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Dear Editor :

We are enclosing herewith manuscript entitled, “Effect of core@shell (Au@Ag) nanostructure on surface plasmon-induced photocatalytic activity under visible light irradiation” by Sunao Kamimura, Shinpei Yamashita, Toshiki Tsubota, and Teruhisa Ohno.

In this paper, we report Au-Ag nanoparticles (NPs) with two different morphologies and clarify the effect of its composite nanostructure on surface plasmon-induced photocatalytic activity; core@shell (Au@Ag) NPs or Au-Ag bimetallic NPs were supported on the SrTiO₃ photocatalyst.

Recently, Au-Ag NPs have attracted considerable attention as photosensitizers of semiconductor photocatalysts under visible light irradiation. However, previous studies were directed towards the control of absorption wavelength by mixing Au and Ag NPs. Thus, it is not clear whether a core@shell (Au@Ag) structure is better than an Au-Ag bimetallic structure for realizing efficient photocatalytic activity.

We revealed that the photocatalytic activity of (Au@Ag)/SrTiO₃ was greater than that of Au-Ag bimetallic/SrTiO₃. We discuss the synthesis and characterization of the morphologies, absorption properties and photocatalytic activities of (Au@Ag)/SrTiO₃ and Au-Ag bimetallic/SrTiO₃ together with results of analysis of its XPS properties.

We would be most grateful if this manuscript could be reviewed and considered for publication in *Applied Catalysis B: Environmental* as soon as possible. Correspondence about the paper should be directed to Teruhisa Ohno at the following address, phone and fax number, and e-mail address.

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Effect of core@shell (Au@Ag) nanostructure on surface plasmon-induced
photocatalytic activity under visible light irradiation

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ABSTRACT

We prepared Au-Ag nanoparticles (NPs) with two different morphologies over SrTiO₃ to investigate the effect of composite nanostructure on surface plasmon-induced photocatalytic activity; core@shell (Au@Ag) NPs were synthesized by a multi-step citric reduction method, and Au-Ag bimetallic NPs were prepared by a photo-reduction method. (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃ showed strong photoabsorption in the visible light response due to a localized surface plasmon resonance (LSPR) of Ag. Moreover, they could oxidize 2-propanol to acetone and CO₂ under visible light irradiation ($440 < \lambda < 800$ nm). From a comparison of action spectra for acetone evolution and the Kubelka-Munk function, it was confirmed that photocatalytic activities of (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃ were induced by photoabsorption based on LSPR excitation of Ag. Interestingly, the rate of acetone evolution over (Au@Ag)/SrTiO₃ was 1.5-times higher than that of over Au-Ag/SrTiO₃, suggesting that the core@shell (Au@Ag) nanostructure contributes to the efficient surface plasmon-induced photocatalytic activity.

1. INTRODUCTION

Surface plasmon resonances in metallic nanoparticles (NPs) are currently being exploited for a variety of applications including molecular sensing [1-5], focusing of light [6], near-field optical microscopy [7], and subwavelength photonics [8]. Surface plasmon-induced charge separation at the interface between metallic NPs and a metal-oxide semiconductor has attracted considerable attention as a potential means of converting light energy into electrical energy in the form of hot electrons, which can be utilized for efficient photovoltaic and photocatalytic devices [9-11]. These research fields were inspired by a report in 2004 by Tatsuma *et al.*, who found that a TiO₂ film loaded with Au and Ag NPs exhibited negative potential changes and anodic currents in response to visible light irradiation [12]. Moreover, they revealed that TiO₂ films loaded with Au NPs (denoted as Au/TiO₂ hereafter) showed photocatalytic oxidation of alcohol under visible light irradiation [13]. After these breakthroughs, tremendous work on surface plasmon-induced photocatalytic reaction has been done by using a metal-oxide semiconductor and precious metal NPs (Au, Ag, Cu, etc.), and these techniques are currently used for water splitting, CO₂ reduction, organic molecule degradation, and selective organic synthesis [14-20].

Recently, we have developed core@shell (Au@Ag) NPs by a multistep citrate reduction method for utilization as a photosensitizer of a TiO₂ photocatalyst [21]. (Au@Ag)/TiO₂ showed strong photoabsorption in a visible light response due to the surface plasmon resonance of Ag in (Au@Ag) NPs. Moreover, (Au@Ag)/TiO₂ exhibited photocatalytic decomposition of 2-propanol under visible light irradiation ($\lambda > 440$ nm), and its photocatalytic reaction rate was greater than that of Ag/TiO₂ and Au/TiO₂. Xu *et al.* and Duan *et al.* also reported that core@shell (Au@Ag) NPs can

significantly enhance photocatalytic activity over semiconductor materials under visible light irradiation, compared to Au NPs [22,23]. Thus, core@shell (Au@Ag) NPs are considered to be a good candidate as a photosensitizer of a photocatalyst. However, it is not clear whether a core@shell (Au@Ag) structure is better than an Au-Ag bimetallic structure for realizing efficient surface plasmon-induced photocatalytic activity. Indeed, Au-Ag bimetallic NPs have attracted considerable attention from the viewpoints of a tunable absorption band, improvement of catalytic activity and photosensitizer of a photocatalyst [24-26]. Zaleska *et al.* reported that bimetallic Au-Ag/TiO₂ showed greater visible light photocatalytic activity than that of Ag/TiO₂ or Au/TiO₂ [27]. However, there is no report concerning the effect of an Au-Ag composite nanostructure on surface plasmon-induced photocatalytic activity. In this study, we examined the photocatalytic activities of SrTiO₃ loaded with core@shell (Au@Ag) NPs and SrTiO₃ loaded with Au-Ag bimetallic NPs in conjunction with optical and structural properties.

2. EXPERIMENTAL

2.1. Synthesis of core@shell (Au@Ag) NPs

(Au@Ag) NPs were synthesized by a multistep citrate reduction method as follows [21]. Au NPs were prepared for use as seeds for the synthesis of (Au@Ag) NPs. Hydrogen tetrachloroaurate (III) tetrahydrate (99.0%, Wako), trisodium citrate (99.0%, Wako) and polyvinylpyrrolidone ((C₆H₉NO)_n; n=27~32, Wako) as starting reagents were mixed thoroughly in distilled water at 70 °C. The mixed solution was stirred for 1 h and cooled to room temperature. The obtained suspension of Au NPs was a dark reddish color with an LSPR band at 522 nm, and average diameter of the Au NPs was 9 nm. The Ag shell was grown on the Au seeds via seed-mediated growth for

(core@shell) Au@Ag NPs. The obtained suspension of Au NPs was heated to reflux and then silver nitrate (99.5%, Wako) and trisodium citrate were simultaneously added. After refluxing for 35 minutes, (Au@Ag) NPs were obtained.

2.2. Loading of (Au@Ag) NPs on SrTiO₃

(Au@Ag) NPs were supported on SrTiO₃ (purchased from Wako) by an impregnation method. The impregnation supporting was carried out by the following procedures. The SrTiO₃ powder and colloidal (Au@Ag) NPs were put into an eggplant-shaped flask. The mixed solution was dispersed by sonication for 5 minutes and then dried by using a rotary evaporator on a water bath. After evaporation, the residue was washed with distilled water several times. The residual water was completely removed by using a vacuum freeze-drying method. Then (Au@Ag)/SrTiO₃ was obtained.

2.3. Loading of Au-Ag bimetallic NPs on SrTiO₃

Au-Ag bimetallic NPs were loaded on SrTiO₃ by a photo-reduction method as described in a previous report [24]. First, 0.4 g SrTiO₃ powder was dispersed in distilled water (10 mL) contained methanol (10 mL). Then, 0.03 M hydrogen tetrachloroaurate (III) tetrahydrate added to the mixed solution after Ar bubbling for 30 min, and the mixed solution was irradiated with UV light was irradiated. Then, 0.05 M silver nitrate was added, and the mixed solution was irradiated with UV light was irradiated. After this process had been repeated for a maximum of 4 times, Au-Ag bimetallic NPs were formed on the SrTiO₃ nanoparticles.

2.4. Characterization

The crystalline phase of SrTiO₃ was characterized by using a powder X-ray diffraction (XRD) instrument (MiniFlex II, Rigaku Co.). The structure of (Au@Ag) NPs was characterized by using a field emission high-resolution transmission electron microscope (HR-TEM; Tecnai G2 F30 S-TWIN, FEI) with a high-angle annular dark-field (STEM-HAADF) detector and by energy-dispersive X-ray spectroscopy (EDS) elemental mapping. The amount of (Au@Ag) NPs loaded on SrTiO₃ was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP-AES). A diffuse reflectance spectrum was acquired at room temperature with a UV/VIS spectrometer (UV-2600, Shimadzu Co.) attached to an integral sphere. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos AXIS Nova spectrometer (Shimadzu Co.) with a monochromatic Al K α X-ray source. The binding energy was calibrated by taking the carbon (C) 1s peak of contaminant carbon as a reference at 284.6 eV.

2.5. Photocatalytic decomposition of 2-propanol

Photocatalytic activity of (Au@Ag)/SrTiO₃ was evaluated by photocatalytic decomposition of 2-propanol. Sample powder (0.22 mg) was spread on a glass dish (4.0 cm²) and placed in a Tedlar bag with a volume of 125 cm³. The 500 ppm of gaseous 2-propanol was injected into the Tedlar bag, where gaseous composition was 79% N₂, 21% O₂, <0.1 ppm of CO₂ and 500 ppm of 2-propanol. After 2-propanol had reached an absorption equilibrium, the sample was irradiated with visible light at room temperature. A xenon lamp was used as a light source, and the irradiation wavelength was controlled by using a Yellow-44 filter and a heat absorbing filter ($440 < \lambda <$

800 nm). The intensity of light was adjusted to 50 mW/cm². The concentrations of 2-propanol, acetone and CO₂ were estimated by gas chromatography (Agilent/Inficon 3000 Micro GC) with a PLOT U column and an OV-1 column. Apparent quantum efficiency (AQE) at each wavelength was calculated from the ratio of the amount of acetone and the amount of incident photons. AQE was measured by using a Xe lamp equipped with a band-pass filter centered at 400 nm, 450 nm, 470 nm, 500 nm, 550 nm and 600 nm, respectively (All band-pass filters were purchased from Asahi Spectra Co., Ltd., and full width at half maximum was 10 nm.).

3. RESULTS AND DISCUSSION

Figure 1a and **1b** show a TEM photograph and distribution of colloidal (Au@Ag) NPs, revealing that (Au@Ag) NPs have an average particle size of 15 nm within a relatively sharp distribution. **Figure 1c** shows STEM-HAADF images of colloidal (Au@Ag) NPs. Since the intensity (brightness) is approximately proportional to the square of the atomic number (Z^2) in a STEM-HAADF image, heavier Au atoms (atomic number: $Z= 79$) give rise to a brighter image than do lighter Ag atoms ($Z= 47$). As shown in **Fig. 1d-1f**, EDS elemental mapping revealed that the Au core is uniformly covered by the Ag shell. These results indicated that (Au@Ag) NPs could be synthesized by a multistep citrate reduction method.

Figure 2a-2f show a STEM-HAADF image of Au-Ag/SrTiO₃ and EDS elemental mapping images. Although data acquisition with high resolution was difficult due to sample drift, STEM-HAADF and EDS images indicated that the Au L edge and Ag L edge were located at same position over the SrTiO₃ particle. These results suggested

that Au-Ag bimetallic NPs could be formed on SrTiO₃ particles by the photo-reduction method.

Figure 3a and **3b** show TEM photographs of 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃, respectively. There was no notable difference in particle size (ca. 15 nm) or shape of metallic NPs. The amount ratio of Au to Ag was estimated by ICP-AES analysis and it was confirmed that 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃ consisted of Au : Ag = 1 : 3.8~4.0 and Au : Ag = 1 : 4.0, respectively. **Figure 3c** shows diffuse reflection spectra of 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃ together with the diffuse reflection spectrum of bare SrTiO₃. Bare SrTiO₃ showed only strong photoabsorption at $\lambda < 380$ nm, which was ascribed to the band-gap excitation. On the other hand, 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃ showed similar absorption spectra in the visible light range with peaks located at 463 nm and 465 nm, respectively. These spectra were considered to be due to localized surface plasmon resonance (LSPR) excitation of Ag [21]. The photoabsorption spectrum of Au NPs was generally observed at around 560 nm due to its LSPR excitation [28]. However, in the case of (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃, the LSPR excitation band of Au NPs could not be detected. One of the reasons for the appearance of a monomodal LSPR band corresponding to Ag is that the Au cores are uniformly covered by Ag shells and the optical contribution from the Au cores is completely screened [29]. Another reason is that the amount ratio of Au to Ag is small.

Photocatalytic activity was evaluated by oxidation of 2-propanol in gas phase. **Figure 4a** and **4b** show time courses of acetone and CO₂ evolution from decomposition of 2-propanol over 1.0 wt% (Au@Ag)/SrTiO₃, 1.0 wt% Au-Ag/SrTiO₃ and SrTiO₃

under visible light irradiation ($440 < \lambda < 800$ nm). Acetone evolution increased almost linearly with irradiation time up to 10 h, followed by gradual saturation with irradiation time due to accumulation of acetone on the surface of (Au@Ag)/SrTiO₃. After prolonged visible light irradiation, the acetone was finally decomposed into CO₂. This behavior is plausible as it is known that 2-propanol decomposes into CO₂, which is the final product, via acetone, the intermediary product [30-32]. It should be noted that acetone and CO₂ were not detected either under dark conditions or under visible light irradiation in the absence of (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃.

In general, surface plasmon-induced photocatalytic reaction can be understood on the basis of the electron injection model: (1) incident photons are absorbed by the metallic NPs through their LSPR excitation, (2) electrons in the metallic NPs are injected into the bulk of the semiconductor photocatalyst, and (3) the resultant electron-deficient metallic NPs can oxidize various organic compounds to be recovered to the original metallic NPs state. Indeed, we have revealed that electron injection occurred from LSPR-excited metallic NPs into the TiO₂ bulk under visible light irradiation [21]. Thus, surface plasmon-induced photocatalytic activity is triggered by photoabsorption of metallic NPs, and metallic NPs greatly contribute to the photocatalytic activity.

An action spectrum is a strong tool for determining whether a photocatalytic reaction observed in samples occurs via photoabsorption of metallic NPs or a thermocatalytic process. To obtain an action spectrum, acetone evolution from decomposition of 2-propanol over 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃ was measured at room temperature under visible light irradiation. The AQE at each wavelength was calculated from the ratio of the amount of acetone and the

amount of incident photons, using the following equation:

$$AQE = \frac{\text{amount of acetone molecules}}{\text{amount of incident photons}},$$

As shown in **Fig. 5a** and **5b**, each AQE plot was in agreement with the Kubelka-Munk function, indicating that photocatalytic activity observed in (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃ was induced by photoabsorption based on LSPR excitation of Ag. Thus, Ag in both types of metallic NPs displayed strong photoabsorption in the visible light range due to LSPR excitation and greatly contributed to photocatalytic activity; (Au@Ag)/SrTiO₃ showed higher photocatalytic activity than that of Au-Ag/SrTiO₃ under visible light irradiation.

Incidentally, it is well known that Ag NPs have great susceptibility to oxidation [33-35]; that is, Ag NPs are oxidized at the interface between Ag and the semiconductor photocatalyst, leading to the formation of silver oxide. The oxidation of Ag gives rise to a decrease in photoabsorption intensity. **Figure 7** shows the results of cycle tests of acetone evolution from decomposition of 2-propanol over 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃ under visible light irradiation ($440 < \lambda < 800$ nm). In both samples, acetone evolution increased almost linearly with irradiation time. As in the first cycle, acetone evolution was increased with irradiation time, indicating that (Au@Ag)/SrTiO₃ continuously decomposed 2-propanol under visible light irradiation without losing their activity. To clarify the valence state of Ag in both types of NPs, XPS measurements were carried out before and after the photocatalytic reaction test. **Figure 9a** and **9b** show Ag 3d XPS spectra of 1.0 wt% (Au@Ag)/SrTiO₃ and 1.0 wt% Au-Ag/SrTiO₃, respectively. Before the photocatalytic reaction test, two peaks located at 368.1 eV and 374.2 eV were observed in (Au@Ag)/SrTiO₃, the peaks being attributed to typical values of Ag(0) 3d_{5/2} and 3d_{3/2}, respectively. These peak profiles

were barely changed after the photocatalytic test, indicating that (Au@Ag)/SrTiO₃ was stable upon photocatalytic reaction or photo-irradiation. For Au-Ag/SrTiO₃, strong peaks located at 367.1 eV and 373.1 eV were observed before the photocatalytic reaction test, in addition to XPS spectra of Ag(0). These strong and broad peaks were identified to be divalent silver ions, suggesting that Au-Ag NPs were partially oxidized to AgO before the photocatalytic reaction test. Sukhishvili *et al.* reported that surface oxidation of Ag NPs hinders charge transfer between Ag NPs and substances [36]. We speculated that partial oxidation of Au-Ag bimetallic NPs suppressed photocatalytic oxidation of 2-propanol, resulting in lower activity than that of compared to (Au@Ag)/SrTiO₃. In the case of (Au@Ag)/SrTiO₃, chemical stability of the Ag shell can be enhanced by coupling the Ag shell to the Au core due to a charge transfer that increases electron density within the Ag shell, yielding a negative Ag oxidation state [37, 38]. Thus, photocatalytic activity of (Au@Ag)/SrTiO₃ was higher than that of Au-Ag/SrTiO₃ under visible light irradiation.

4. CONCLUSIONS

We prepared core@shell (Au@Ag)/SrTiO₃ and bimetallic Au-Ag/SrTiO₃ to clarify the effect of composite nanostructure on surface plasmon-induced photocatalytic activity. (Au@Ag)/SrTiO₃ and bimetallic Au-Ag/SrTiO₃ showed similar photo-absorptions in the visible light range, which were attributed to localized surface plasmon resonance (LSPR) excitation of Ag in both types of metallic NPs. The (Au@Ag)/SrTiO₃ and bimetallic Au-Ag/SrTiO₃ could oxidize 2-propanol to acetone and CO₂ under visible light irradiation ($440 < \lambda < 800$ nm), and the rate of acetone evolution over (Au@Ag)/SrTiO₃ was greater than that of Au-Ag/SrTiO₃. From the action

spectra, it was confirmed that photocatalytic activities of (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃ were induced by photoabsorption based on LSPR excitation of Ag in both types of metallic NPs. Based on the results of XPS spectra, it was revealed that a chemical stability of Ag was improved by forming core@shell structure, which leads to efficient surface plasmon-induced photocatalytic activity.

ACKNOWLEDGEMENTS

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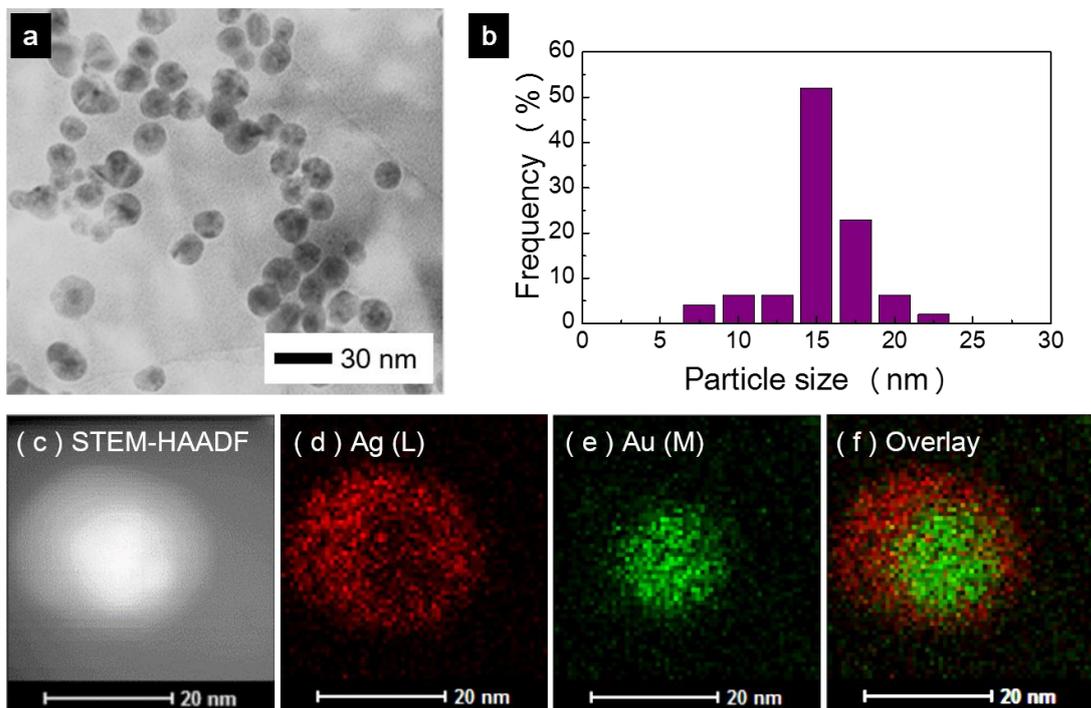


Figure 1. (a) TEM photograph and (b) size distributions of colloidal (Au@Ag) NPs. (c) STEM-HAADF image and (d-f) EDS elemental mapping images of colloidal (Au@Ag) NPs.

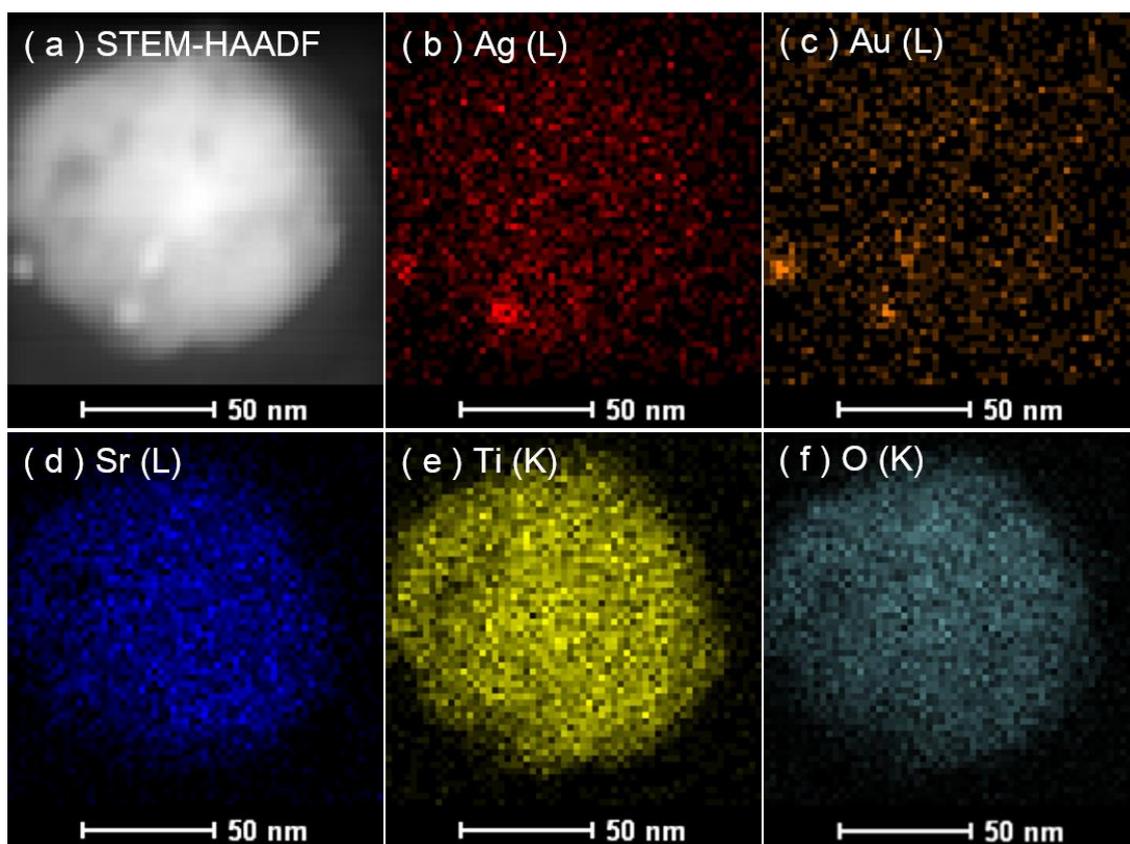


Figure 2. (a) STEM-HAADF image and (b-f) EDS elemental mapping of 1.0 wt% Au-Ag/SrTiO₃ prepared by a photo-reduction method.

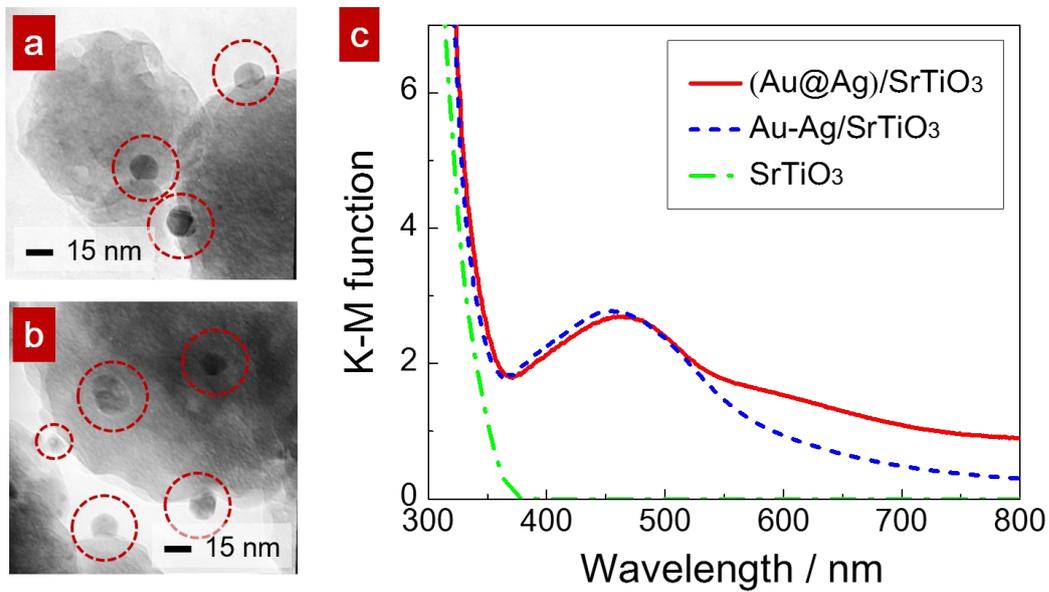


Figure 3. TEM photograph of (a) SrTiO₃ loaded with 1.0 wt% (Au@Ag) NPs, and (b) SrTiO₃ loaded with 1.0 wt% Au-Ag bimetallic NPs. (c) K-M functions of 1.0 wt% (Au@Ag)/ SrTiO₃ (solid line), 1.0 wt% Au-Ag/ SrTiO₃ (broken line) and bare SrTiO₃ (chain line).

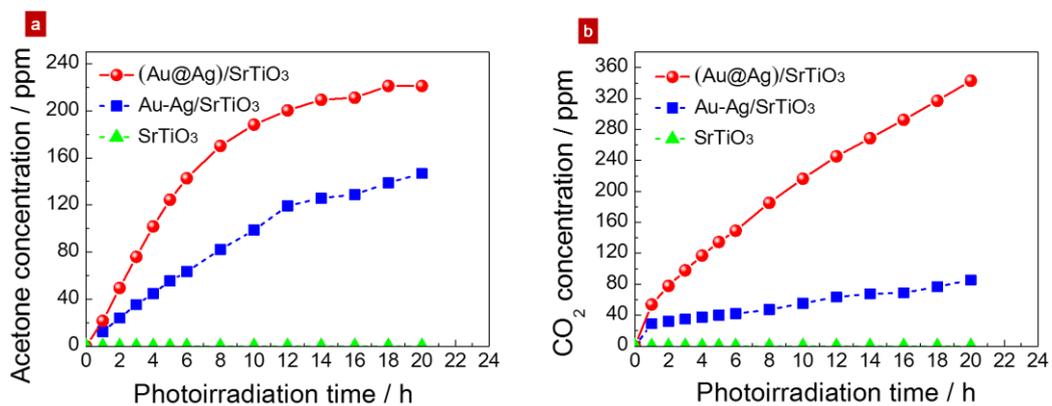


Figure 4. Time courses of (a) acetone evolution and (b) CO₂ evolution from 2-propanol decomposition over 1.0 wt% (Au@Ag)/SrTiO₃, Au-Ag/ SrTiO₃ and SrTiO₃ under visible light irradiation ($440 < \lambda < 800$ nm, intensity = 50 mW/cm²).

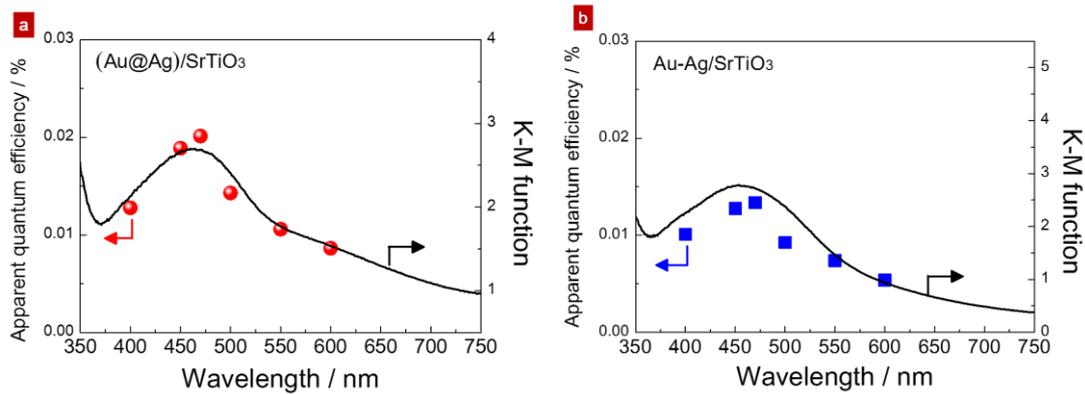


Figure 5. Action spectra of acetone evolution from 2-propanol decomposition over (a) 1.0 wt% (Au@Ag)/SrTiO₃ and (b) 1.0 wt% Au-Ag/SrTiO₃ together with Kubelka-Munk functions.

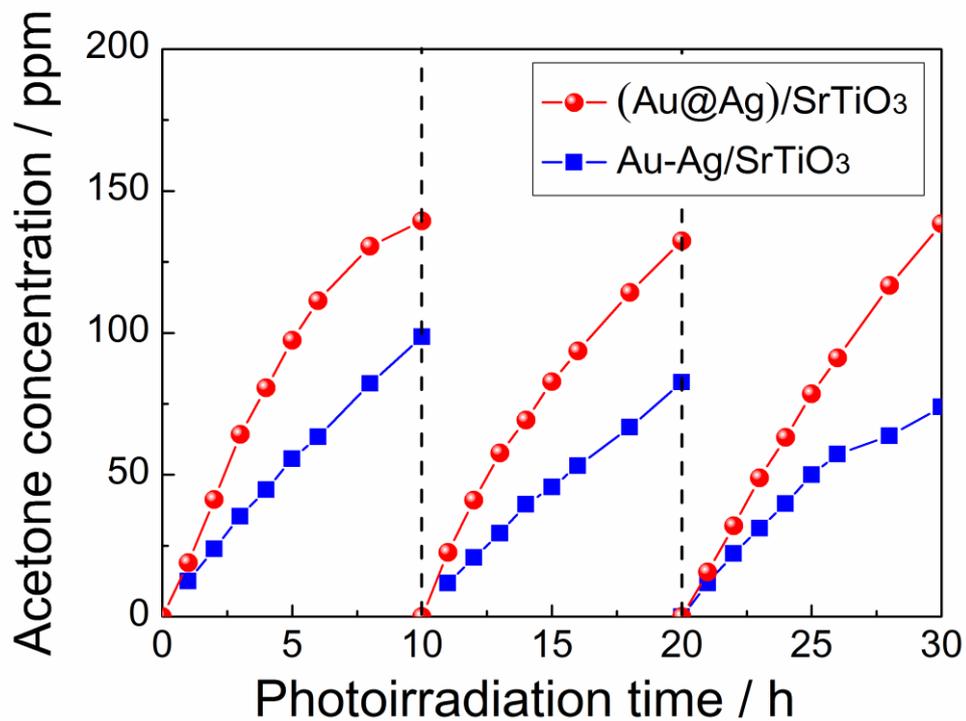


Figure 6. Time courses of acetone evolution from 2-propanol decomposition over 1.0 wt% (Au@Ag)/SrTiO₃ (solid circle) and 1.0 wt% Au-Ag/SrTiO₃ (solid square) under visible light irradiation ($440 < \lambda < 800$ nm, intensity = 50 mW/cm²) measured up to 3 cycles. After 10 h and 20 h, residual gas was evacuated and additional 2-propanol (500 ppm) was injected and photo-irradiated again.

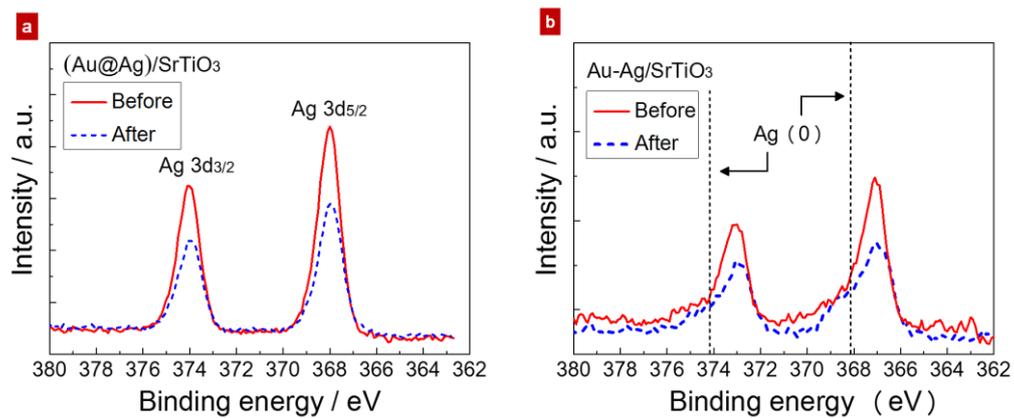


Figure 7. XPS spectra of Ag 3d of (a) (Au@Ag)/SrTiO₃ and Au-Ag/SrTiO₃ before (solid lines) and after (broken lines) photocatalytic reaction tests for decomposition of 2-propanol.

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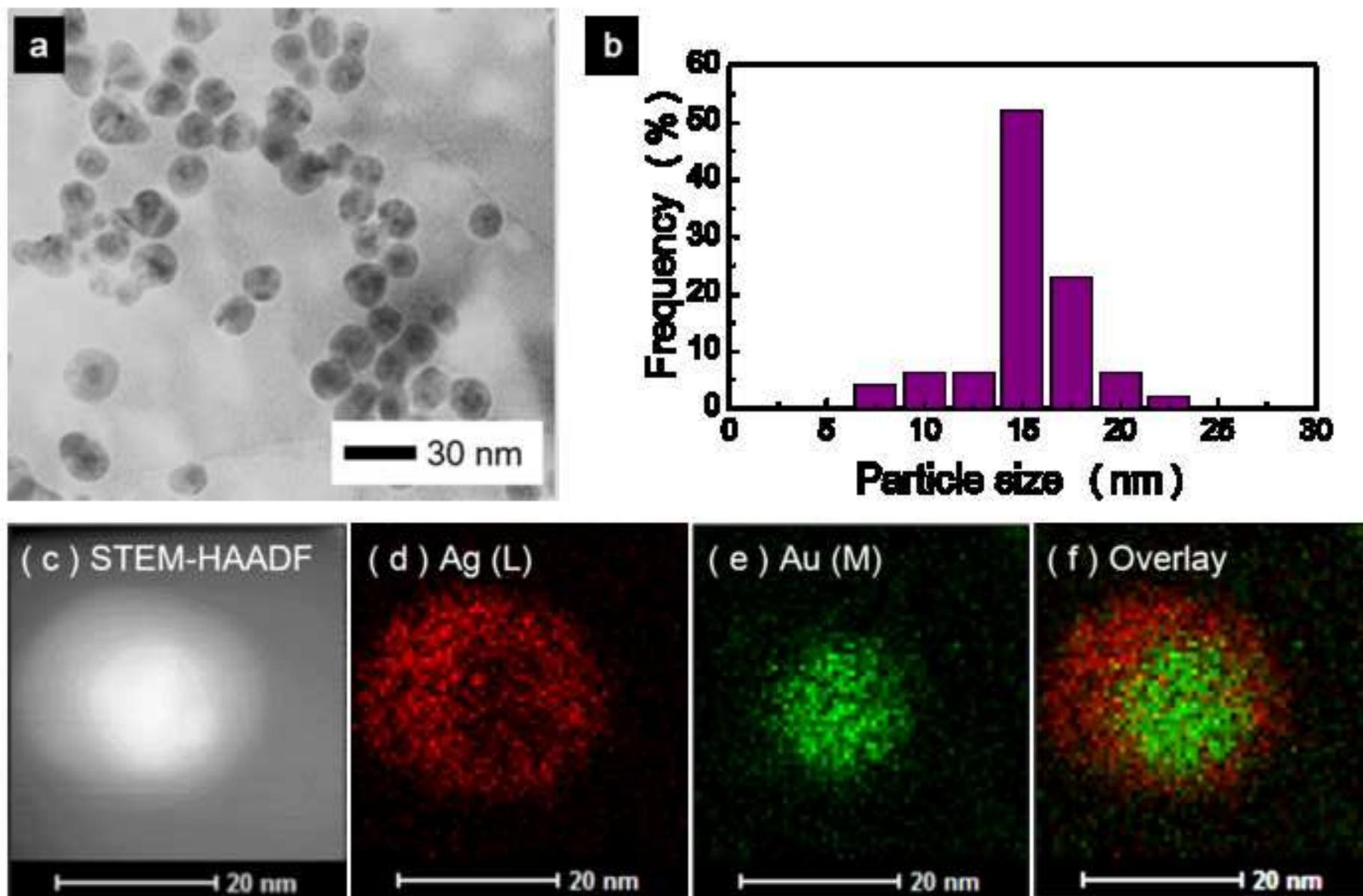


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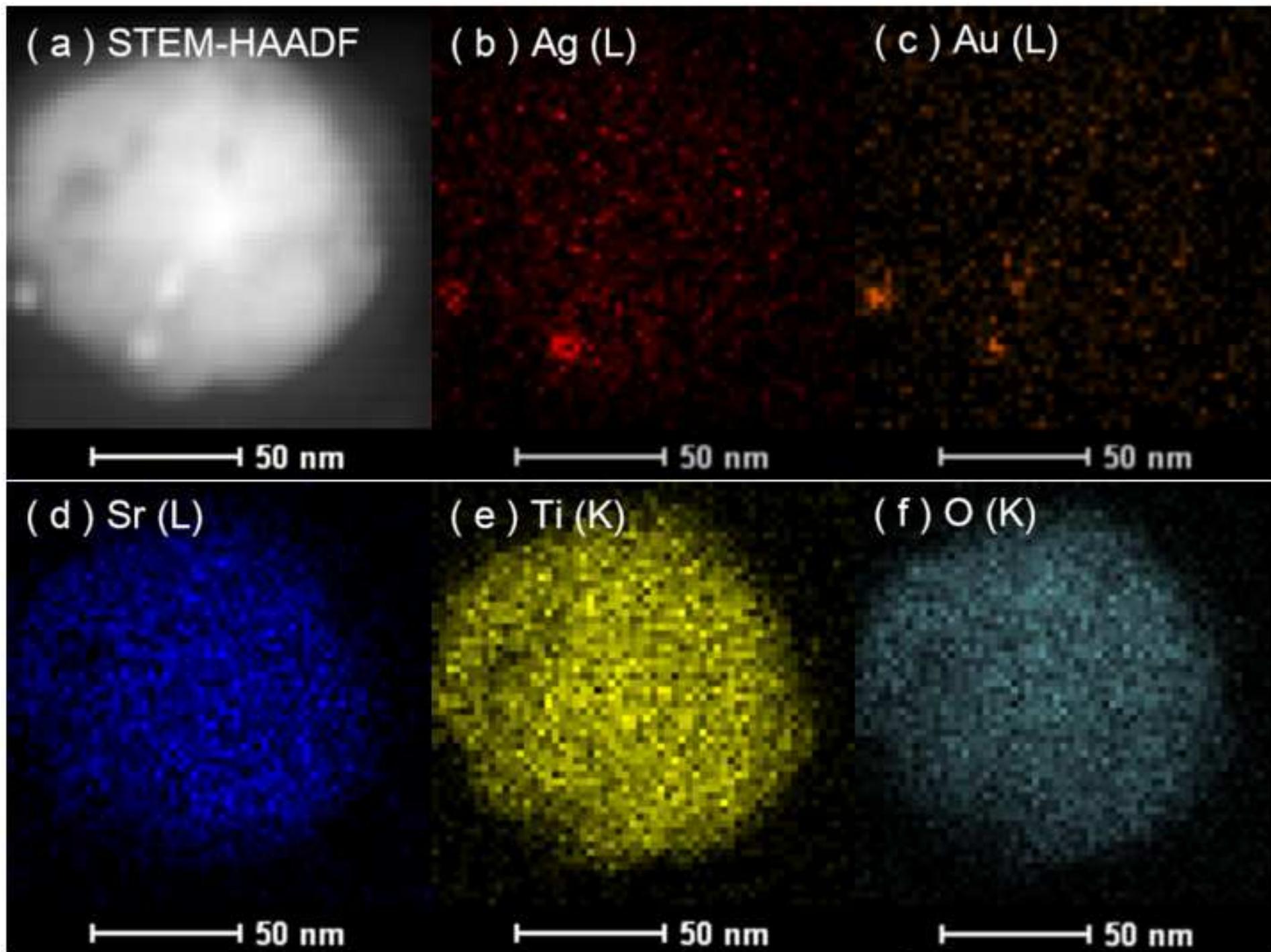


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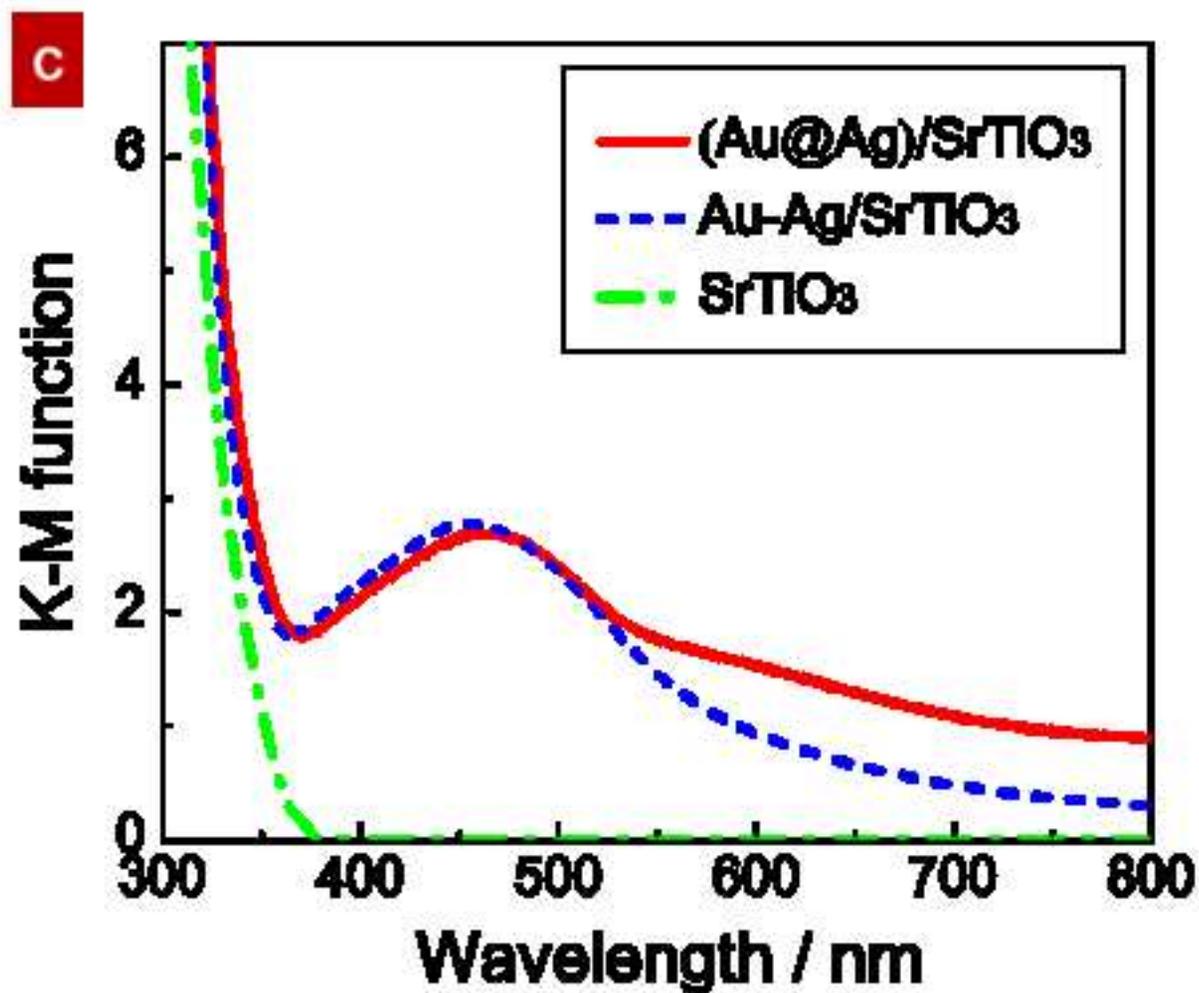
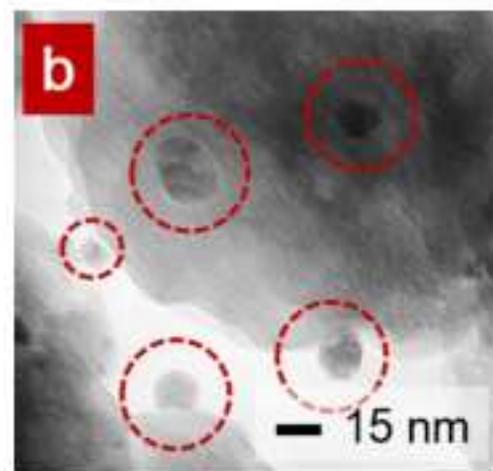
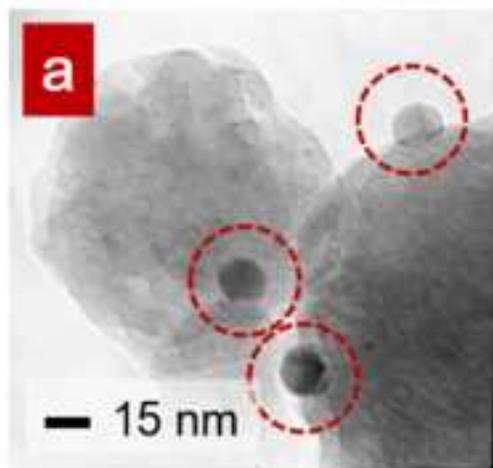


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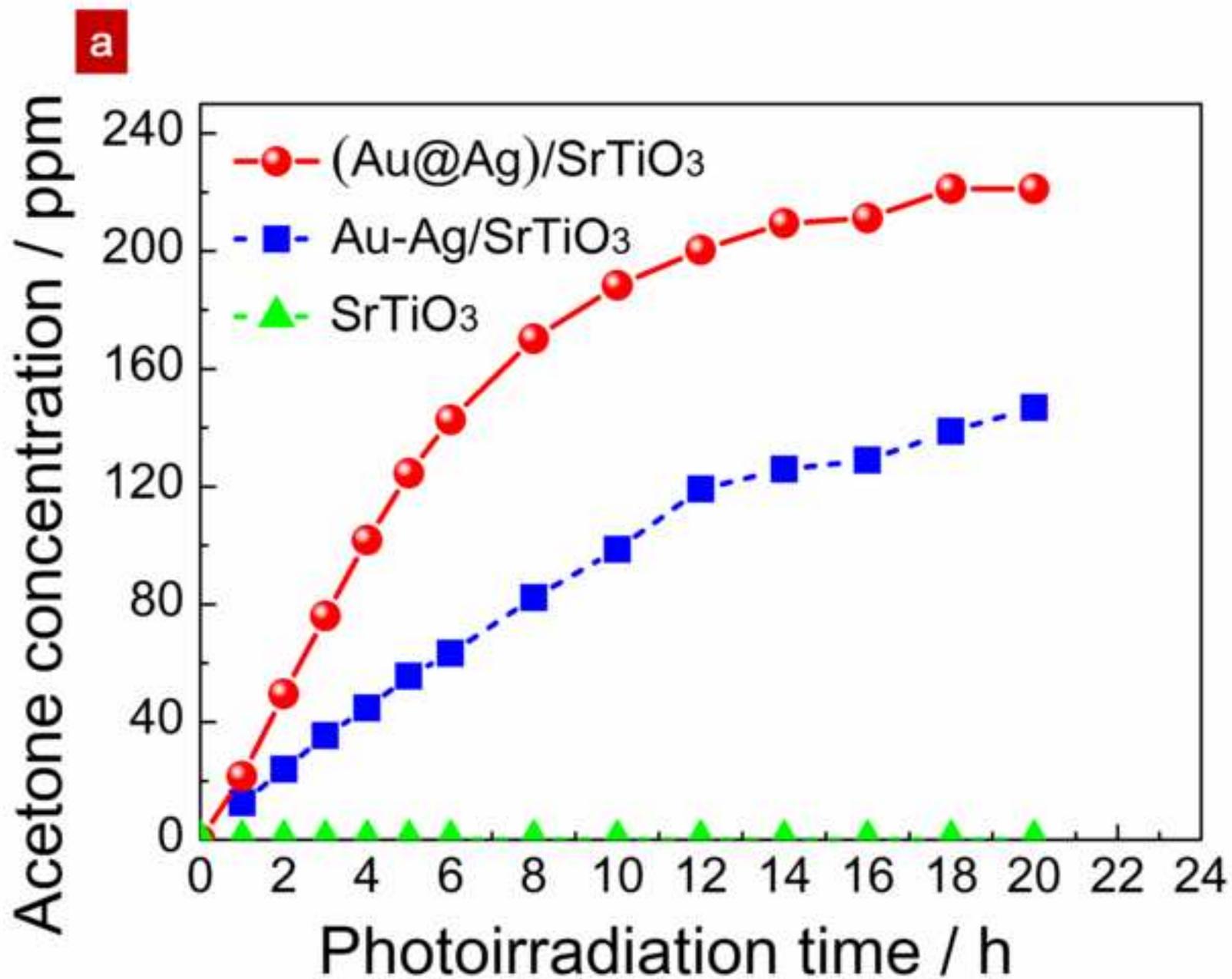


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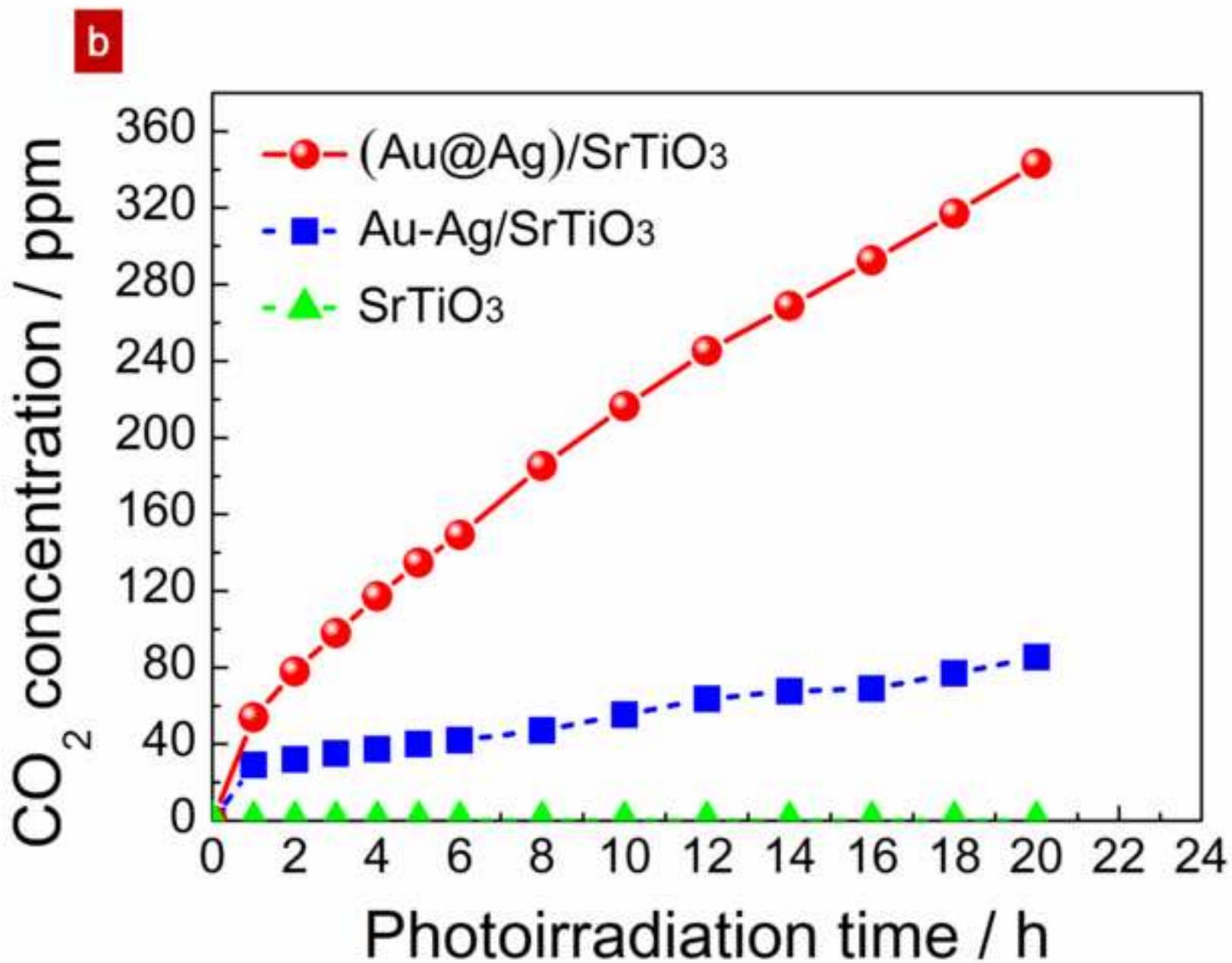


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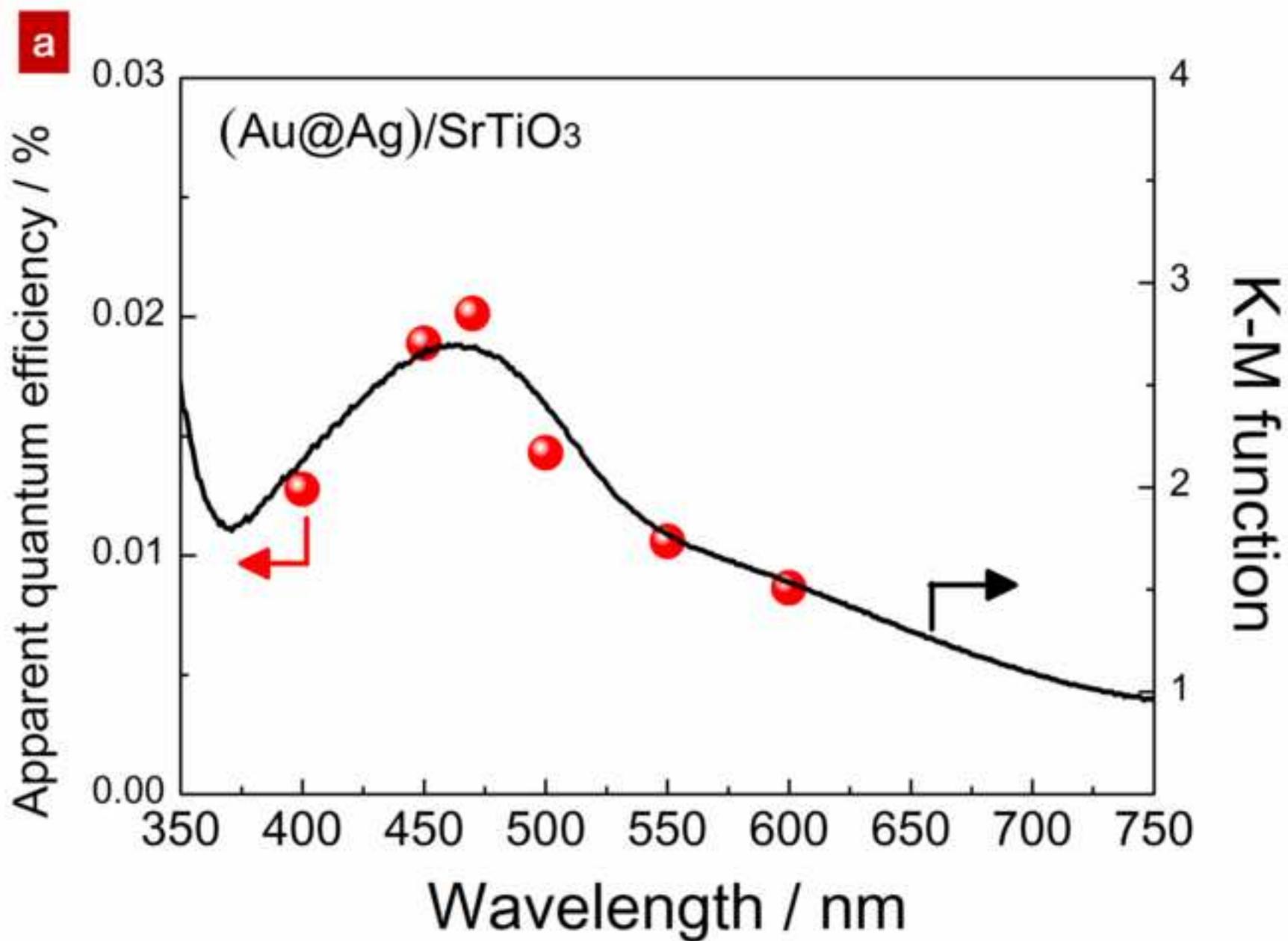


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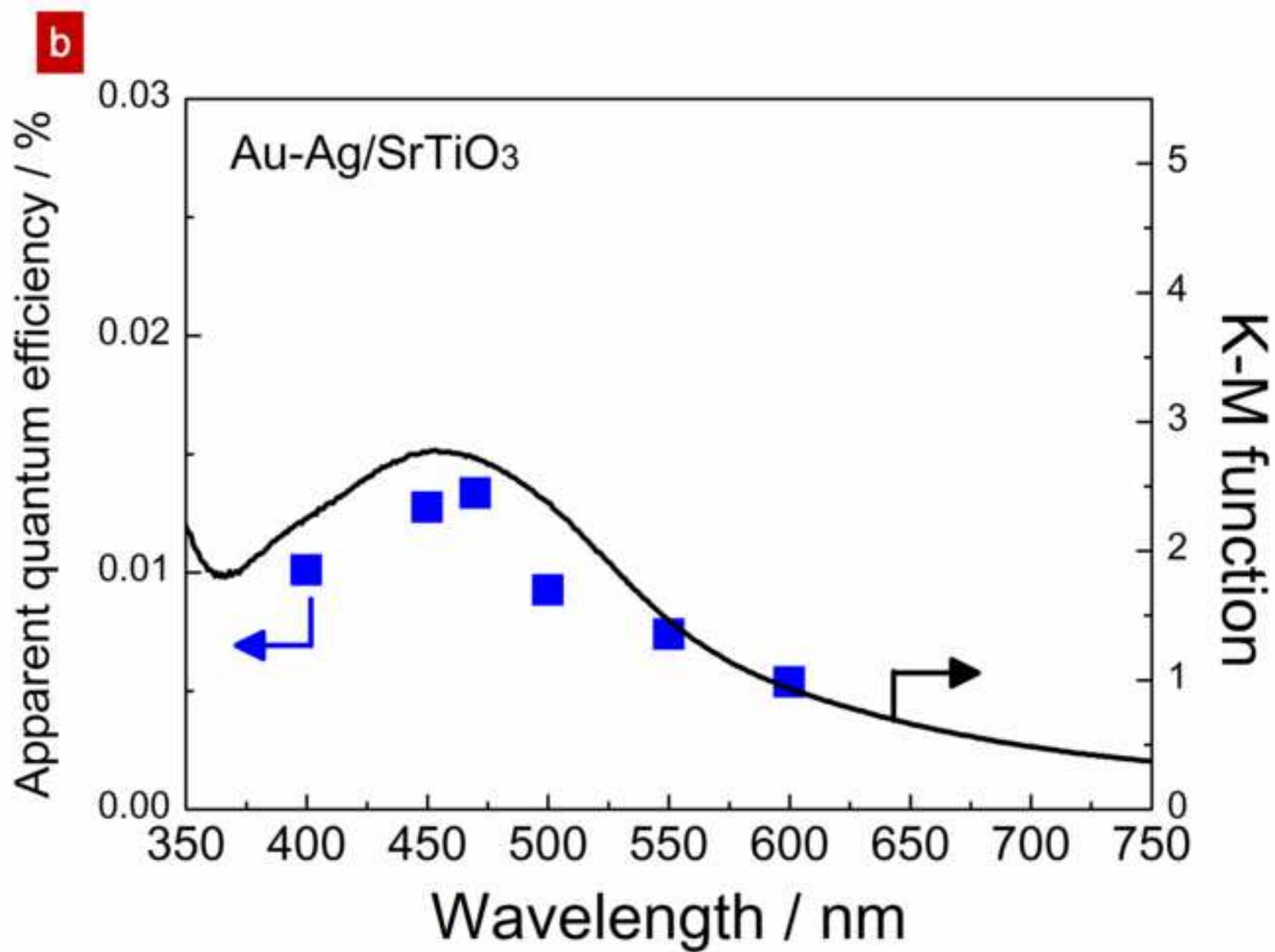


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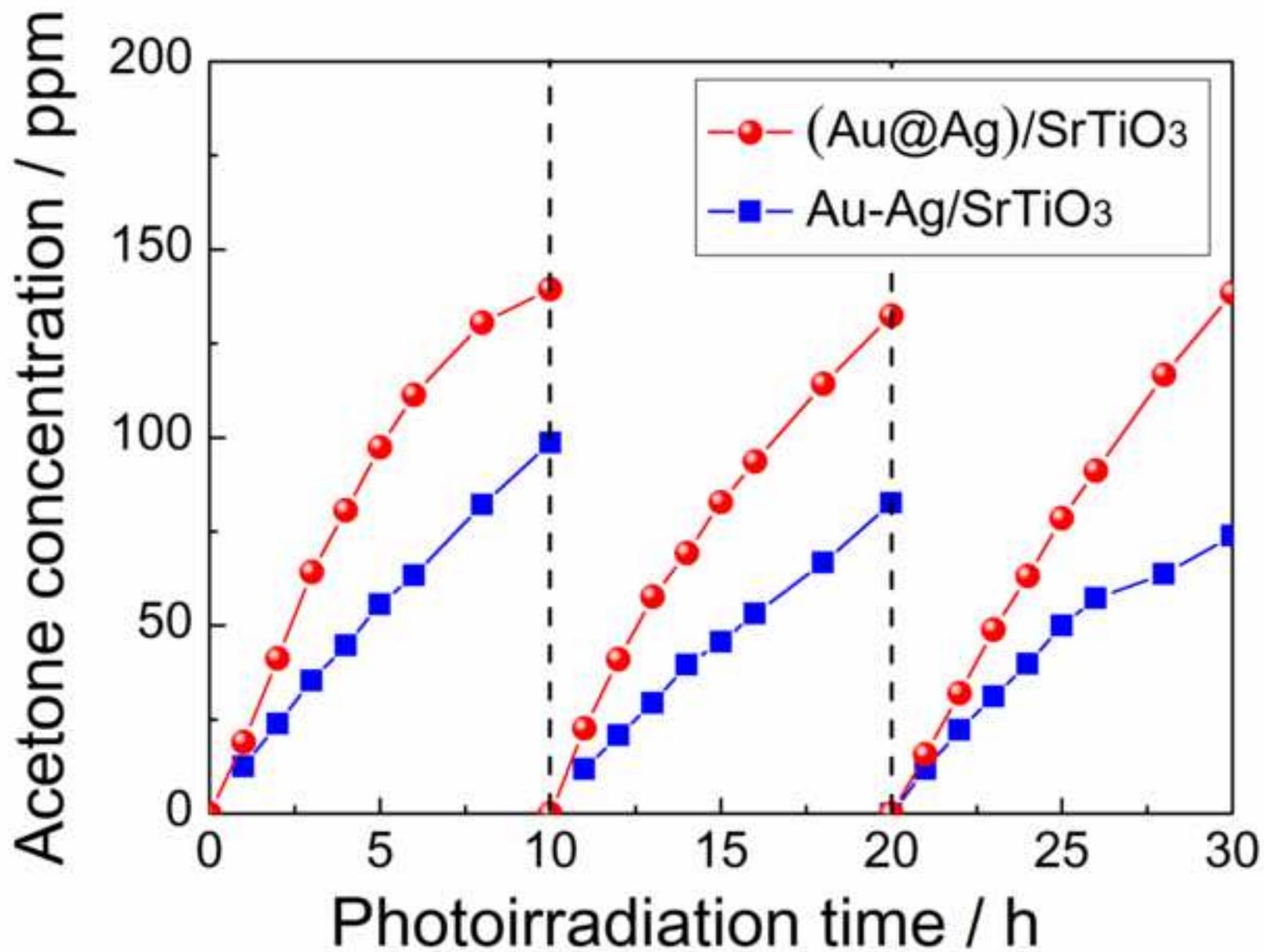


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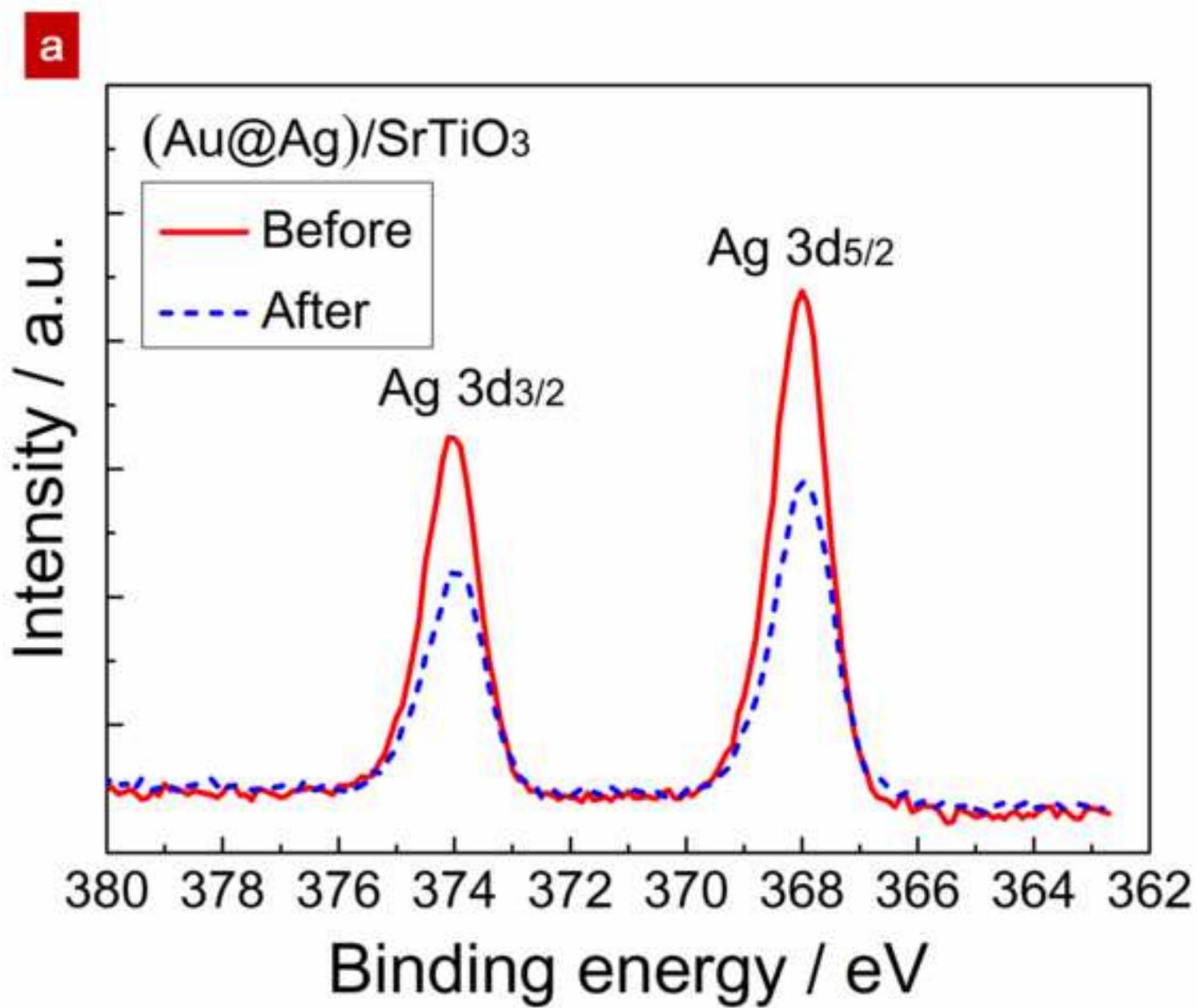
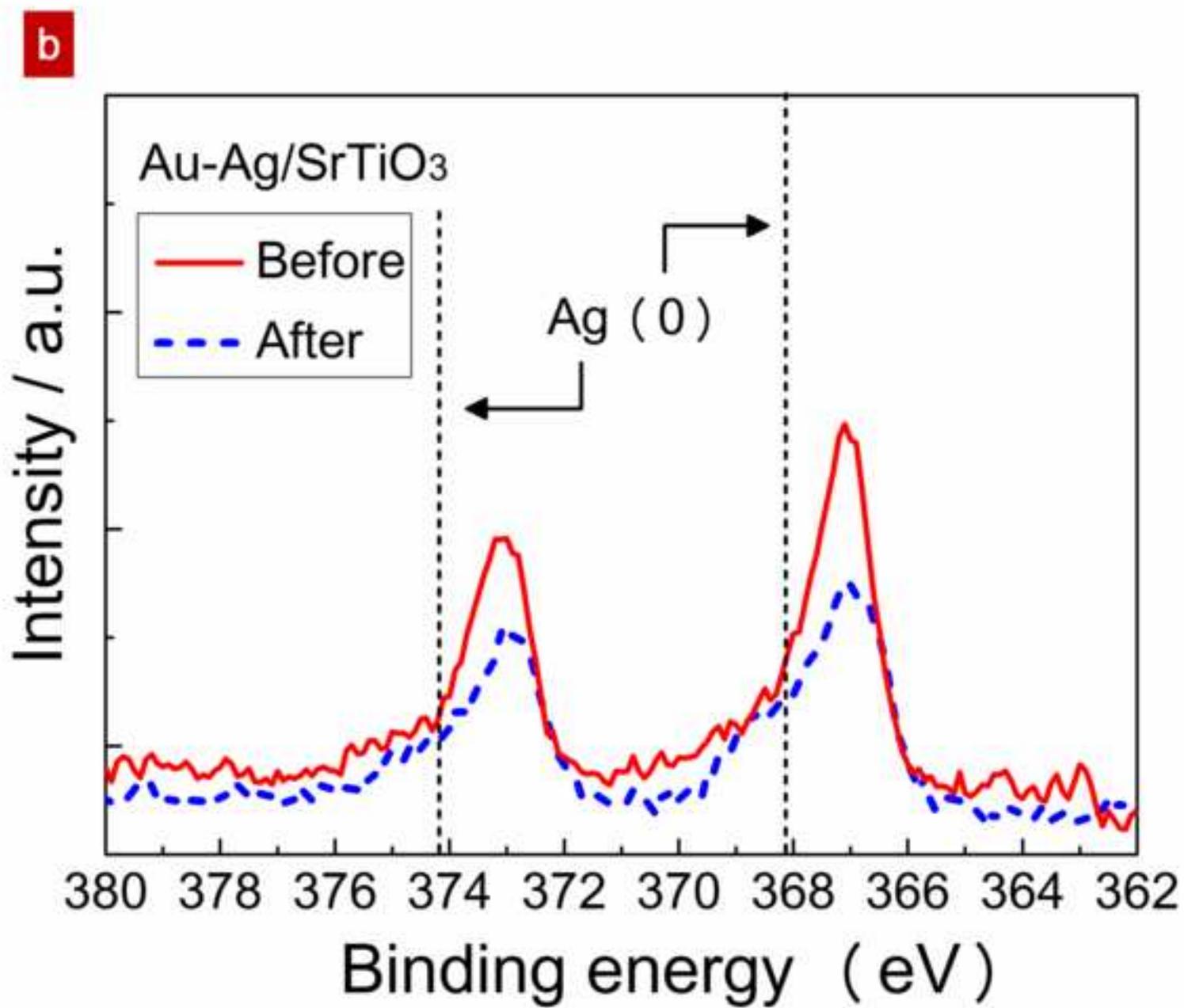
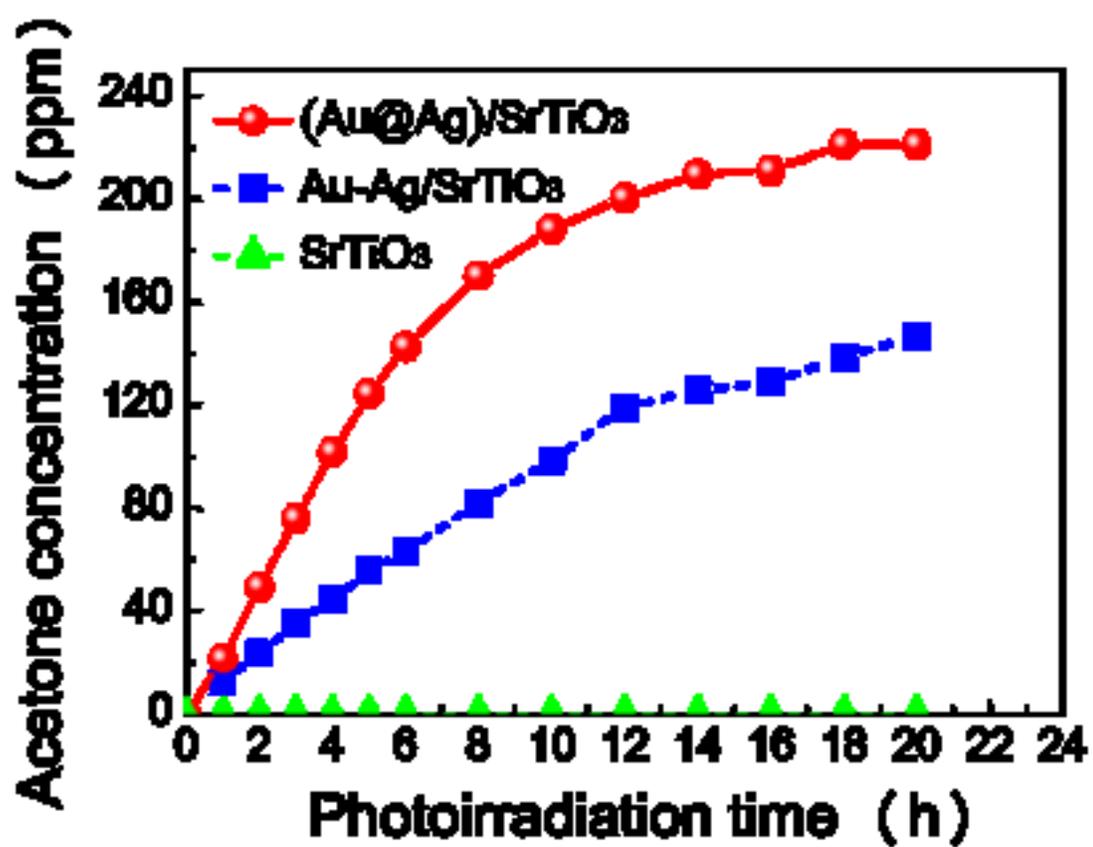
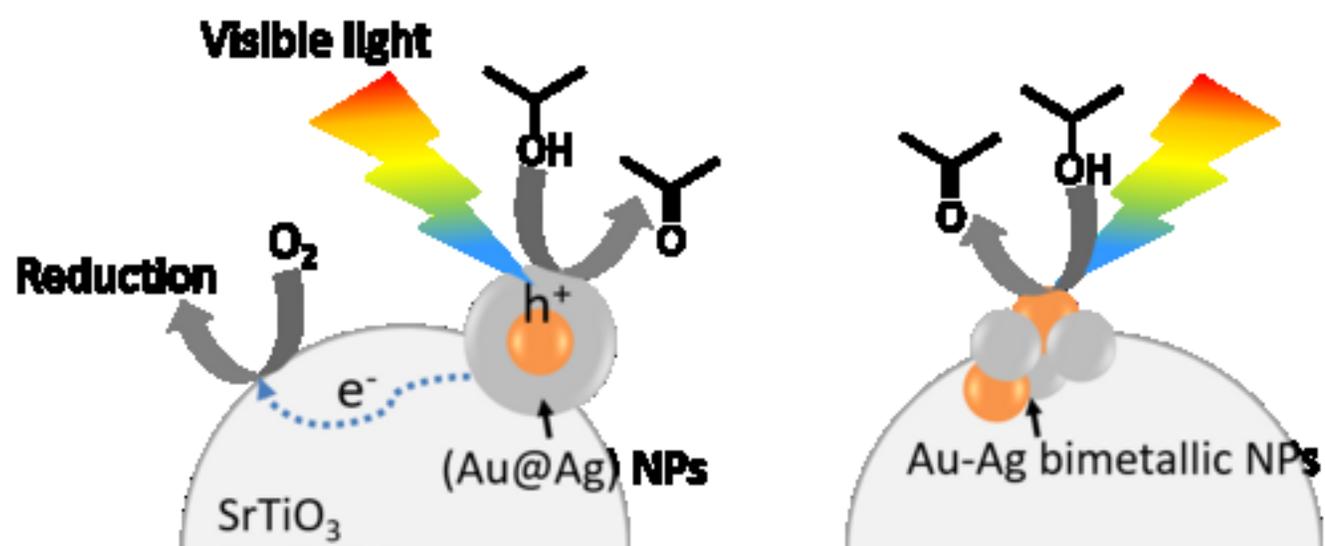


Figure 7b
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1

Highlights

- 2 1. (Au@Ag)/SrTiO₃ can oxidize 2-propanol to acetone and CO₂ under visible light
3 irradiation.
- 4 2. (Au@Ag)/SrTiO₃ showed higher photocatalytic activity than that of bimetallic
5 Au-Ag/SrTiO₃.
- 6 3. The core@shell nanostructure contributes to the chemical stability of the Ag shell.