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Surface plasmon enhanced ethylene glycol electrooxidation based on hollow platinum-silver nanodendrites structures.

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Highlights

1. The dendritic Pt-Ag hollow nanocrystals have been successfully engineered.
2. Plasmonic nanostructures can serve as highly efficient photocatalysts.
3. Surface plasmon resonance enhance photoelectrocatalytic EGOR.
4. Facile design over the plasmonic metals endow them superior catalytic activity.

1 **Surface plasmon enhanced ethylene glycol electrooxidation based on**
2
3 **hollow platinum-silver nanodendrites structures**
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21 **Abstract**
22

23 The surface plasmon resonance (SPR) effect on noble metals to convert solar energy
24 into chemical has attracted a lot of interest. However, the lack of highly efficient
25 photocatalysts is still the forbidden obstacle as well as their large-scale development.
26 Therefore, we focus on plasmon resonance enhanced electrocatalytic oxidation of
27 liquid fuel employing photocatalysts to develop unique hollow platinum-silver (Pt-Ag)
28 nanocrystals. The hollow Pt-Ag is formed of nanodendrites (Pt₁-Ag₁) which display a
29 great enhancement in catalytic activity towards ethylene glycol oxidation with the
30 mass and specific activity found to be: 7045.2 mA mg⁻¹ and 14.1 mA cm⁻²,
31 respectively. This is due to: the SPR effect, efficient electronic distribution and
32 synergistic properties, together with the unique hollow dendritic nanostructures.
33 Impressively, the SPR effect also induces the optimum Pt-Ag nanocatalyst under
34 visible light irradiation conditions to display 1.7-fold enhancements in catalytic
35 activity compared to that under dark conditions. In addition, 6.2 and 7.0-fold
36 enhancements were obtained when the optimized Pt-Ag was employed as
37 photoelectrocatalyst compared to the commercial Pt/C. Therefore, we present a
38 unique catalyst which produces a high catalytic activity and long-term stability
39 compared to those previously reported. More importantly, we also introduce a
40 promising approach towards the designing of a plasmonic metal nanocatalyst with
41 ideal nanostructures for liquid fuel oxidations.
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1 **Keywords:** Plasmonic nanostructures; SPR effect; Hollow Pt-Ag dendrites; Ethylene
2 glycol oxidation; Visible light
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4 **1. Introduction**

5 The production and conversion of solar energy have received much attention in
6 recent years [1]. The use of different photocatalysts to directly convert solar energy
7 into chemical has attracted a great interest. Although most of the photocatalysts are
8 semiconductors, it has also been well demonstrated that plasmonic nanostructures of
9 noble metals such as gold and silver also serve as efficient photocatalysts [2, 3].
10 Plasmonic metallic nanostructures are featured with their strong interactions with
11 resonant photons *via* exciting the SPR [4, 5]. In addition, the SPR can be
12 characterized by the collective oscillation of valence electrons induced by resonance
13 photons [6, 7]. Therefore, the investigation of SPR induced photoelectrocatalytic
14 effect based on plasmonic metallic nanostructures is of vital significance for exploring
15 highly efficient photoelectrocatalysts for electrocatalytic oxidation reactions.
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18 It has been demonstrated that controlling the shape and size of the plasmonic
19 metallic nanocrystals precisely can regulate their properties to meet the requirements
20 of different reactions, for which the SPR is largely dependent on the size and shape of
21 nanocrystals [8]. For instance, the localized surface plasmon resonance (LSPR)
22 wavelengths of Au can be efficiently tuned from the visible light to near-infrared
23 region by controlling the size and morphology of Au nanoparticles [9-11]. The SPR of
24 Ag can also be controlled by adjusting the shape and size of the Ag nanoparticles [12].
25 Accordingly, by manipulating the compositions, sizes and morphologies of the
26 plasmonic metals, it is possible to engineer the nanocatalysts with enhanced
27 photoelectrocatalytic activity and durability towards various chemical reactions
28 [13-15].
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30 The distinctive capability of plasmonic metallic nanostructures to concentrate
31 scatter electromagnetic fields, biosensing, or convert the energy of photons into
32 chemical energy make them suitable for various applications [16-18]. The SPR effects
33 have been widely reported to enhance the catalytic activities of a series of reactions
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1 such as: water splitting [10], reduction of CO₂ [13] and degradation of organic
2 molecules [8] among others. During these processes, the SPR effect of plasmonic
3 metallic nanostructures play a significant role in the substantial enhancement of
4 catalytic activities [18-20]. However, the applications of the photoelectrocatalytic
5 processes in liquid fuel oxidation reactions induced by the SPR effects have remained
6 unexplored.
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12 Therefore, we herein report a facile Pt-Ag hollow nanodendrites synthesis. And
13 the as-prepared hollow Pt-Ag nanodendrites displayed a significant enhancement in
14 the electrocatalytic performances compared with the commercial Pt/C catalyst. These
15 outstanding properties are attributed to the unique hollow dendritic structure as well
16 as synergistic and electronic effects between Pt and Ag. More importantly, we took
17 advantage of the plasmonic Ag combination with the SPR to enhance the catalytic
18 activity towards the oxidation of ethylene glycol (EG) by Pt-Ag hollow nanodendrites
19 under visible light illumination. The resulting Pt₁Ag₁ nanocatalysts achieved 1.7-fold
20 enhancements in mass and specific activities, showing a class of ideal
21 photoelectrocatalysts towards liquid fuel oxidation.
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33 **2. Experimental section**

34 **2.1 Chemicals**

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36 Silver nitrate (AgNO₃, 99%), chloroplatinic acid (H₂PtCl₆, 99.9%),
37 hexadecyltrimethylammonium chloride (CTAC, 99%), L-ascorbic acid (AA, C₆H₈O₆,
38 99%), potassium hydroxide (KOH), dehydrate trisodium citrate (Na₃C₆H₅O₇·2 H₂O),
39 acetone (C₃H₆O, 99%), ethanol (C₂H₅OH, A.R. grade, > 99.5 %) and EG ((CH₂OH)₂, A.R.
40 grade, > 99.5 %) were purchased from Sinopharm Chemicals Reagent Co., Ltd, China.
41 Doubly distilled water was used throughout the experiments.
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51 **2.2 Preparation of Pt-Ag hollow nanodendrites**

52 The Ag seeds were firstly prepared according to the method described by our
53 previously reported work [21]. In the standard synthesis of Pt-Ag hollow
54 nanodendrites, 1.4 mL H₂PtCl₆ (7.7 mM) was firstly injected into 10 mL aqueous
55 solution in a glass vial, which contained 10 mg CTAC. After vigorous stirring for 10
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1 min, 4 mL of AA (10 mg) was added dropwise to the above solution to serve as the
2 reducing agent. After continuous reaction for 3 min, 5 mL of freshly-prepared Ag
3 seeds were dropped into this aqueous solution. Then, the aqueous solution was
4 violently shaken and capped, and then sonicated at ambient temperature for another 2
5 h. For comparison, the Pt₁Ag_{0.5} and Pt₁Ag_{1.5} hollow nanodendrites were also prepared
6 by tuning the amounts of Ag seeds to 2.5 and 7.5 mL, respectively, while keeping the
7 other reaction parameters unchanged.
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10 **2.3 Characterizations**

11 In this work, we firstly used the Tecnai G220 (FEI America) to investigate the
12 morphology and structure of the samples. After that, the FEI Tecnai F20 transmission
13 electron microscope operated at an accelerating voltage of 200 kV was employed to
14 record the scanning transmission electron microscopy (STEM), high-magnification
15 transmission electron microscopy (HR-TEM) and EDX elemental mapping images.
16 An X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K α X-ray
17 source ($\lambda = 1.540598 \text{ \AA}$) was used to obtain the powder X-ray diffraction (PXRD)
18 patterns of the samples. The compositions and elemental valences were characterized
19 by X-ray photoelectron spectroscopy (XPS), which was performed on a VG Scientific
20 ESCALab 220XL electron spectrometer using 300 W Al K α radiation.
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37 **2.4 Electrochemical measurements**

38 Cyclic voltammetry (CV) was employed to investigate the electrocatalytic
39 performances carried out in a standard three-electrode system, which included a Pt
40 wire, glassy carbon electrode (GCE), a saturated calomel electrode (SCE) and as
41 counter, working and reference electrodes, respectively. In the standard preparation of
42 catalysts-coated electrode, the catalysts should firstly be re-dispersed in a mixture
43 solvent containing Nafion and isopropanol and to form a homogeneous catalyst ink by
44 sonicating for 30 min. Next, five microlitres of the dispersion was transferred onto the
45 GC electrode and dried naturally. The CV was operated using in 1 M KOH + 1 M EG
46 at the potential ranging from -0.9 to 0.3 V with the sweeping rate of 50 mV/s. Every
47 time before examination, the GCE was polished with alumina powder and then rinsed
48 with doubly deionized water and ethanol for several times. Besides, the measurements
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1 of successive CVs of 500 cycles were also conducted for investigating their long-term
2 durability. To achieve precise results, all the electrochemical measurements were
3 repeated five times. The photocurrent responses of the modified electrode in 1 M EG
4 + KOH solution were measured with a potential of -0.2 V at a scan rate of 50 mV s^{-1}
5 under visible light illumination. The illumination was interrupted every 100 s.
6 Electrochemical impedance spectroscopy (EIS) measurements were carried out at -0.2
7 V with an AC perturbation signal of 5.0 mV over the frequency range from 100 kHz
8 to 0.1 Hz. It was worth noting that all the visible light in particular,
9 photo-electrochemical measurements were operated by using a xenon lamp (150 W)
10 with UV cut-off filter (>400 nm) at the distance of 28 cm to irradiate all the working
11 electrodes.
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23 **3. Results and discussion**

24 **3.1 Materials characterizations**

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29 The unique Pt-Ag hollow nanodendrites have been prepared by employing a facile
30 wet-chemical method, where CTAC and AA serve as the stabilizers and reducing
31 agents, respectively (See the Experimental Section for details). The as-obtained
32 products were firstly characterized by employing the TEM. The morphological and
33 structural features were characterized *via* TEM and HAADF-STEM. Fig.1a and b
34 show that the products consist of the uniform hollow nanostructure with the
35 dendrite-like surface. In addition, the nanocrystals were highly dispersed with an
36 average size of 53.8 nm (Supporting Information, Fig.S1). The HRTEM image of the
37 individual nanodendrite illustrates that the lattice fringe spacing is calculated to be
38 0.230 nm (Fig.1c), which is associated with the (111) facet of Pt-Ag alloy [23]. The
39 PXRD patterns of the Pt-Ag hollow nanodendrites exhibit the typical face centered
40 cubic (*fcc*) structure with the diffraction peaks located between those of the standard
41 Pt and Ag (Fig.1d), which are associated with the HRTEM result, further confirming
42 the formation of Pt-Ag alloy phases in the Pt-Ag hollow nanodendrites. The atomic
43 ratio of Pt/Ag is $52.3/47.7$, as revealed by inductively coupled plasma atomic
44 emission spectroscopy (ICP-AES), which is also consistent with the scanning electron
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microscope energy dispersive X-ray spectroscopy (SEM-EDS) (51.4/48.6, Fig.1e).

Besides, the composition distribution of Pt₁Ag₁ hollow nanodendrites was investigated by employing the EDX elemental mapping analysis, where both Pt and Ag were distributed uniformly over the whole Pt-Ag hollow nanodendrite (Fig.1f), as confirmed by the line-scan analysis (Fig.1g).

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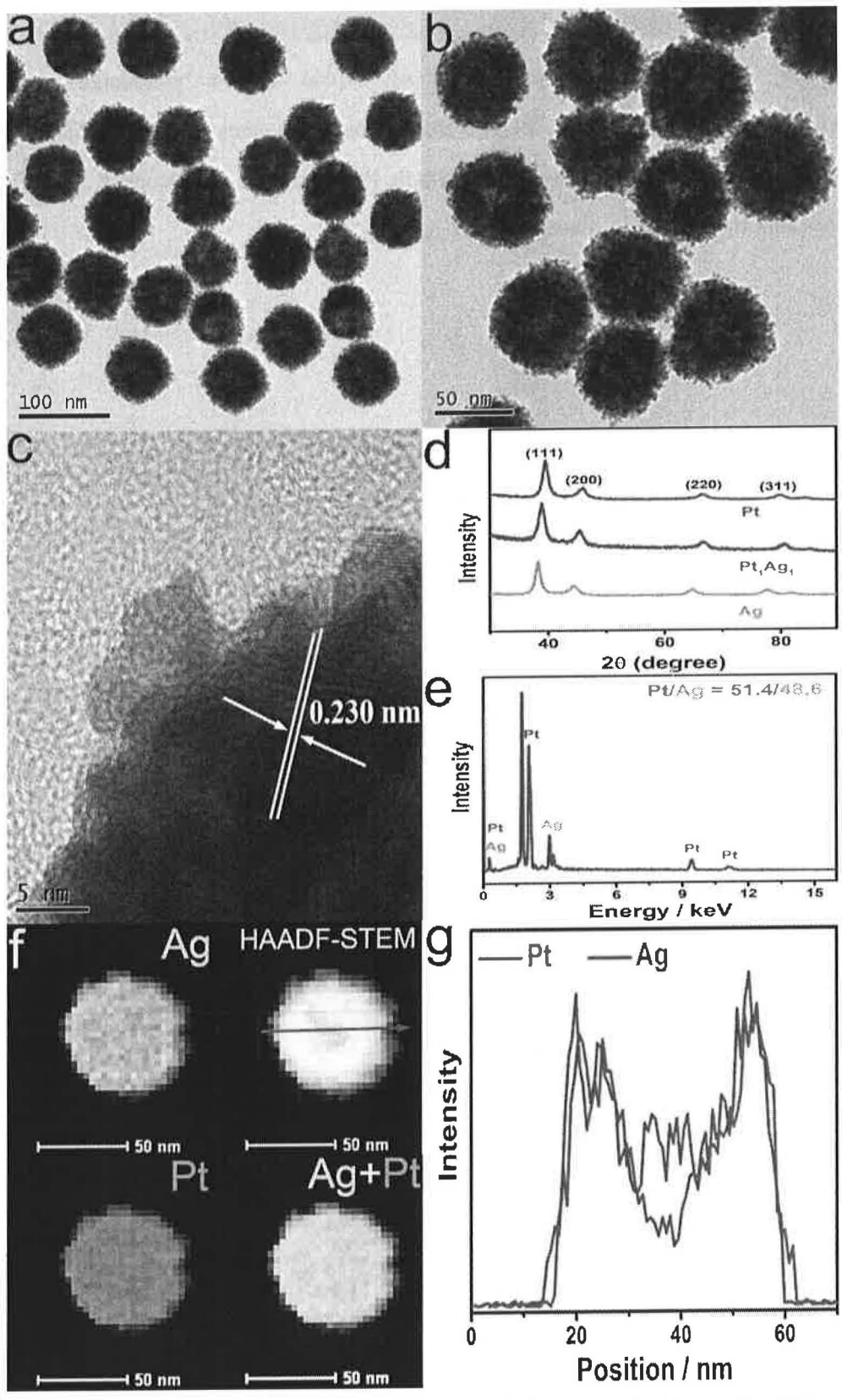


Fig.1 (a, b) Representative TEM images of Pt₁Ag₁ hollow nanodendrites with different magnifications. (c) HRTEM image of an individual Pt₁Ag₁ hollow nanodendrite. (d) XRD patterns

1 of Pt₁Ag₁ hollow nanodendrites, Pt and Ag. (e) The TEM-EDX elemental mapping,
2 HAADF-STEM and corresponding (f) line-scan of individual Pt₁Ag₁ hollow nanodendrites for
3 element distribution analyses.

4 Moreover, in order to understand the compositions and elemental valences of the
5 Pt₁Ag₁ hollow nanodendrites, the XPS measurements were also employed. As
6 displayed in Fig.2a, the typical peaks at the binding energy (B.E.) of 71.5 and 74.3 eV
7 were assigned to the Pt 4f_{7/2} and Pt 4f_{5/2} states, respectively. The XPS of Pt 4f_{7/2} in the
8 Pt₁Ag₁ hollow nanodendrites shifted positively to a higher B.E. and Ag 3d shifted to a
9 lower B.E. compared with that of standard Pt and Ag, indicating the changes in the
10 electronic structure, which may be attributed to the occurrence of charge transfer from
11 Ag to Pt [24-26]. More importantly, both of the metallic states of Pt and Ag (Fig.2b)
12 were the predominant states in Pt₁Ag₁ hollow dendrites.

13 Next, we analyzed the optical properties of the as-obtained Pt₁Ag₁ hollow
14 nanodendrites, by measuring the UV-vis adsorption spectra of the samples, as is
15 displayed in Fig.2c. The Pt₁Ag₁ hollow nanodendrites showed an absorption edge at
16 *ca.* 420 nm, which is associated with the adsorption of Ag nanoparticles, revealing the
17 distinct absorptions of visible light [27]. While the adsorption edge at *ca.* 650 nm may
18 be ascribed to some unremoved residues. These results suggest that the as-prepared
19 PtAg hollow nanodendrites catalyst possess the outstanding optical properties, which
20 might be beneficial for photoelectrocatalytic ethylene glycol oxidation reaction
21 (EGOR). In addition, we conducted the photocurrent response measurement to study
22 the photoelectric properties of the resulted Pt₁Ag₁ hollow nanodendrites. Fig.2d
23 showed the photocurrent-time (I-t) curve on the Pt₁Ag₁ hollow nanodendrites
24 modified electrode. Remarkably, a responsive photocurrent with intensity of *ca.* 200
25 mA mg⁻¹ was observed for the EGOR when the electrode was upon visible light
26 illumination. Besides, the photocurrent response was also repeatable during on/off
27 cycles upon light illumination, indicating that the SPR and electronic effects between
28 Ag and Pt were favorable for the enhancement of current density [28].

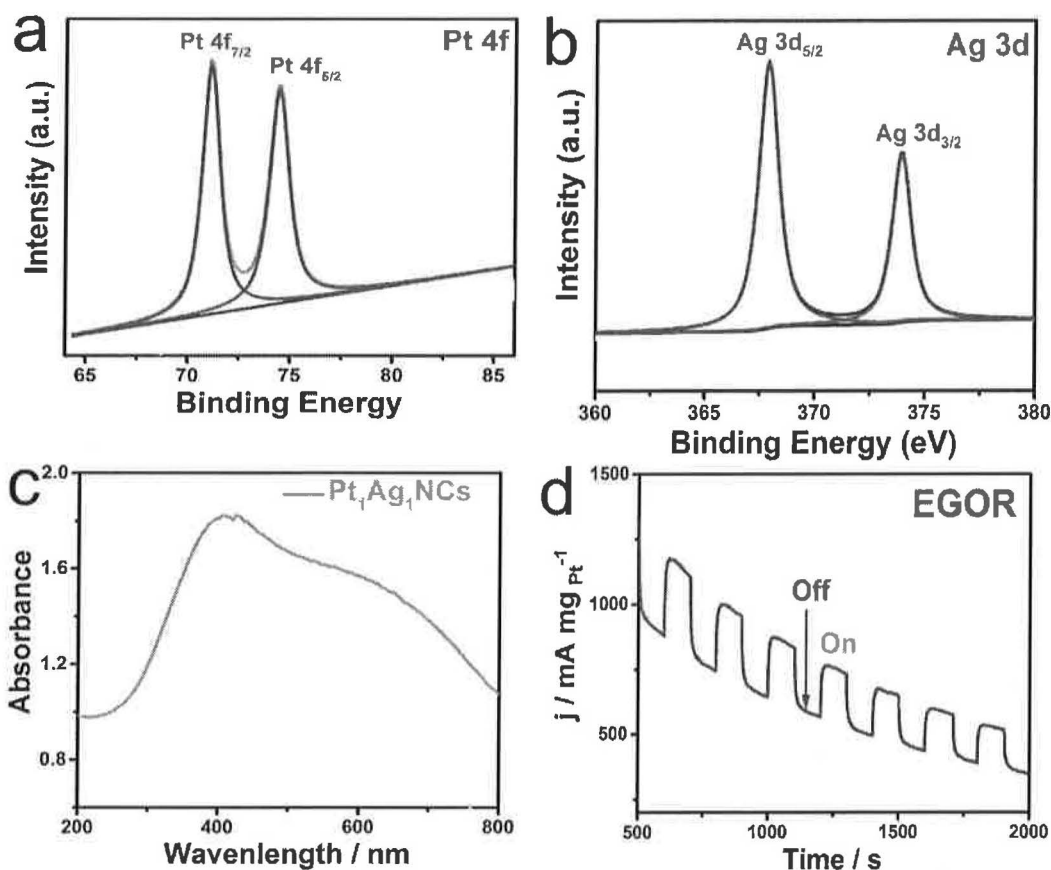


Fig. 2 The XPS spectra of (a) Pt 4f and (b) Ag 3d in Pt_1Ag_1 hollow nanodendrites. (c) UV-vis spectra of dendritic Pt_1Ag_1 hollow nanodendrites, and (d) photocurrent responses of Pt_1Ag_1 hollow nanodendrites towards EGOR in 1 M EG and 1 M KOH solution at a potential of -0.2 V under visible light illumination. The illumination from a Xe lamp was interrupted every 100 s.

To uncover the influences of composition on the final shape, we herein synthesized the other two types of $Pt_1Ag_{1.5}$ and $Pt_1Ag_{0.5}$ hollow nanodendrites by simply varying the amount of Ag seeds while keeping the concentration of H_2PtCl_6 solution the same. According to the Fig.S2 (Supporting Information), Pt_1Ag_1 hollow nanodendrites were similar to both $Pt_1Ag_{1.5}$ and $Pt_1Ag_{0.5}$, indicating the synthesis of Pt-Ag hollow nanodendrites was not dependable on the atomic ratio.

3.2 Electrochemical tests

The visible-light-enhanced electrocatalytic oxidation reaction can be applied due to the distinctive hollow dendritic nanostructure, optical properties and the strong SPR effects of the resulted Pt-Ag hollow nanodendrites. Therefore, we herein chose the electrocatalytic oxidation of EG to evaluate the photoelectrocatalytic properties of the dendritic Pt-Ag hollow nanodendrites under the visible light irradiation. The CV

operated in 1 M KOH solution (Fig.3a) was significant for evaluating the electrochemically active surface areas (ECSA) of the electrocatalysts, which can provide some crucial information regarding the number of available active sites. Therefore, a higher ECSA value means more available surface active sites [29, 30]. The ECSA value for Pt₁Ag₁ hollow nanodendrites was calculated to be 50.2 m² g⁻¹, which was much higher than those of Pt₁Ag_{0.5} hollow nanodendrites (46.2 m² g⁻¹) and Pt₁Ag_{1.5} hollow nanodendrites (48.3 m² g⁻¹) (Fig.3b). The higher ECSA of Pt₁Ag₁ hollow nanodendrites was attributed to the combination of the roughly dendritic surface and hollow nanostructures [31].

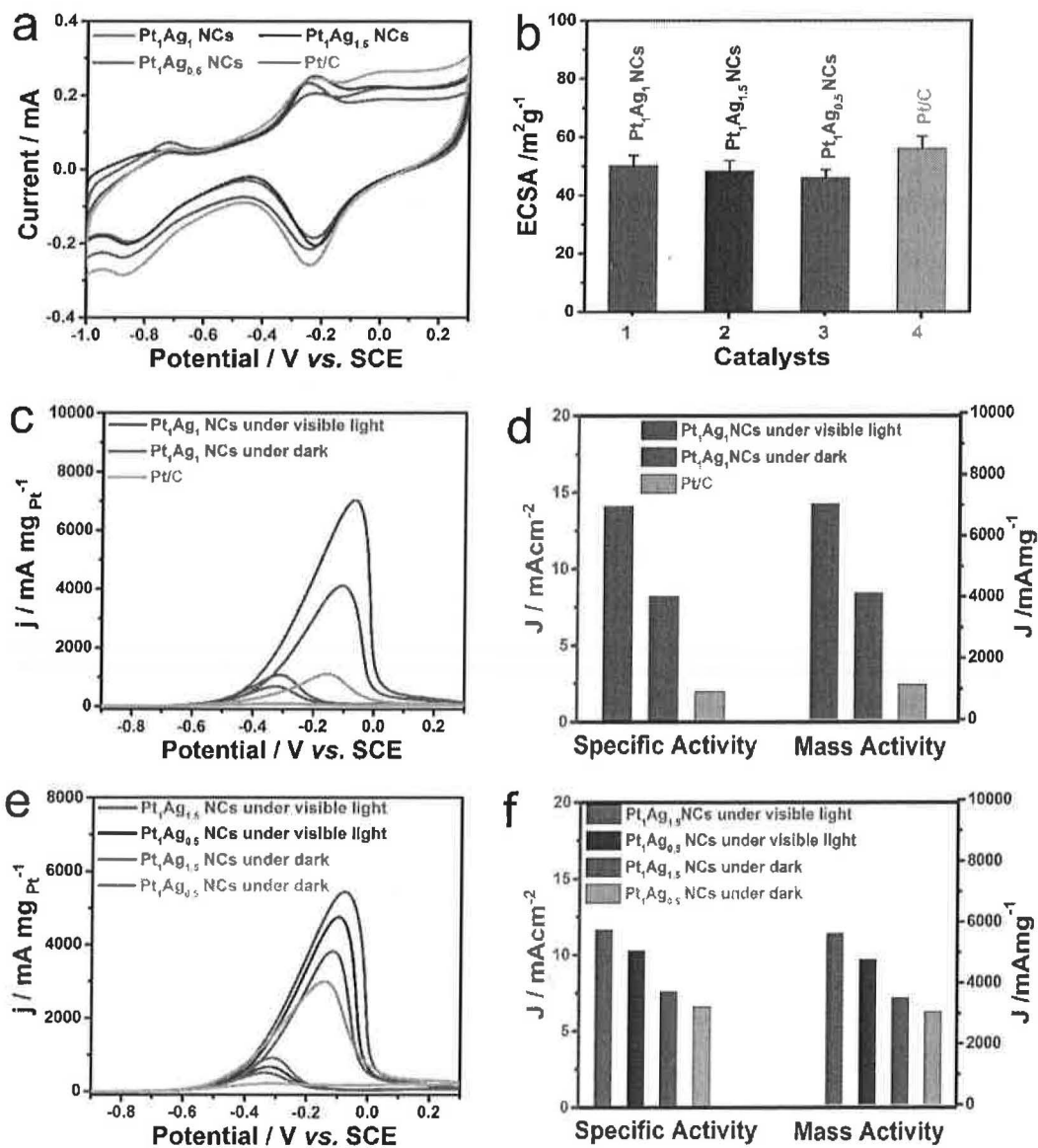


Fig. 3 (a) CV curves of Pt₁Ag₁, Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites and commercial Pt/C in 1

1 M KOH solution. (b) The calculated ECSA of Pt₁Ag₁, Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites and commercial Pt/C. (c) CV curves of Pt₁Ag₁ hollow nanodendrites under visible light illumination and dark, as well as commercial Pt/C. (d) The calculated specific and mass activities Pt₁Ag₁ hollow nanodendrites under visible light illumination and dark, as well as commercial Pt/C towards EGOR. (e) CV curves of Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites towards EGOR under visible light illumination and dark. (f) The calculated specific and mass activities of Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites towards EGOR under visible light illumination and dark condition were illustrated. These electrochemical measurements were repeated five times to achieve precise results.

The electrocatalytic performances of the Pt-Ag hollow nanodendrites were then carried out in 1 M KOH and 1 M EG solution at the sweeping rate of 50 mV/s. For comparison purposes, the peak current densities were normalized to both the ECSA and the mass of Pt loading on the surface of the modified electrodes. As it can be seen in Fig.3c, the Pt₁Ag₁ hollow nanodendrites displayed a remarkably superior peak current density under visible light irradiation than that under dark conditions. Fig.3d shows the histogram for the specific and mass activities of commercial Pt/C and Pt₁Ag₁ hollow nanodendrites under visible light irradiation or dark conditions. Among these, the Pt₁Ag₁ hollow nanodendrites under visible light irradiation displayed the highest mass and specific activities of 7045.2 mA mg⁻¹ and 14.1 mA cm⁻². In addition, 6.2 and 7.0-fold enhancements were found compared to those of the commercial Pt/C (1135.2 mA mg⁻¹ and 2.05 mA cm⁻²). More interestingly, the Pt₁Ag₁ hollow nanodendrites under visible light irradiation also displayed 1.7 times higher than under dark (4129.1 mA mg⁻¹ and 8.2 mA cm⁻²).

The electrocatalytic activities of the other two types of Pt-Ag hollow nanodendrites with different compositions were also investigated. As it can be seen in Fig. 3e and f, both Pt₁Ag_{1.5} and Pt₁Ag_{0.5} nanocatalysts displayed excellent electrocatalytic performances towards EGOR under visible light irradiation with the specific activities found to be 11.7 and 10.3 mA cm⁻², which are 1.54 and 1.56 times higher than those under dark conditions, respectively. Apart from the specific activity, both Pt₁Ag_{1.5} and Pt₁Ag_{0.5} hollow nanodendrites also displayed an enhancement in mass activity, 5628.7 mA mg⁻¹ and 4756.8 mA mg⁻¹ towards EGOR when the modified electrodes were upon the visible light irradiation. The electrocatalytic activities towards EGOR were enhanced greatly by the SPR effects, unique dendritic

structure and the synergistic properties between Pt and Ag [32, 33].

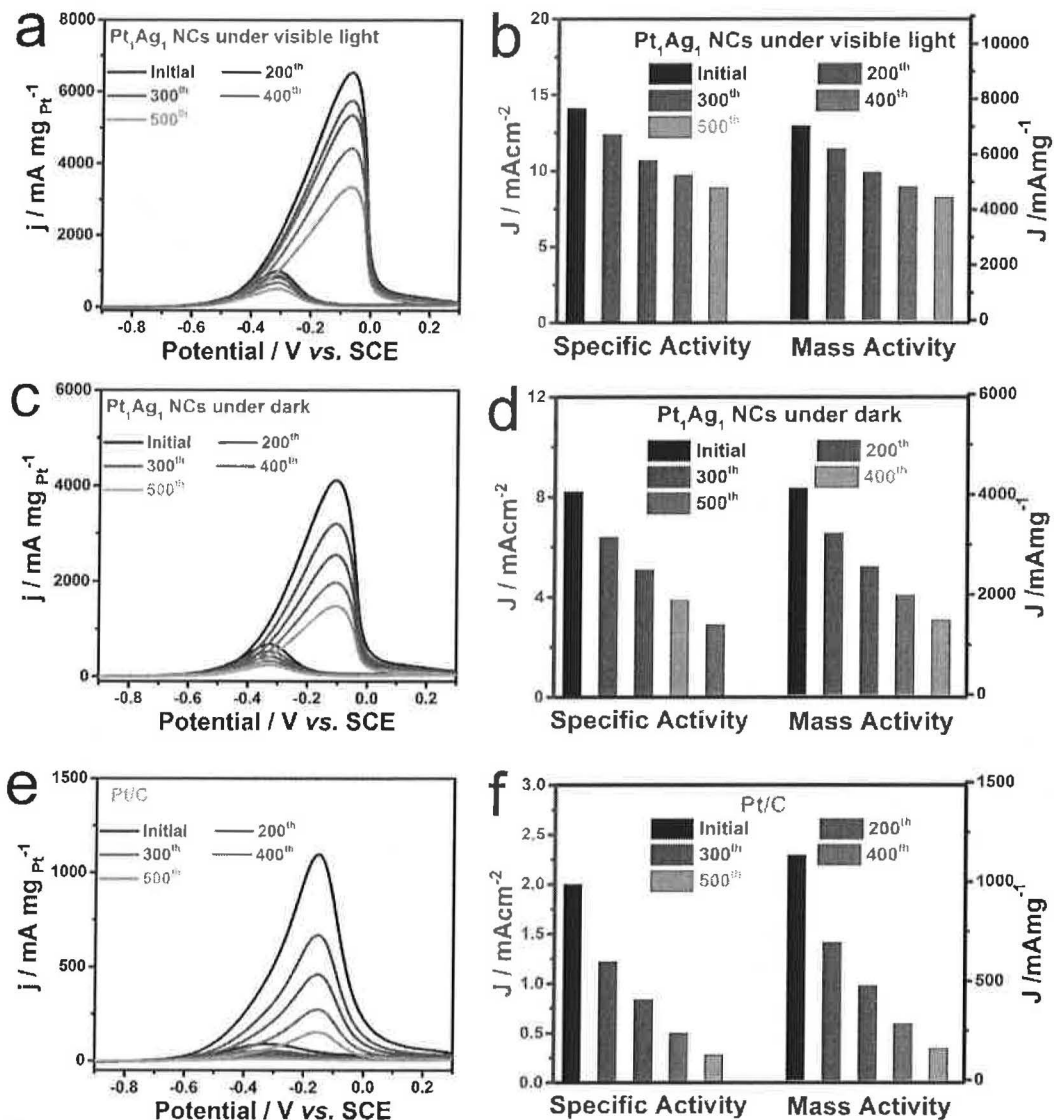
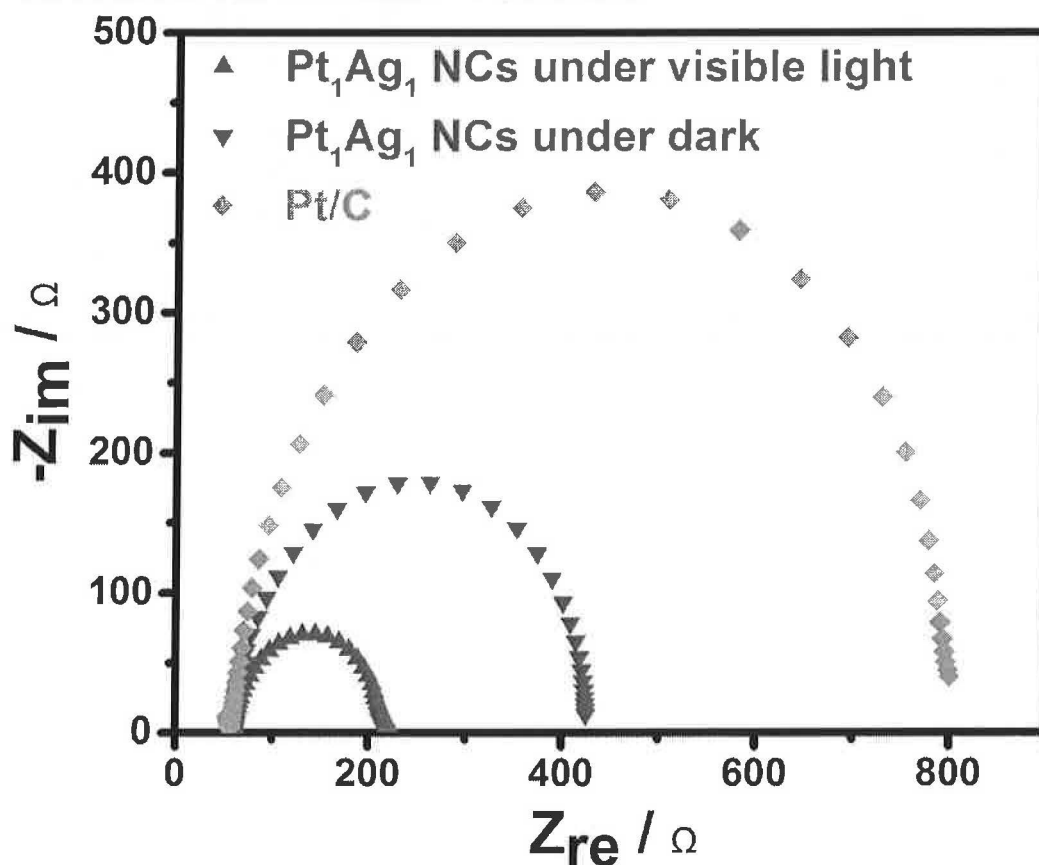


Fig.4 Durability comparison of (a and b) $\text{Pt}_1\text{Ag}_{0.5}$ hollow nanodendrites under visible light irradiation, (c and d) $\text{Pt}_1\text{Ag}_{0.5}$ hollow nanodendrites under ambient reaction and (e and f) commercial Pt/C for the successive CVs of 200th, 300th, 400th and 500th cycles together with the retained specific and mass activities. These electrochemical measurements were repeated five times to achieve precise results.

The durability of the catalyst is also another significant parameter for evaluating the properties of an electrocatalyst in fuel cells. An electrocatalyst with better durability means a much longer lifetime, which is crucial for practical applications [34]. Therefore, we conducted the continuous 500 cycles CV to investigate their electrocatalytic durability, which were carried out in the solution of 1 M KOH + 1 M EG solution. According to the Fig.4, although the peak current densities of these

1 catalysts decayed rapidly in the initial period, the Pt₁Ag₁ hollow nanodendrites upon
2 the visible light irradiation displayed the slowest current decay over time and retained
3 the highest activity among these catalysts after 500 cycles. For more detailed
4 the highest activity among these catalysts after 500 cycles. For more detailed
5 comparison, the normalized current densities of these electrocatalysts are also
6 recorded. As seen, the Pt₁Ag₁ hollow nanodendrites nanocatalysts under visible light
7 irradiation retained the catalytic activities of 63.1 % of the initial value towards
8 EGOR, which is much higher than that of commercial Pt/C (14.3 %) and Pt₁Ag₁
9 hollow nanodendrites (36.2 %) under dark conditions. The retained mass and specific
10 activities of Pt₁Ag₁ hollow nanodendrites nanocatalysts under visible light irradiation
11 were calculated to be 4438.5 mA mg⁻¹ and 8.9 mA cm⁻², respectively, both of which
12 are much higher than the other electrocatalysts, indicating the superior long-term
13 stability. The greatly enhanced durability of Pt₁Ag₁ hollow nanodendrites upon the
14 visible light irradiation can mainly be ascribed to the highly exposed surface active
15 sites, synergistic and electronic effects between Pt and Ag, as well as the
16 photoelectrical synergistic effects from SPR effects.



1 Fig.5 The Nyquist plots of commercial Pt/C, Pt₁Ag₁ hollow nanodendrites modified electrodes
2 under visible light irradiation or dark conditions at the potential of -0.2 V.

3 Next, we have also conducted EIS at the potential of -0.1 V, for which the
4 diameter is a crucial parameter, to evaluate the electrical resistance and conductivity
5 of the as-prepared electrocatalysts. As it can be observed in Fig.5, the diameter
6 impedance arc (DIA) of Pt₁Ag₁ hollow nanodendrites under visible light illumination
7 is much smaller than that under dark conditions and that of the commercial Pt/C
8 catalyst. This indicated that Pt₁Ag₁ hollow nanodendrites nanocatalysts modified
9 electrode possessed smaller electron transfer resistance. In addition, the best electrical
10 conductivity under visible light illumination is attributed to the SPR effect and the
11 charge transfer between Pt and Ag [35-39].
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22 In general, the greatly enhanced electrocatalytic performances of Pt-Ag hollow
23 nanodendrites towards EGOR can be mainly attributed to the following combined
24 features: (1) the unique hollow dendritic nanostructures can efficiently provide high
25 surface active areas available for the EG molecules [40]. (2) The electronic and
26 synergistic effects originated from the Pt and Ag are also beneficial for enhancing
27 their electrocatalytic activity and durability [41-45]. (3) Most importantly, the
28 photoelectrical effects induced by SPR upon the visible light irradiation are crucial for
29 the substantial enhancements of electrocatalytic performances towards EGOR [46].
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38 4. Conclusions

39 In summary, a simple method has been successfully demonstrated for the
40 synthesis of an advanced class of Pt-Ag photoelectrocatalysts. Owing to the unique
41 hollow nanodendrite structure, as well as the synergistic and electronic effects
42 between Pt and Ag, the as-prepared Pt-Ag hollow nanodendrite can expose more
43 surface active area. In addition, it can display remarkable electrocatalytic activity
44 towards EGOR with the unprecedentedly high mass and specific activities of 7045.2
45 mA mg⁻¹ and 14.1.1 mA cm⁻². Furthermore, 6.2 and 7.0-fold enhancements were
46 obtained compared to those of the commercial Pt/C. More significantly, owing to the
47 SPR effects based on the Ag, the Pt-Ag hollow nanodendrites under the visible light
48 irradiation also showed an enhancement of 1.7 times in catalytic activity than that
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1 under dark conditions. A number of excellent Pt-Ag photocatalysts have been
2 prepared, the one we obtained is the best with both high catalytic activity and
3 long-term stability, which can be well applied as highly efficient photoelectrocatalysts
4 for fuel cells. This manuscript opens up a promising and novel approach for designing
5 highly efficient photoelectrocatalysts towards liquid fuel electrooxidation and other
6 chemical reactions, which would greatly alleviate the serious energy crisis and
7 environment pollution.
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10 11 12 13 14 **Acknowledgements**

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Figure

Fig.1 (a, b) Representative TEM images of Pt₁Ag₁ hollow nanodendrites with different magnifications. (c) HRTEM image of an individual Pt₁Ag₁ hollow nanodendrite. (d) XRD patterns of Pt₁Ag₁ hollow nanodendrites, Pt and Ag. (e) The TEM-EDX elemental mapping, HAADF-STEM and corresponding (f) line-scan of individual Pt₁Ag₁ hollow nanodendrites for element distribution analyses.

Fig. 2 The XPS spectra of (a) Pt 4f and (b) Ag 3d in Pt₁Ag₁ hollow nanodendrites. (c) UV-vis spectra of dendritic Pt₁Ag₁ hollow nanodendrites, and (d) photocurrent responses of Pt₁Ag₁ hollow nanodendrites towards EGOR in 1 M EG and 1 M KOH solution at a potential of -0.2 V under visible light illumination. The illumination from a Xe lamp was interrupted every 100 s.

Fig. 3 (a) CV curves of Pt₁Ag₁, Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites and commercial Pt/C in 1 M KOH solution. (b) The calculated ECSA of Pt₁Ag₁, Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites and commercial Pt/C. (c) CV curves of Pt₁Ag₁ hollow nanodendrites under visible light illumination and dark, as well as commercial Pt/C. (d) The calculated specific and mass activities Pt₁Ag₁ hollow nanodendrites under visible light illumination and dark, as well as commercial Pt/C towards EGOR. (e) CV curves of Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites towards EGOR under visible light illumination and dark. (f) The calculated specific and mass activities of Pt₁Ag_{1.5}, Pt₁Ag_{0.5} hollow nanodendrites towards EGOR under visible light illumination and dark condition were illustrated. These electrochemical measurements were repeated five times to achieve precise results.

Fig.4 Durability comparison of (a and b) Pt₁Ag_{0.5} hollow nanodendrites under visible light irradiation, (c and d) Pt₁Ag_{0.5} hollow nanodendrites under ambient reaction and (e and f) commercial Pt/C for the successive CVs of 200th, 300th, 400th and 500th cycles together with the retained specific and mass activities. These electrochemical measurements were repeated five times to achieve precise results.

Fig.5 The Nyquist plots of commercial Pt/C, Pt₁Ag₁ hollow nanodendrites modified electrodes under visible light irradiation or dark conditions at the potential of -0.2 V.

Fig.1

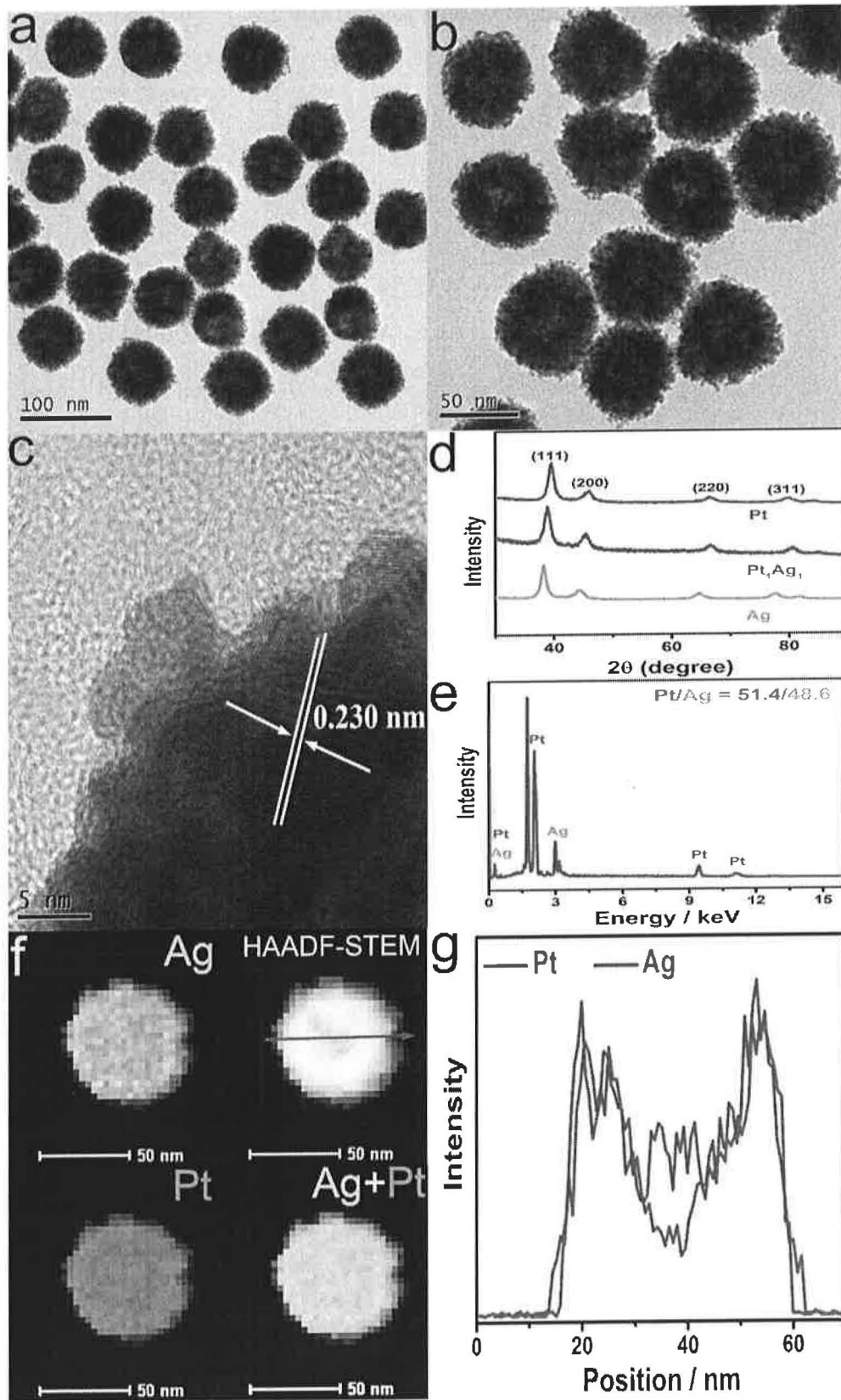


Fig.2

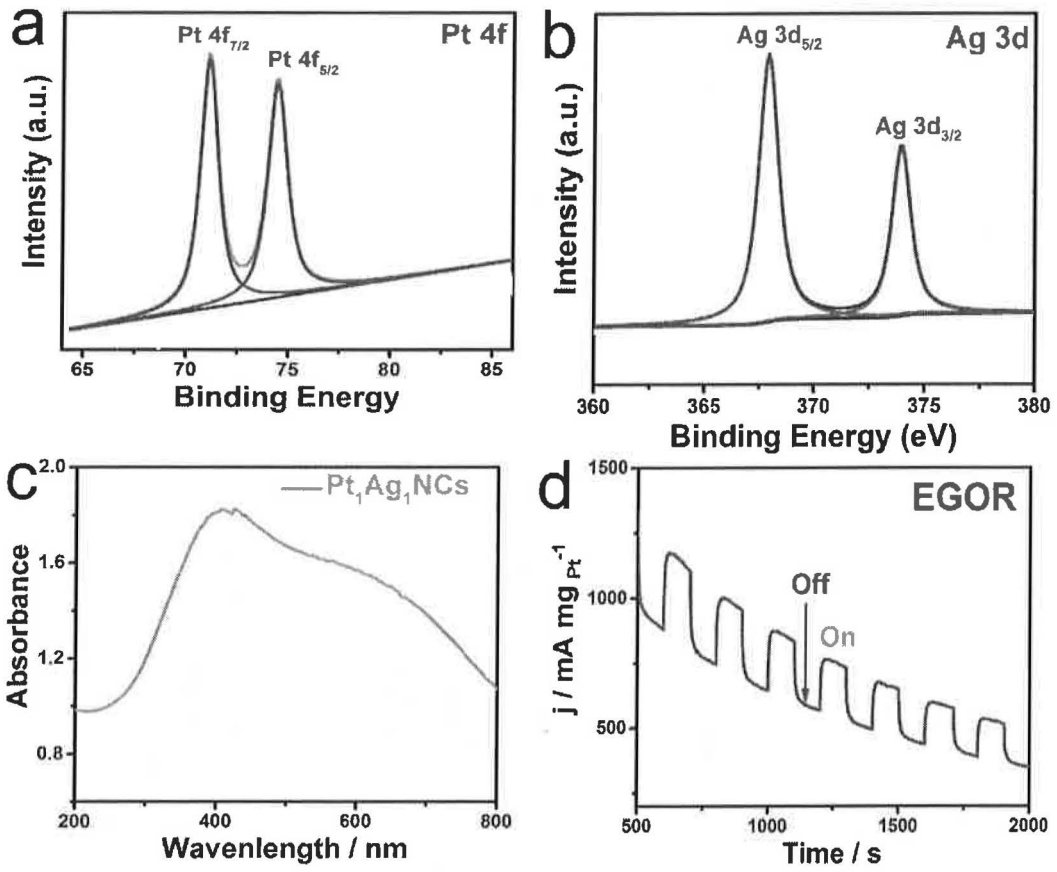


Fig.3

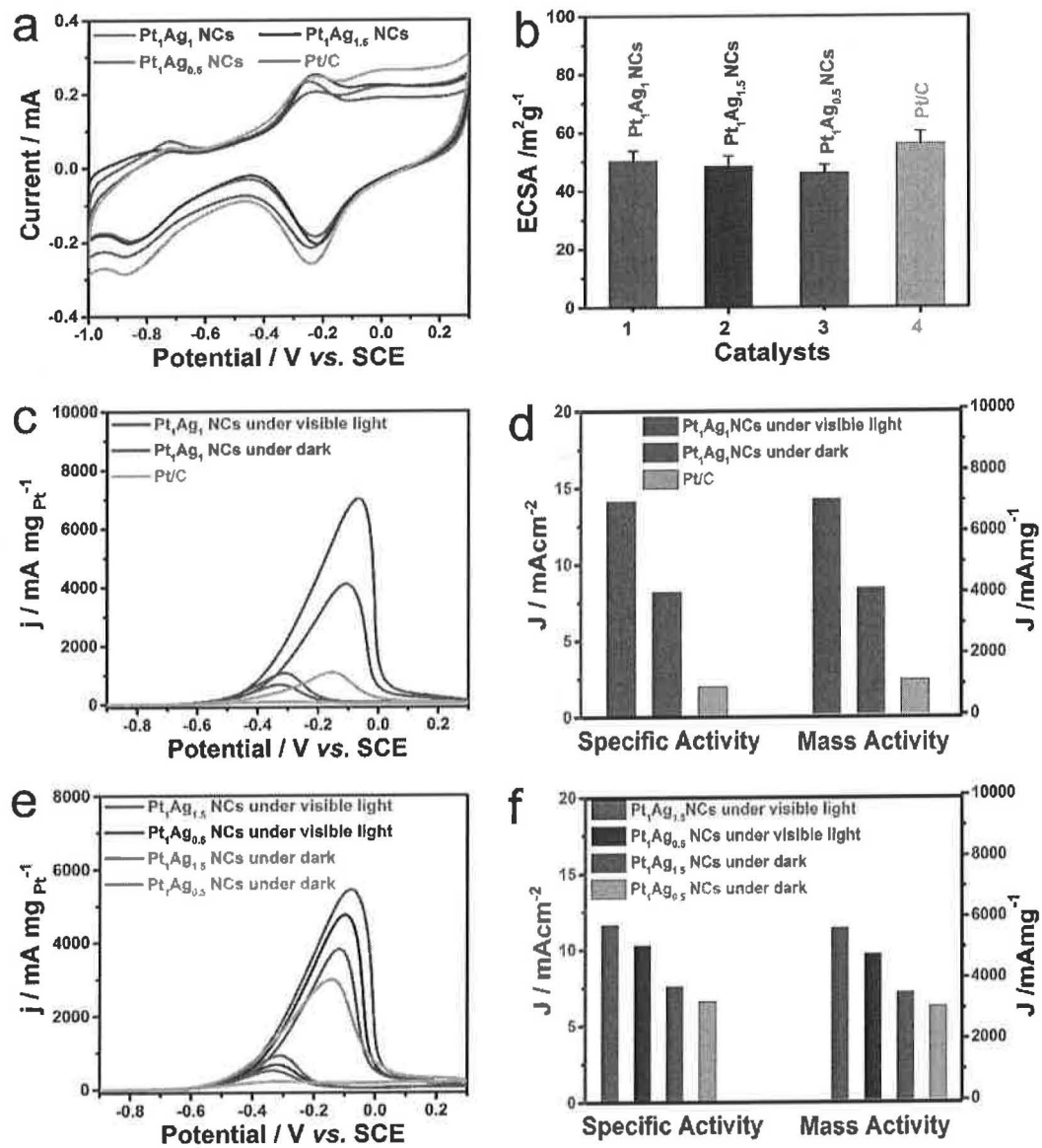


Fig.4

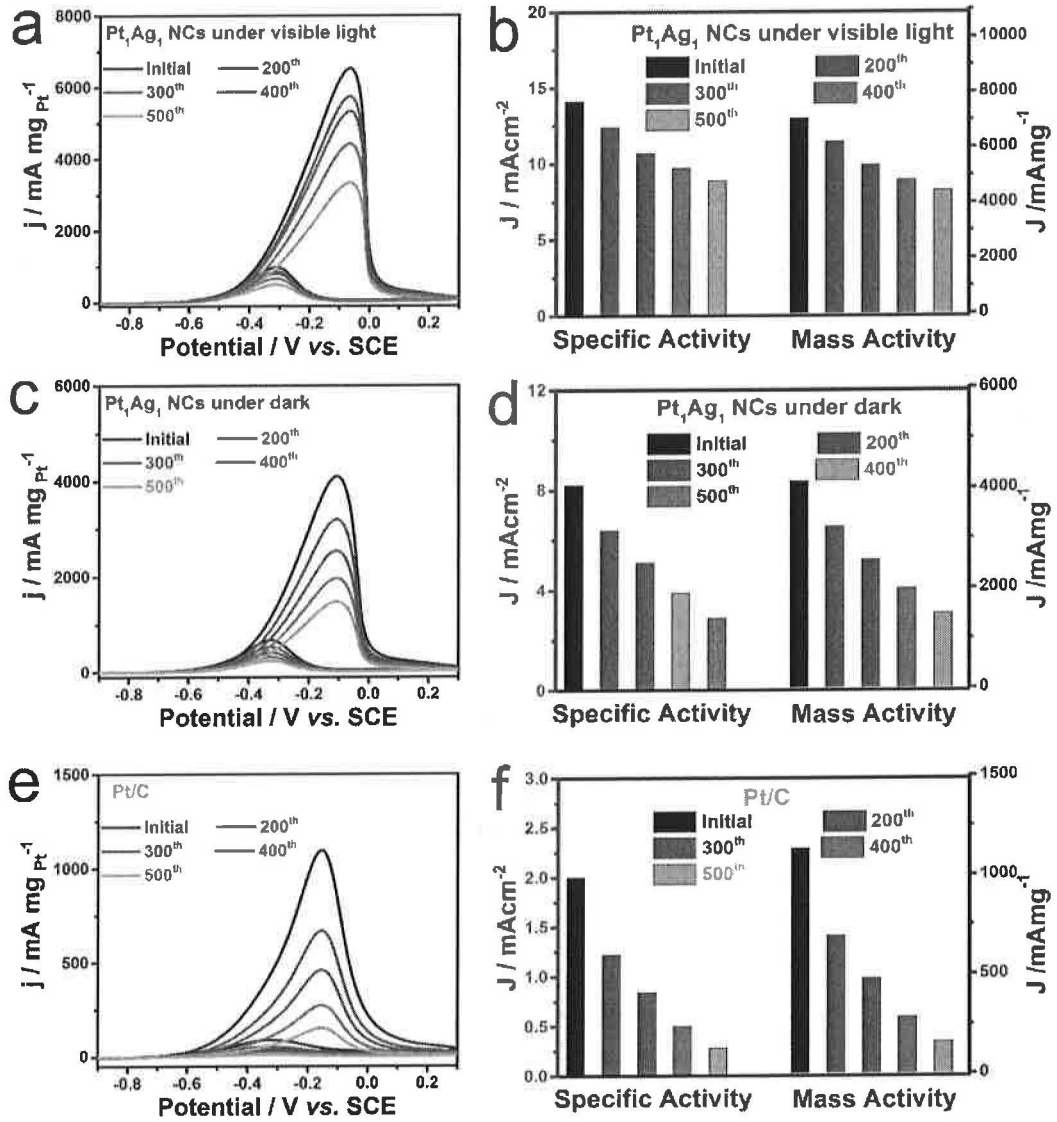
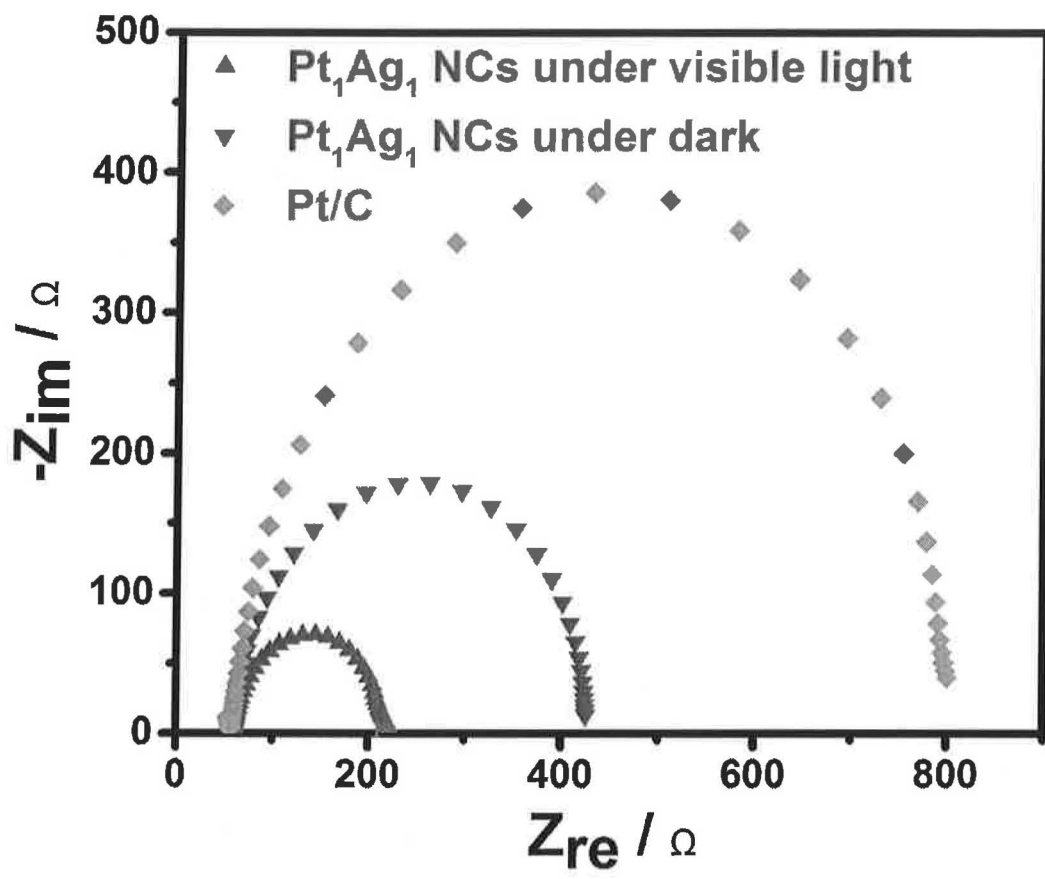


Fig.5



Supplementary Material

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Graphical Abstract

