local high-resolution element mapping characterization (see Figure 3). The as-synthesized Co/TiO₂ sample shows a good magnetic response when exposed to an external magnetic field, as shown by the photograph inset in Figure 2d. These indicate that the Co nanoparticles have been well decorated onto the hierarchical TiO₂ nanostructures.

Figure 3 shows the typical morphology, structure, and composition of the Co@Au/TiO₂ nanostructures that are prepared with the mole ratio of HAuCl₄:CoCl₂:TiO₂ = 0.015:0.15:1. The SEM image in Figure 3a, b shows that the nanoparticles with an average diameter of about 80 nm are uniformly covered on the tips of TiO₂ nanorods, and the morphology of the Co@Au/TiO₂ particles looks like fireworks in full bloom. Both dark-field TEM image in Figure 3c and bright-field TEM image in Figure 3d show that most of the nanoparticles attached on tips of TiO₂ nanorods are spherical. The high-resolution bright and dark TEM images in Figure 3d, e, f, g, h clearly show that most of the nanoparticles are core-shell nanostructures as indicated by arrows in the figures. Meanwhile, some nanoparticles are well-defined core-shell structures as shown by arrows in Figure 3d, e, while some nanoparticles are complete hollow shell structures as shown by arrows in Figure 3f. In addition, there are many nanoparticles with diameters less than 10 nm adsorbed on the side of nanorods as shown in Figure 3e, f. These different structures of nanoparticles tell us that the replacement process is complex. The Co nanoparticles attached on the tip of nanorods have more opportunities to react with Au³⁺, and they are replaced more absolutely, and, as a

result, the hollow Au shells are formed [15]. However, the Co nanoparticles attached on the middle sites of nanorods have few chances to contact with Au³⁺ due to space limitation, and they are replaced incompletely, and, as a result, core/shell structures are not formed. In order to identify the bimetallic core-shell structure, the composition and structure of nanoparticles on the surface or tips of TiO₂ nanorods are further characterized by high-resolution TEM and the elemental mapping as shown in Figure 3g, h, i. It can be found from Figure 3g that the Co@Au nanoparticles are core/shell structures but they are not uniform. Some ones are well-defined core-shell structures, some are hollow, while some solid nanoparticles have a very thin shell. These different structures of nanoparticles indicate that the replacement process is complex. The local element mapping of this region shows the Co@Au/TiO₂ mainly contains Ti, Sn, Pd, Co, and Au. Meanwhile, the nanorods are mainly made of Ti element and small amounts of Sn and Pd elements. The nanoparticle on the tip is composed of Co and Au elements, and small amounts of Sn and Pd elements. In particular, the Co and Au distribution clearly shows the core/shell structure, which is in accordance with the TEM observation in bright-field and dark-field. Figure 3j gives the EDX analysis of this local element mapping region. The content of Ti, Sn, Pd, Co, and Au is 47.39, 0.80, 1.62, 28.55, and 21.53 at %, respectively. On the basis of these characterizations, it can be identified that hierarchical TiO₂ nanostructures decorated with core-shell Co@Au nanoparticles have been successfully prepared. The resulting Co@Au/TiO₂ also shows a good magnetic response when exposed to an applied external magnetic field as shown by the photograph inset in Figure 3j.

Figure 4 shows the morphology and the structure of a typical sample of Co@Ag/TiO₂ with a mole ratio of AgNO₃:CoCl₂:TiO₂ = 0.03:0.1:1. The SEM images (Figure 4a, b) show many light nanodots are adsorbed on urchin-like TiO₂ microspheres with the diameters about 3 μm. The TEM images (Figure 4c, d, e, f) show the nanodots cover on TiO₂ nanorods homogeneously, and the average diameters of the nanodots are about 10 to 20 nm. The composition and structure of nanoparticles on the tips of TiO₂ nanorods are mainly composed of Ti, Sn, Pd, Co, and Ag elements as shown in Figure 4g, h. The content of Ti, Sn, Pd, Co, and Ag is 48.16, 1.46, 1.15, 36.96, and 12.27 at%, respectively.

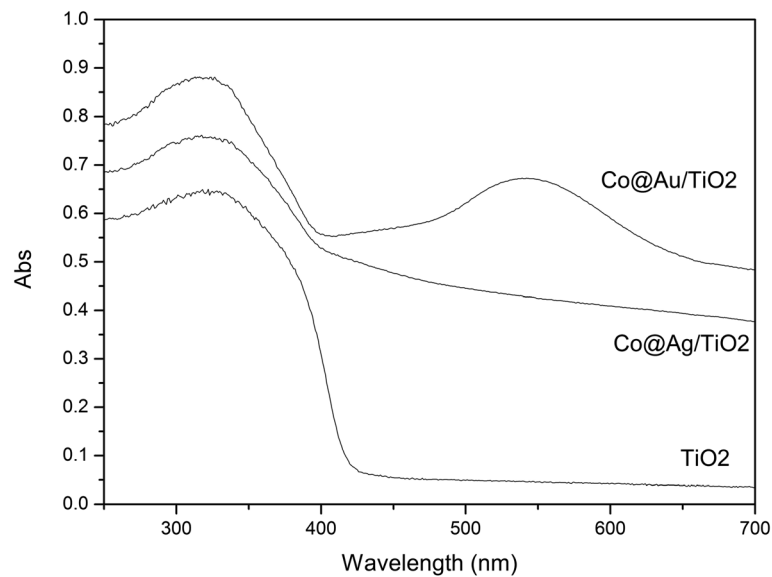


Figure 5 UV-visible absorption spectra of the hierarchical TiO_2 , Co@Au/TiO_2 , and Co@Ag/TiO_2 nanostructures.

The UV-vis absorption spectra of the urchin-like hierarchical TiO_2 , Co@Au/TiO_2 , and Co@Ag/TiO_2 nanostructures are shown in Figure 5. Obviously, decorating with Co@Au or Co@Ag bimetallic nanoparticles can enhance light-harvesting efficiency. Besides the absorption band of TiO_2 at the wavelength lower than 400 nm, a wide absorption band in the range of visible light can be observed in the spectra of Co@Au/TiO_2 and Co@Ag/TiO_2 nanostructures. Especially, the Co@Au/TiO_2 nanoparticles show a strong absorption peak at about 550 nm corresponding to the surface plasmon resonance of Au

nanoparticles. The Co@Ag/TiO_2 nanostructures do not show a strong absorption peak mainly because the corresponding surface plasmon resonance of Ag nanoparticles is located at a lower wavelength than 400 nm.

Finally, the Co@Au/TiO_2 and Co@Ag/TiO_2 nanostructures are also evaluated for decolorization of methyl blue (MB) solution, a model dye in wastewater of the dyeing industry. The removal of MB molecules from the aqueous solution using Co@Au/TiO_2 and Co@Ag/TiO_2 nanostructures is monitored by UV-vis spectroscopy as shown in Figure 6. It is found that the intensity of the

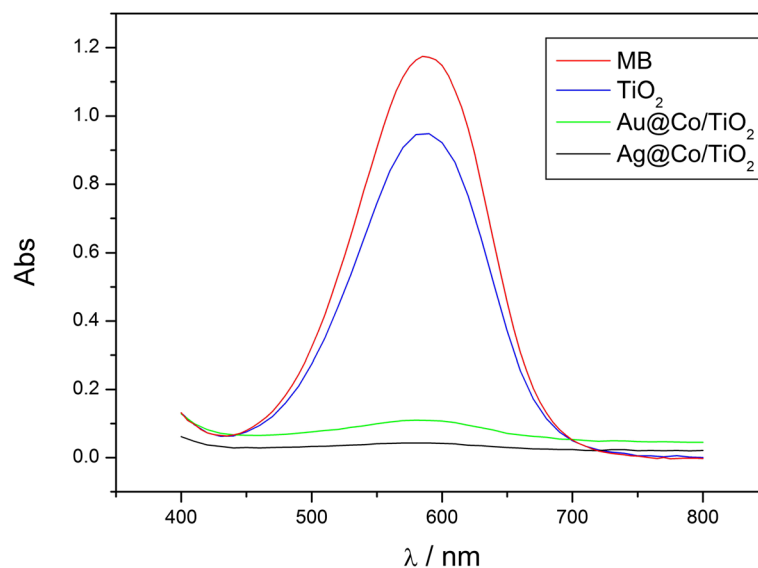


Figure 6 UV-visible absorption spectra of MB after interaction with hierarchical TiO_2 , Co@Au/TiO_2 , and Co@Ag/TiO_2 nanostructures. The spectra were measured after daylight lamp irradiation for 15 min.

characteristic absorption peak of MB at 590 nm significantly decreases in the presence of Co@Au/TiO₂ or Co@Ag/TiO₂ nanostructures, indicating the rapid decolorization of MB. In particular, compared to urchin-like TiO₂ nanostructures, the Co@Au/TiO₂ or Co@Ag/TiO₂ nanostructures show faster decolorization rate. For example, after daylight lamp irradiation for 15 min, the decrease of peak intensity of MB at 590 nm exceeds 90% in the presence of Co@Au/TiO₂ nanostructures and exceeds 95% in the presence of Co@Ag/TiO₂ nanostructures, which is distinctly faster than 19% of decolorization by pure urchin-like TiO₂. According to the N₂ adsorption-desorption isotherm, the special surface area of pure TiO₂, Co@Au/TiO₂, and Co@Ag/TiO₂ nanostructures is 35, 31, and 34 m²/g, respectively. The difference in the surface area of three samples is not significant. Therefore, the faster decolorization of MB solution in the presence of Co@Au/TiO₂ and Co@Ag/TiO₂ nanostructures can be mainly attributed to Co@Au and Co@Ag nanoparticles decorated on TiO₂, which have enhanced light-harvesting ability and improved the photocatalytic efficiency. The Co@Au/TiO₂ and Co@Ag/TiO₂ nanostructures can also retain their activity in repeated decolorization cycles. For example, after cycling decolorization for five times, the typical Co@Au/TiO₂ nanostructures still maintain 85% of decolorization after irradiation for 15 min, while Co@Ag/TiO₂ nanostructures maintain 90% of decolorization. In addition, it should be noted that the Co@Au/TiO₂ or Co@Ag/TiO₂ is also suitable for decolorization of other dyes, such as methyl orange (MO), etc., but the decolorization rate for MO is much slower compared to that for MB. The similar phenomenon has also been reported in other references, which can be attributed to the difference of molecular structure between MO and MB [16].

Conclusions

In this paper, we have presented a type of 3D urchin-like hierarchical TiO₂ nanostructures decorated with magnetically bimetallic core-shell nanoparticles. The urchin-like TiO₂ nanostructures are used as templates, magnetic Co nanoparticles are introduced onto TiO₂ nanostructures by electroless plating, and finally, the Au or Ag shell is formed on Co nanoparticles by *in situ* replacement reaction. The resulting Co@Au/TiO₂ and Co@Ag/TiO₂ nanostructures not only possess a good magnetic response to an applied external magnetic field but also show enhanced light-absorption ability due to surface plasmon absorption of Au and Ag in the visible region. Decolorization experiments show that the Co@Au/TiO₂ and Co@Ag/TiO₂ nanostructures can decolorize methyl blue more effectively compared to pure TiO₂ nanostructures. The unique structures and enhanced multifunctional characteristics will allow the 3D bimetallic core-shell

nanoparticle-decorated TiO₂ nanostructures to have potential applications in a wide range of fields.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

LX carried out the preparations and characterization and drafted the manuscript. SL participated in parts of the materials preparations and characterization. JY performed the mechanism analysis of the novel structures. XZ conceived the study and participated in its design and coordination and helped to draft the manuscript. All authors read and approved the final manuscript.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Nos. 11174234 and 51272215) and NPU Foundation for Fundamental Research (No. JC201159).

Received: 28 November 2014 Accepted: 9 February 2015

Published online: 27 February 2015

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