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# Shell/Core Au/$CeO_2$ Nanospheres Attached to Indium Tin Oxide Surface for Electro-oxidation of Methanol in Alkaline Media

*Weihua Wang, Lijun Li, Yu Zhou, Yanfang Gao*, Zhenzhu Cao, Hong Wang, Caihong Li,*
*Zhaojun Wu, Jinrong Liu**

College of Chemical Engineering, Inner Mongolia University of Technology, Hohhot 010051,
P. R. China
*E-mail: yf_gao@imut.edu.cn; liujr@imut.edu.cn

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Although nanosized gold (Au) nanoparticles show a greater electrocatalytic activity than bulk gold, improving the electrocatalytic activity of gold still remains a challenge. In order to improve the performance of Au nanoparticles towards electro-oxidation of methanol, we use $CeO_2$ nanospheres as the catalyst support to obtain a $CeO_2$/Au core shell structure. In this paper, we demonstrate an interesting way to prepare catalysts by using $CeO_2$ nanoporous spheres as the supporting material, with Au nanoparticles assembled on the surface of the $CeO_2$ nanoporous spheres using 3-mercaptopropyltrimethoxysilane. The morphology and structure of these as-prepared materials are characterized by transmission electron microscopy (TEM), electron diffraction (ED) and scanning electron microscopy (SEM). The electrocatalytic properties of Au/indium tin oxide (ITO) and Au@$CeO_2$/ITO electrodes for methanol oxidation are investigated. The results indicate that the prepared Au@$CeO_2$/ITO electrode exhibits greater electrocatalytic activity and stability than the Au/ITO electrode.

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**Keywords:** Methanol electro-oxidation; $CeO_2$ nanosphere; Au nanoparticles

## 1. INTRODUCTION

Platinum (Pt) and Pt-based alloys are commonly employed as anode materials for electro-oxidation of methanol in direct methanol fuel cells. However, the major problem associated with Pt and Pt-based catalysts is the poisoning that occurs by CO-like species adsorbed on the catalyst surface, which are produced during the electro-oxidation of methanol in acidic media [1-3]. To overcome this problem, Au has been examined as a possible alternative substrate metal for the electro-oxidation of methanol in alkaline media. It has recently been shown that an Au electrode does not undergo poisoning during methanol electro-oxidation, because it does not electrogenerate $CO_{ads}$ [4, 5].

Bulk gold is considered to be a poor catalyst, but recent studies have shown that nanosized Au particles exhibit high catalytic activity, especially when Au is used as an anode catalyst towards methanol electro-oxidation [6, 7]. For nanoparticle catalysts, a support material is necessary. However, although various supporting materials such as carbon nanotubes, graphite, activated carbon fibers, and various kinds of porous carbon and carbon networks have been extensively investigated as potential supports for electrocatalysts, developing alternative electrode materials for better activity and stability for methanol electro-oxidation still remains a challenge. It has been reported that not only titanium carbide nanoparticles and tungsten carbide microspheres, but also titanium dioxide nanotubes and spheres, vanadium oxide nanotubes and manganese oxide nanotubes, have found use as supporting materials with good electrocatalytic properties [8-14]. As such, these results open up a new way to find excellent catalyst substrates.

Herein, we have used $CeO_2$ nanospheres as a catalyst support, since nanosphere structured materials have attracted much attention due to their high specific surface area and unique pore structure, which is anticipated to yield a high dispersion of Au nanoparticles. Although the resultant $Au/CeO_2$ catalyst has been reported by several researchers in traditional temperature-programmed reduction reactions and fuel cells [15-18], the type of shell and core structure of the $Au@CeO_2$ nanospheres used in methanol electro-oxidation in alkaline media has rarely been reported.

## 2. EXPERIMENTAL

### *2.1 Preparation of Au nanoparticles*

All glassware used in the preparation of colloidal nanoparticles was cleaned with freshly prepared aqua regia and rinsed thoroughly with deionized water. [Caution:] The Au nanoparticles was prepared following the method of Dan *et al* [19] with a few modifications. 1 mL of polyvinyl pyrrolidone (PVP) (10mg $mL^{-1}$) solution was mixed with 200 ml of 0.25 mmol $L^{-1}$ $HAuCl_4$ solution for 1h under vigorous stirring. Then, 5 ml of 0.1 mol $L^{-1}$ fresh $NaBH_4$ solution was dropwise added to the Au/PVP solution and the solution was continually stirred for 2h to produce an Au colloid seed solution. The resultant colloid nanoparticles were stored at 4 °C prior to use.

### *2.2 Fabrication of Au nanoparticle film electrodes*

Fabrication of Au nanoparticle electrodes were synthesized according to the literature method with a slight modification [20, 21]. A piece of ITO glass was cleaned with acetone and ethanol by ultrasonic cleaning, and then the carefully cleaned ITO glass was activated in 0.05 mol $L^{-1}$ NaOH for 30 min. The carefully treated ITO glass was first placed in a dilute solution of 3-mercaptopropyltrimethoxysilane (MPTS) (0.3 ml of MPTS in 3 ml of ethanol) for 12 h and then rinsed with copious amounts of ethanol upon removal.

The MPTS-modified ITO glass was subsequently immersed into the Au colloid seed solution and left for 12 h to allow the Au seed particles to attach to the ITO glass surface. After the ITO glass had been removed from the Au seed solution, the ITO glass surface was washed by flushing it with pure water several times, and was immediately immersed in a growth solution as follows: 10 ml of 0.25 mmol $L^{-1}$ $HAuCl_4$, 0.1 mol $L^{-1}$ cetyltrimethylammonium bromide (CTAB) solution and 0.05 ml of 0.10 M ascorbic acid solution [22]. The ITO glass treated in the Au colloid seed solution was immersed in the growth solution and left for 12h. The resultant Au nanoparticle-attached ITO substrate was removed from the growth solution, washed several times with pure water, and then dried for scanning electron microscopy (SEM) characterization and electrochemical measurements.

### *2.3 Synthesis of $CeO_2$ nanospheres and preparation of Au@$CeO_2$ working electrode*

In a typical reaction for $CeO_2$ spherical crystallites [23], 1 mmol of $Ce(NO_3)_3$ and 1 mmol of PVP (repeating unit) were dissolved in 40 ml of distilled water and the mixture was stirred magnetically for 30 min to obtain good homogeneity. The resultant solution was transferred to a 50ml Teflon-lined stainless steel autoclave, which was heated and maintained at 160 °C for 24 h. After cooling to room temperature naturally, the resultant light-yellow precipitate was filtered off, washed with distilled water and alcohol several times, and dried in a vacuum at 80°C for 12h.

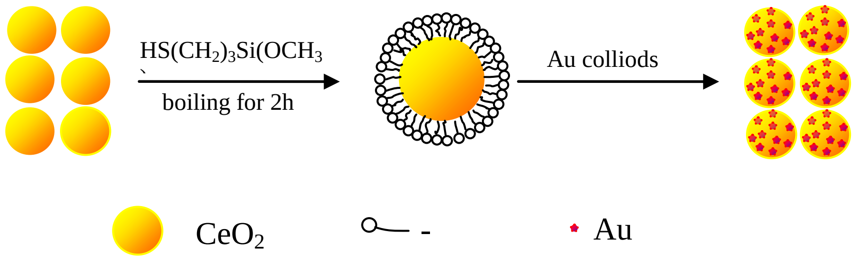
Formation of Au nanoparticles on an MPTS-modified $CeO_2$ nanosphere surface According to a similar process reported elsewhere [24,25], and as shown in scheme 1, 0.18 g of $CeO_2$ nanospheres were dispersed in 50 ml absolute ethanol and then sonicated for 20 min. The resultant colloidal solution was transferred into a three-neck flask equipped with a condenser, and 5 ml of methacryloxypropyltrimethoxysilane was injected into the flask, and the mixture was vigorously stirred at room temperature for about 1 h before being heated to reflux for 2 h under protection with nitrogen. After the mixture was cooled to room temperature, the solid product was filtered and washed with absolute ethanol six times, and then dispersed in 10 ml of ethanol by sonication for 10 min.

Thirty milliliters of Au colloid solution was introduced into a round-bottom flask containing 10ml of an ethanol dispersion of functional $CeO_2$ nanospheres, and the mixture was stirred overnight at room temperature. The solid product was filtered and washed with ethanol and distilled water. The obtained product was characterized by SEM and transmission electron microscopy (TEM).

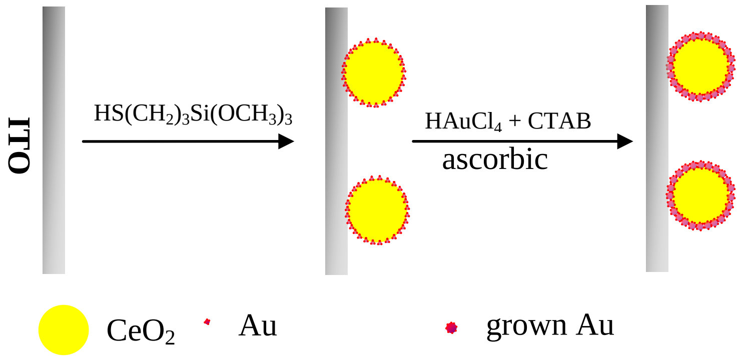
In order to achieve a stable working electrode, the Au@$CeO_2$/ITO electrode was immersed into the Au growth solution, as shown in scheme 2. The above obtained product was dispersed in 2 ml ethanol, and the suspension was uniformly pipetted onto the surface of an MPTS-modified ITO electrode. After drying, the Au@$CeO_2$/ITO electrode was immersed into the Au growth solution, as described in the preparation above for the Au/ITO electrode. The Au@$CeO_2$/ITO electrode with Au nanoparticles grown on the surface was characterized by electrochemical measurements.

### *2.4 Electrochemical Measurements*

Cyclic voltammetric (CV) measurements were performed using a CHI 660 electrochemical workstation (CH Instruments, Austin, TX) in a conventional three-electrode electrochemical cell using a twisted platinum wire as the auxiliary electrode and a KCl-saturated Ag/AgCl electrode as the reference electrode. The working electrode was an Au/ITO electrode or an Au@$CeO_2$/ITO electrode. Before taking the CV measurements, the working electrode was immersed in $N_2$ saturated electrolyte solution for 15 min to achieve a stable system.



**Scheme 1.** Schematic representation of the self-assembled Au nanoparticles on an MPTS-modified $CeO_2$ nanosphere



**Scheme 2.** Schematic representation of preparation of Au@$CeO_2$ working electrode

## 3. RESULTS AND DISCUSSION

Au colloids were synthesized according to a typical process [19]. Briefly, $HAuCl_4$ was reduced in $NaBH_4$ in the presence of PVP as a protecting reagent to yield Au nanoparticles with particle sizes of around 5 nm (Figs. 1A and 1B). These Au nanoparticles were then used as seed colloids. Cleaned ITO glass substrates were modified by immersion into an ethanolic solution of MPTS, yielding mercapto-terminated surface functionalities, as described by Jena *et al* [7] for assembling gold nanoparticles. Then, the freshly prepared gold nanoparticles were immobilized onto the MPTS-modified ITO surface by immersion of the latter into the growth solution for 12 h. The growth solution was employed to amplify the response current, which was otherwise hard to detect. In a study of the electrocatalytic activity of methanol oxidation by us, the gold nanoparticle film electrode modified by 5 nm Au nanoparticles achieved a response current of 0 ampere after several CV sweeps. If the ITO glass was treated in the seed solution, which was immersed in the growth solution and left for 12h, the Au /ITO showed a good electro-catalytic activity and stability of methanol oxidation. When the ITO glass substrate was removed from the growth solution, the surface bound Au nanoparticles attached to the ITO glass substrate appeared as a continuous red-violet film. In the growth solution, the ascorbic acid acted as a reducing agent and the CTAB acted as a dispersing agent.

We can clearly find that the Au nanoparticles are successfully attached to the surface of ITO electrodes, and the sizes of the Au nanoparticles grew to 50 nm (Figs.1C and 1D). As shown in Fig.1D, the Au nanoparticles show a good dispersion, and the distribution of nanoparticle sizes is very uniform due to the addition of CTAB. It was found that the greater the uniformity of dispersed Au nanoparticles, the higher the electro-catalytic activity shown by the Au catalysts [19].

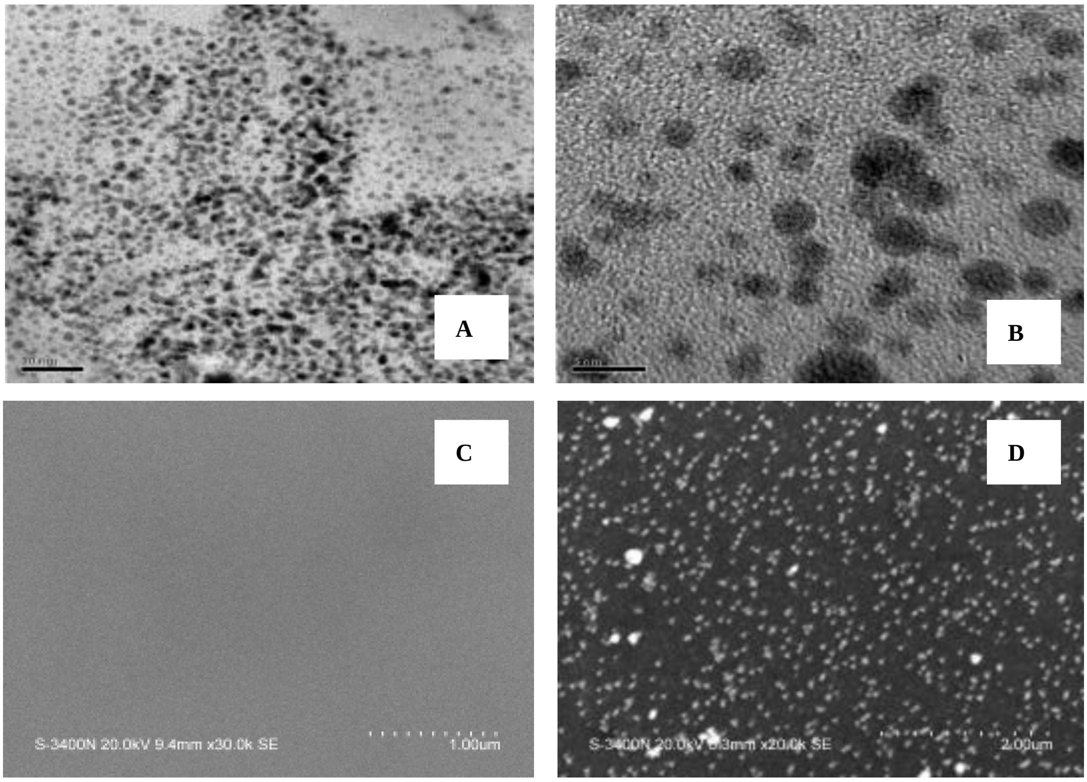


**Figure 1.** TEM images of A) and B) Gold nanoparticles, SEM micrographs of surfaces of C) bare ITO electrode and D) Au/ITO electrode.

$CeO_2$ nanospheres were synthesized by a hydrothermal treatment method as described elsewhere [23]. SEM images show that the morphology of the $CeO_2$ particles is spherical, with a size distribution of around 120 nm (Fig.2A). Fig. 2B shows an SEM image of the Au@$CeO_2$ nanospheres after Au nanoparticles were assembled on the surface of the $CeO_2$ nanospheres. The corresponding EDS spectrum is displayed on the right of Fig. 2B, which confirms that the Au nanoparticles were successfully anchored to the surface of the $CeO_2$ nanospheres by MPTS. The size of the Au nanoparticles is around 5 nm smaller than that of the $CeO_2$ particles, while the size of the Au@$CeO_2$ nanospheres is around the same as the $CeO_2$ nanospheres.

Figs. 2C and 2D show TEM images of the $CeO_2$ nanospheres and Au@$CeO_2$ nanospheres after assembly with 5 nm Au nanoparticles. The morphology of the $CeO_2$ nanospheres is spherical, which is in agreement with Fig. 2A. The $CeO_2$ nanospheres were aggregated with many smaller $CeO_2$

nanoparticles on the inside of the $CeO_2$ nanospheres. In this regard, the $CeO_2$ nanospheres have high specific surface areas, which is good for improving the dispersion of Au catalysts. Fig. 2D shows an amplified image of the Au@$CeO_2$ nanospheres. Compared with the $CeO_2$ nanospheres, the Au@$CeO_2$ nanospheres have a hierarchical structure consisting of interconnected small nanoparticles with a pore size of several nanometers. The numerous individual dark nanodots spread along the nanoporous spheres in Fig. 2D are Au nanoparticles, which indicates that the well-dispersed Au nanoparticles decorate the $CeO_2$ nanospheres quite uniformly. This also reveals that the -SH groups on the surface of the $CeO_2$ nanospheres play a key role in the attachment of the Au nanoparticles.

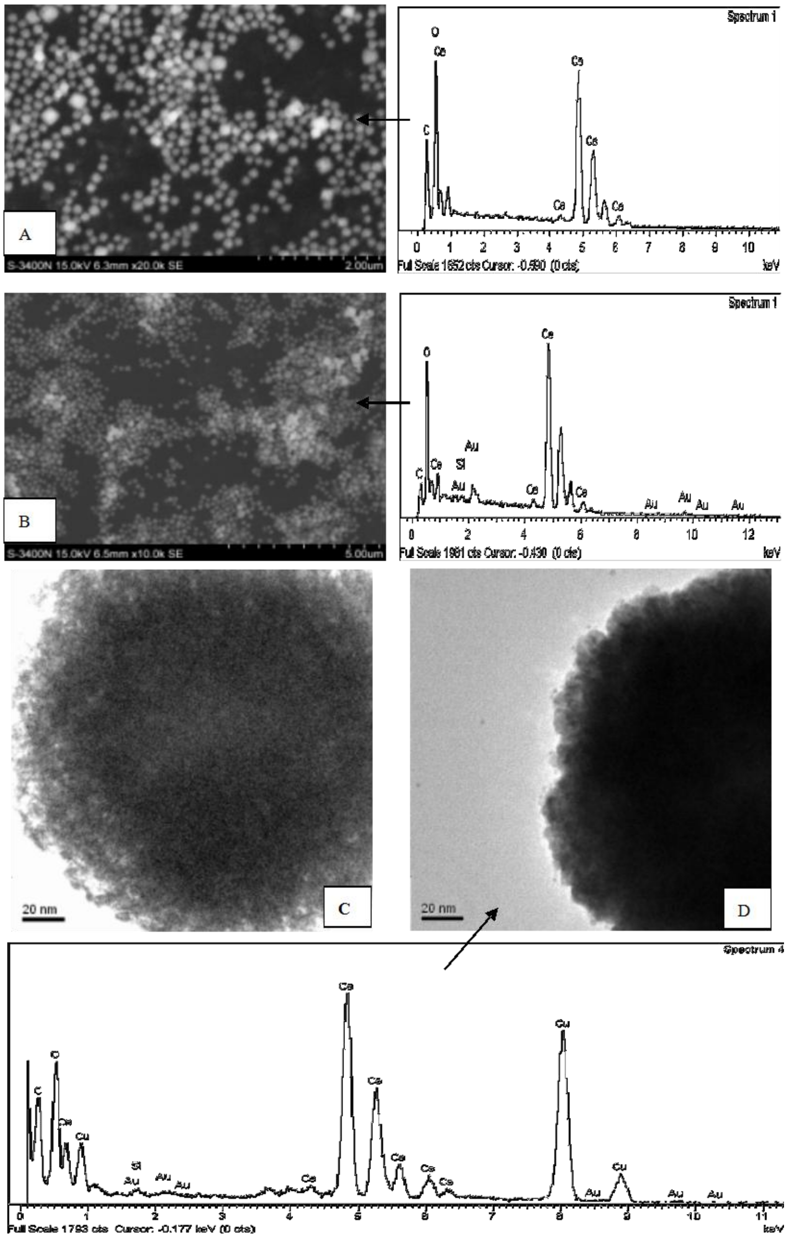


**Figure 2.** SEM images and the corresponding EDS spectra of A) $CeO_2$ nanospheres and B) Au@$CeO_2$ nanospheres; TEM images of C) $CeO_2$ nanospheres and D) Au@$CeO_2$ nanospheres and the EDS spectrum of D) Au@$CeO_2$ nanospheres. In these images, Au nanoparticle size is 5 nm.

The chemical composition of the Au@$CeO_2$ nanoparticles was determined using EDX spectroscopy, in which the main peaks of Ce, Au, and O were observed. Obviously, the strong Ce and O peaks are ascribed to the $CeO_2$ nanospheres and the Au peak is attributed to the Au nanoparticles decorated on the $CeO_2$ supports.

Fig. 3A shows the CV curves recorded in 0.1 mol $L^{-1}$ KOH solution for an Au nanoparticle/ITO electrode, $CeO_2$/ITO electrode and an Au@$CeO_2$/ITO electrode. A broad oxidation peak in the potential range from 0.3 to 0.6 V and a large reduction wave at 0.1 V, corresponding to the formation of surface oxides and their reduction were observed. The oxidation peak corresponded to oxidation of the gold. The results can be described by the following reaction [4, 5]:

$$Au + OH^- = Au(OH)_{ad} + e^- \quad (1)$$

$$Au(OH)_{ad} + OH^- = AuO_{ad} + H_2O + e^- \quad (2)$$

The reduction wave corresponded to the reduction of surface oxides:

$$AuO_{ad} + H_2O + 2e^- = Au + OH^- \quad (3)$$

Such a voltammetric response was not observed for the $CeO_2$/ITO electrode, revealing that the voltammetric features of the Au-nanoparticle-attached ITO electrode are due to the presence of nanostructured Au particles on the surface of the ITO electrode.

The gold particle area was calculated by using the charge involved in the reduction of the electrochemically formed Au oxide in the cyclic voltammograms recorded between -0.2 and 0.6 V in 0.1 M KOH, assuming the charge density for the reduction of the Au oxide is 723 μC/ $cm^2$[26].

Gold particle area ($cm^2$) = Au oxide reduction charge (μC)/723 (μC/$cm^2$)

The cyclic voltammetric response observed at the Au@$CeO_2$/ITO electrode is grater than that for Au/ITO, which may be because it is easy to generate $OH_{ads}$ functional groups on the surface of the $CeO_2$ nanospheres at low potentials in alkaline media, where the $OH_{ads}$ species formed following the adsorption of $OH^-$ anions, as shown in equation (4) [27].

$$CeO_2 + OH^- = CeO_2\text{-}OH_{ads} + e^- \quad (4)$$

Here, many more $OH^-$ anions were adsorbed at the interface between Au and $CeO_2$, which is considered an advantage for improving the current density of the oxidation peak and the reduction peak.

All the working Au@$CeO_2$ electrode material was grown in Au growth solution in this paper, details of which are given in the experimental part. Fig. 3B illustrates the typical CV curves obtained for methanol oxidation on the Au@$CeO_2$/ITO electrode with different concentrations of methanol. It can be seen that the oxidation peak current density of the positive scan increases with increasing methanol concentration in the solution. However, the oxidation peak potential of methanol shifted slightly. This may be attributed to the influence of the formation of surface gold oxides [6].

The process of methanol oxidation on Au in alkaline media has been proposed as follows [5]:

$$CH_3OH + 5OH^- \longrightarrow HCOO^- + 4H_2O + 4e^- \qquad (1)$$

And the intermediate steps are shown in the following reaction equations:

$$CH_3OH + {}^{-\delta}HOAu \longrightarrow (HOH_2C\ldots H\ldots{}^{-\delta}HOAu)_{ad} \qquad (2)$$

$$(HOH_2C\ldots H\ldots{}^{-\delta}HOAu)_{ad} + OH^- \longrightarrow {}^*CH_2OH + e^- + H_2O + {}^{-\delta}HOAu \qquad (3)$$

$$^*CH_2OH + 4OH^- \longrightarrow HCOO^- + 3e^- + 3H_2O \qquad (4)$$

It can be seen from the reaction equations that the adsorbed $OH^-$ anions play a governing role in methanol electro-oxidation on Au in alkaline media. In alkaline solution containing methanol, the oxidation current of the positive scan arises from the oxidation of Au and methanol. Firstly, plenty of $OH^-$ anions were chemisorbed by the Au@$CeO_2$/ITO electrode to assist the generation of abundant Au oxides. Then, methanol was oxidized on the surface of the Au oxides with the association effect of the $OH^-$ anions at a higher anodic potential scan [6, 7]. At low concentration of methanol in alkaline solution, there was an electrochemical reduction peak at the cathodic scan in Fig. 3B, which was attributed to the reduction of the remaining Au oxides. Nevertheless, the cathodic reduction peak gradually decreased with increasing concentration of methanol, causing the cathodic reduction peak to disappear and a cathodic oxidation wave to appear in its place with the further increasing concentration of methanol. It is confirmed that the Au oxides involved in the catalytic oxidation of methanol and the surface oxides function as an electron-transfer mediator in the oxidation process [6, 7].

Fig. 3C compares the electrocatalytic activity of the Au@$CeO_2$/ITO electrode and the Au/ITO electrode toward the direct oxidation of methanol. The Au@$CeO_2$/ITO electrode shows the oxidation peak and reduction peak at a more negative potential than the Au/ITO electrode does, indicating the better electrocatalytic activity of the Au@$CeO_2$/ITO electrode. Fig.3C also shows that $CeO_2$ has no electrocatalytic ability towards methanol electrooxidation, it indicates that the Au is the key catalyst for the methanol electrooxidation on the Au@$CeO_2$. The catalytic current for methanol oxidation on the Au/ITO electrode is much lower than that on the Au@$CeO_2$/ITO electrode. There may be several reasons for this. Firstly, the $CeO_2$ nanospheres have a high specific surface area, which enables a high dispersion of gold catalyst. Secondly, the catalytic effect of the Au@$CeO_2$/ITO electrode can also be attributed to the generated surface Au oxides and $OH^-$ anions adsorbed on the surface between the $CeO_2$ and Au. These $OH^-$ anions are known to act as an electron-transfer mediator in the oxidation process [4]. As is known, the generation of $OH_{ads}$ functional groups on the surface of the $CeO_2$ nanospheres is relatively easy at low potentials in alkaline media. Moreover, the $OH_{ads}$ species formed from the adsorption of $OH^-$ anions indicates that the $CeO_2$ nanospheres strongly favor the formation of surface gold oxides and $OH^-$ chemisorption [27]. Lastly, the $CeO_2$ nanospheres can adsorb methanol and formaldehyde at low temperature, which is considered good for improving the oxidation current for the electro-oxidation of methanol [28, 29].

The chronoamperometric technique is an effective method to evaluate the electrocatalytic activity and stability of an electrode material. Fig. 3D shows typical current density–time responses for methanol oxidation measured at a fixed potential of 0.7 V on Au/ITO and Au@CeO$_2$/ITO electrodes. To each electrode, the methanol electro-oxidation current decreases moderately with time. The current measured for the Au@CeO$_2$/ITO electrode is higher for all corresponding potentials than the Au/ITO electrode. This result proved that the Au@CeO$_2$/ITO electrode has better activity, which is consistent with the results obtained from the cyclic voltammograms of methanol electro-oxidation.

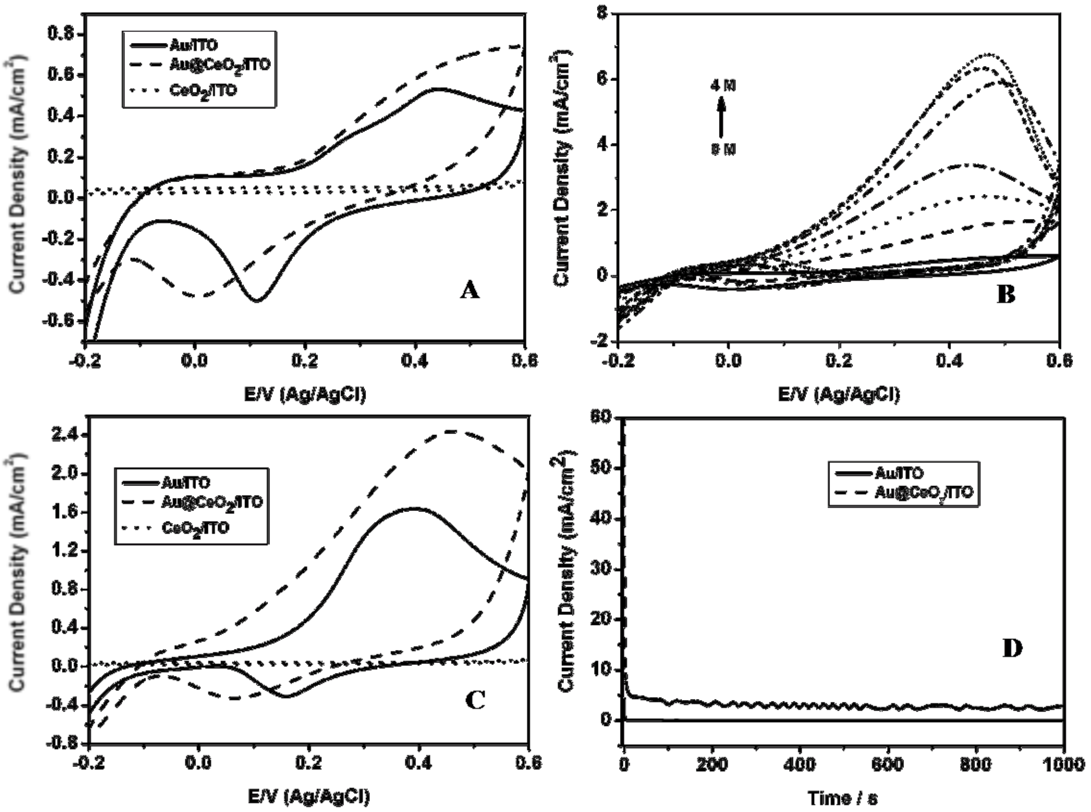


**Figure 3.** A) Cyclic voltammograms (CV) at an Au/ITO electrode, CeO$_2$/ITO electrode and an Au@CeO$_2$/ITO electrode in 0.1 mol L$^{-1}$ KOH solution. Scan rate: 10 mV S$^{-1}$. B) CV curves of 0, 0.5, 1, 2, 3 and 4 mol methanol in 0.1 mol L$^{-1}$ KOH solution on Au@CeO$_2$/ITO electrode, scan rate is 10 mV S$^{-1}$. C) CV curves for the oxidation of methanol at Au/ITO, CeO$_2$/ITO electrode and Au@CeO$_2$/ITO electrodes in 0.1 mol L$^{-1}$ KOH solution and 1mol L$^{-1}$ CH$_3$OH solution. Scan rate: 10 mV s$^{-1}$. D) Chronoamperometry curves for Au/ITO electrodes and Au@CeO$_2$/ITO in 0.1 mol L$^{-1}$ KOH solution and 1mol L$^{-1}$ CH$_3$OH solution at 0.7 V for 1000 s.

## 4 .CONCLUSIONS

Au@CeO$_2$ shell core structures were successfully obtained and used as a kind of electrocatalyst in the electro-oxidation of methanol in alkaline media. An electrochemical study indicated that the Au@CeO$_2$ electrode had better electrocatalytic activity for methanol oxidation in KOH solution than the Au/ITO electrode. Although the current density of the Au-based catalyst is much lower than a Pt-based catalyst, it was found that the catalytic activity will be improved greatly by achieving unique morphologies and nanosizes of the $CeO_2$ nanospheres and Au nanoparticles. It also implies that $CeO_2$ nanospheres may be good candidates for noble metal catalyst supports, and have potential application in preparing catalysts for direct methanol fuel cells. Further experimental and theoretical studies are needed to identify mechanisms leading to the enhancement of catalytic activity by the supporting materials.

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