



Synthesis, characterization and electrochemical properties of mesoporous zirconia nanomaterials prepared by self-assembling sol–gel method with Tween 20 as a template

Yongjun Chen^{a,b,**}, Suzanne K. Lunsford^c, Yongcheng Song^a, Huangxian Ju^b, Polycarpus Falaras^d, Vlassis Iikodimos^d, Athanassios G. Kontos^d, Dionysios D. Dionysiou^{e,*}

^a Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, PR China

^b Key Laboratory of Analytical Chemistry for Life Science (Ministry of Education of China), Department of Chemistry, Nanjing University, Nanjing 210093, PR China

^c Department of Chemistry, Wright State University, Dayton, OH 45435, USA

^d Institute of Physical Chemistry, NCSR Demokritos, 15310 Aghia Paraskevi, Attiki, Greece

^e Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221-0071, USA

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ABSTRACT

Zirconium dioxide nanomaterials, including nanoparticles and their derived films, were synthesized using a new surfactant self-assembling sol–gel route, which involves complexation of zirconium alkoxide precursor with acetylacetone as a chelating agent and Tween 20 as a structural directing agent. The properties of the synthesized material were studied using XRD, SEM, SAXS, HRTEM and N₂ adsorption and desorption analysis. It was found that Tween 20 can greatly increase the BET surface area and pore volume, inhibit crack formation in the derived film and retard particle growth at some extent. There exists tetragonal crystalline network with narrow pore size distribution in the ZrO₂ nano-materials prepared with Tween 20 in the sol. Furthermore, a mechanism on the formation of mesopore ZrO₂ structure via the Tween 20 self-assembling sol–gel process is presented. With the selection of the sono-gel carbon electrode modified by the mesoporous ZrO₂ film (M-ZrO₂ film) prepared with 1.10 g Tween 20/ml zirconia sol, enhanced electrochemical responses (i.e., enhanced peak currents) to catechol and ascorbic acid were confirmed using cyclic voltammetry (CV). Moreover, the modified electrode demonstrated additional improved electrochemical properties, such as good reversibility ($i_{pc}/i_{pa} \approx 1$) and high selectivity (exceptionally resolved oxidation peaks between catechol and ascorbic acid), good stability and repeatability.

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1. Introduction

The field of mesoporous materials has been extensively investigated since the discovery of ordered mesoporous materials by the scientists of Mobil Corporation in 1992 [1–3]. Recently, synthesis of mesoporous materials in thin film configuration has attracted significant interests due to their unique characteristics, such as high BET surface area and large pore volume [4], which has in fact brought a great technological potential in their applications in many fields including membrane separation [3–5], chemical sensors [3,5,6], surfaces for heterogeneous catalysis [3,7], and optical devices [4]. Among various popular film preparation techniques, such as etching technology [8], electrodeposition [9], sol–gel

[10–17], spraying methods [18], electrochemical anodization [19], chemical vapor deposition [20] and atomic layer deposition [21], the self-assembling sol–gel route based on the supramolecular assembly of templates as structure-directing agents, a “bottom-up” approach, is considered to be an excellent method for the preparation of mesoporous oxide films with controllable crystallinity and film morphology, tailor-designed pore structure, high BET surface area, and controlled film thickness [10–12,14,15]. For such preparation routes, the soft templates (i.e., surfactants) play a vital role in directing the formation of mesoporous structure via the formation of self-aggregated organization (i.e., surfactant micelles) in the solution [11,12,14,15,22].

Recently, there is significant activity in the development of smart nanosensors for *in situ* detection of chemicals of interests due to their simplicity, fast response and high sensitivity [6,23–25]. Since metal oxide semiconductors (i.e., ZrO₂, TiO₂) as electrode materials have many advantages including robustness, chemical and thermal stability, low cost, biocompatibility, and relatively high electronic conductivity [23–25], synthesis of mesoporous oxide

* Corresponding author. Tel.: +1 513 556 0724; fax: +1 513 556 2599.

** Co-corresponding author. Tel.: +86 411 84708015; fax: +86 411 84708460.

E-mail addresses: chenyjuc@gmail.com (Y. Chen), dionysios.d.dionysiou@uc.edu (D.D. Dionysiou).

semiconductors has become an important issue in the construction of smart nanosensors equipped with the electrode decorated by metal oxides [23–26].

Encouraged by the promising electrochemical properties of ZrO_2 , a wide gap semiconductor [27,28], of which its synthesis method was reported in our previous study [25], in this study, we report the synthesis of mesoporous ZrO_2 nanoparticles and films by employing a new surfactant self-assembling sol–gel method associated with incorporating an environmentally friendly surfactant Tween 20 as a structure-directing agent into the sol we had employed before [25]. The advantage of employing such a type of modified sol is due to its beneficial characteristics including good mixing of precursor materials at molecular level, good stability (i.e., it is stable for more than one month) for film preparation and relatively high sol viscosity induced by Tween 20, which is beneficial to the increase in the film thickness by dip coating process [14]. The result in this study demonstrated that Tween 20 is an effective structure-directing agent to synthesize mesoporous ZrO_2 nanoparticles and films with improved structural properties. Electrochemical characterization of the mesoporous ZrO_2 films using cyclic voltammetry showed that such films exhibit improved electrochemical response to catechol, a phenolic chemical and a well known neurotransmitter [6]. There were few reports on employing Tween 20 as a structural directing agent in the synthesis of some oxides such as TiO_2 and $TiO_2-Al_2O_3$ [14,29]. However, to the best of our knowledge, there is no report on the synthesis of mesoporous ZrO_2 nanomaterials by incorporating Tween 20 surfactant as a new structure directing agent into the zirconia sol containing zirconium alkoxide precursor stabilized by acetylacetone as a chelating agent and on the study of their electrochemical properties using cyclic voltammetry (CV).

2. Experimental

2.1. Materials

Zirconium (IV) propoxide solution 70 wt.% in 1-propanol (Aldrich), ethanol (200 proof, Aldrich), acetylacetone (99%, Fisher Scientific) and de-ionized water were used for the preparation of the zirconia sol. The molar ratio of zirconium (IV) propoxide:water:acetylacetone:ethanol was 2:4:1:62. Surfactant Tween 20 (Sigma ultra) with different loadings (0.55, 1.10, 1.65, and 2.20 g/ml zirconium sol) was added into zirconium sol. After vigorous stirring, a transparent and homogenous sol was formed. ZrO_2 nanoparticles were prepared using 5 ml sol. The sols on the borosilicate glass dishes were dried at room temperature ($\sim 23^\circ C$) and at relative humidity (RH%) of 44–50% for 8 h and then put into a programmable high temperature furnace (Paragon Model HT-22-D, Thermcraft Inc., Winston-Salem, North Carolina) for calcination. The materials and method to prepare sonogel carbon (SGC) electrode are the same as those reported in our former study [25]. The ZrO_2 gel was coated on the tip of the SGC electrode by dipping the carbon electrode into the sol followed by its careful withdrawal from the sol. A withdrawal velocity of ~ 12.3 cm/min was employed to prepare ZrO_2 films coated on the glass substrates. After the coated gels were “dried” at room temperature, they were calcined in a furnace. The furnace temperature was incremented at a ramp rate of $15^\circ C\ min^{-1}$ to $100^\circ C$ and hold for 15 min, then continued to increase at a ramp rate of $3.0^\circ C\ min^{-1}$ until $500^\circ C$ and was held at this value for 30 min. Finally, the films were cooled naturally to room temperature.

2.2. Characterization of ZrO_2 nanomaterials

The crystal phase composition of ZrO_2 nanomaterials prepared with different Tween 20 loadings was determined by X-ray

diffraction (XRD) using a Siemens Kristalloflex D500 diffractometer with $Cu\ K\alpha$ radiation ($\lambda = 0.154$ nm). Small-Angle X-ray Scattering (SAXS) measurements were performed using a SAXSess instrument at accelerating voltage of 40 kV and current of 50 mA. A nickel filtered $Cu\ K\alpha$ radiation source ($\lambda = 0.154$ nm) was employed. During the sample analysis, sandwich holders with Kapton films were used for containing the as-prepared ZrO_2 samples. The crystal and pore morphology of ZrO_2 nanomaterials were determined by a JEM-2010F (JEOL) High Resolution-Transmission Electron Microscope (HR-TEM) with field emission gun at 200 kV. All powder samples were dispersed in methanol (High Performance Liquid Chromatography (HPLC) grade, Pharmco) using an ultrasonic cleaner (2510R-DH, Branson) for 5 min and fixed on a carbon-coated copper grid (LC200-Cu, EMS). The BET surface area and pore structure of ZrO_2 nanoparticles were determined using a Micromeritics TriStar 3000 Gas Adsorption Analyzer. The surface morphologies of ZrO_2 films coated on the borosilicate glasses were characterized by an environmental scanning electron microscope (ESEM, Philips XL 30 ESEM-FEG) with accelerating voltage of 10 K. A UV–vis spectrophotometer (HP 8452A) was employed to obtain information on the optical properties of the as-prepared mesoporous ZrO_2 films.

2.3. Electrochemical sensor response

Electrochemical behavior of catechol at the electrodes was carried out using an Electrochemical Workstation (Epsilon, Bioanalytical Systems) based on cyclic voltammetry (CV) with a three-electrode compartment cell [25]. The electrochemical compartment cell was composed of a Pt auxiliary electrode (Bioanalytical Systems), Ag/AgCl reference electrode (Bioanalytical Systems), and the working electrode (i.e., sono-gel carbon electrode modified by ZrO_2 films). Catechol ($C_6H_4(OH)_2$, Fluka) solutions at different concentrations were prepared in 0.1 M sulfuric acid (Aldrich) with de-ionized water. In addition, a 5.0 mM catechol solution mixed with 5.0 mM ascorbic acid ($C_6H_8O_6$, Aldrich), a common interferent, was prepared in 0.1 M sulfuric acid (Aldrich) with de-ionized water. The scan rate of CV was $100\ mV\ s^{-1}$.

3. Result and discussion

3.1. Surface morphology of ZrO_2 films

It has been well established that good structural integrity of the metal oxide film is beneficial to obtaining good long-term mechanical stability of the films [14]. For the application of electrochemical sensor using the electrode coated by metal oxide film, a continuous conducting network of metal oxide media is necessary for an effective electron transfer. Therefore, the fabrication of ZrO_2 film with good structural integrity becomes an important issue to the construction of a robust and effective electrode for sensor application. In order to investigate whether Tween 20 addition into the sol can improve structural integrity of the film, two types of ZrO_2 films prepared without and with Tween 20 were coated on the borosilicate glass to compare their surface morphologies. It was found that there was no formation of cracks on the ZrO_2 film prepared with Tween 20 loading of 1.10 g/ml Zirconia sol (M- ZrO_2 film), while many cracks were seen on the ZrO_2 film prepared without Tween 20. Therefore, incorporating Tween 20 into the sol is beneficial to avoiding crack formation of the ZrO_2 film. The mechanism of crack formation for sol–gel-derived inorganic films is attributed to the formation of tensile stresses induced by capillary force during the period of drying and densification process [30–32]. Tween 20 has a low volatility due to its high boiling point (above $100^\circ C$) and can hold a certain amount of solvent (i.e., ethanol) and water. As a result, it is believed that Tween 20 can decrease the evaporation

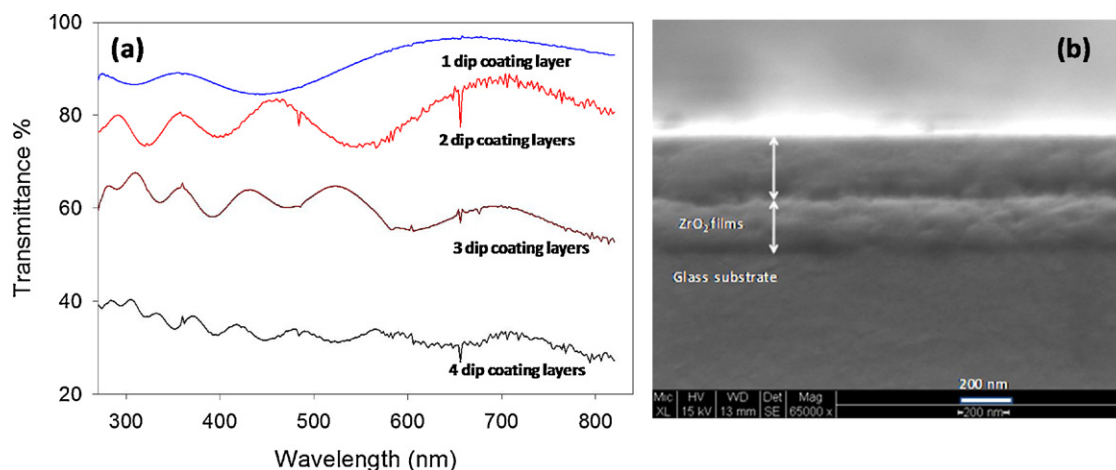


Fig. 1. (a) UV-visible transmission spectra of M-ZrO₂ films coated on borosilicate glass and (b) cross-section SEM image of M-ZrO₂ films coated on borosilicate glass.

rate of solvent and enhance stress relaxation in the gel. Therefore, incorporating Tween 20 into the sol can inhibit crack formation for the ZrO₂ film.

3.2. Optical properties of the mesoporous ZrO₂ film

UV-vis spectroscopy analysis was performed to obtain information on the optical properties of mesoporous ZrO₂ films prepared by such a surfactant self-assembling sol-gel route. During the period of UV-vis spectroscopy measurements, the borosilicate glass without any coating was used as a reference. The results on transmittance of ZrO₂ films prepared with Tween 20 loading of 1.10 g/ml Zr sol (M-ZrO₂ films) at different number of dip coating layers are shown in Fig. 1(a). It can be observed that the ZrO₂ films with one dip coating layer (two layers at both sides) were highly transparent, reaching 85–97% at the range of wavelength from 280 nm to 800 nm. High transmittance of the films can be explained by small crystalline size and high porosity of the film, which will be discussed later. In order to obtain information on the film thickness associated with the transmittance of mesoporous ZrO₂ films, the film thickness was also measured by cross-section SEM analysis, which is shown in Fig. 1(b). It can be seen that the thickness of M-ZrO₂ film at the first dip coating layer and the second dip coating layer was ~200 nm and ~250 nm, respectively. The increase in the number of dip coating cycles leads to a remarkable decrease in the transmittance of the films, for example, a 9% decrease in the transmittance of M-ZrO₂ film at wavelength of 365 nm when each film thickness increased from 200 nm to 450 nm. At the same time, it was observed that as the number of dip coating cycles increases, more interference fringes appeared in the transmittance curves as a result of the increase in film thickness [33]. It should be noted that for *in situ* sensor applications, absorption of sunlight by semiconducting electrodes should be eliminated in order to avoid possible photocatalytic degradation of the target chemicals of interests. Thus, optimizing film thickness of our mesoporous ZrO₂ films in order to eliminate UV light absorption should not be ignored in their employment as sensors.

3.3. Crystalline structure of the as-prepared ZrO₂

The crystalline structures of ZrO₂ nanomaterials were investigated using powder X-ray diffraction analysis. The results are shown in Fig. 2. The presence of four sharp peaks at 2θ angle of 30.2°, 34.9°, 50.2°, and 58.9° indicates the existence of tetragonal zirconium dioxide (t-ZrO₂) [25,27]. Increasing Tween 20 loading in the sol leads to the enhancement of the full width at half-maximum

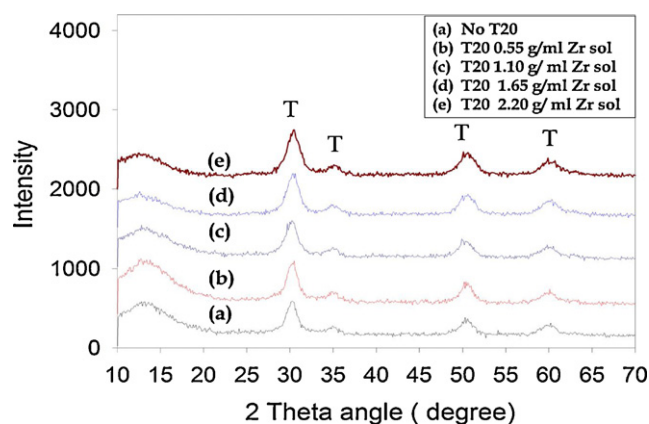


Fig. 2. X-ray diffraction spectra of ZrO₂ powders prepared at different Tween 20 loading.

intensity (FWHM) of t-ZrO₂ (1 0 1) at 2θ of 30.2° [27,34,35], suggesting that Tween 20 can inhibit particle growth at some extent during hydrolysis and condensation process, which is in agreement with our former report [14,15]. Fig. 3 shows small angle XRD analysis for ZrO₂ nanomaterials prepared at different Tween 20 loadings. The ZrO₂ samples prepared with Tween 20 loading of 1.10 g/ml zirconia sol presented peaks at $Q = \sim 0.50 \text{ nm}^{-1}$ corresponding to a 2θ

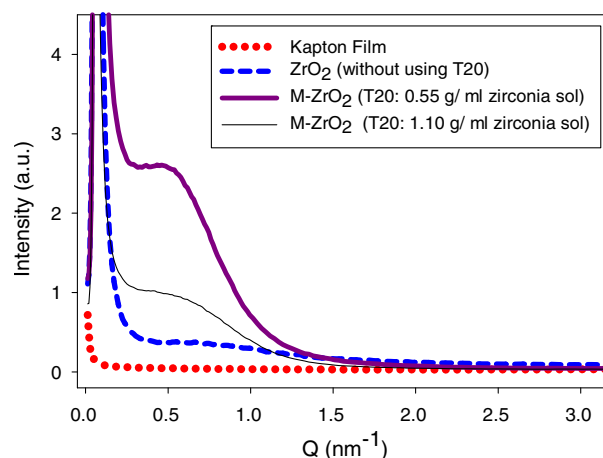


Fig. 3. Small angle XRD analysis of ZrO₂ nanoparticles at different Tween 20 loading. $Q = 4 \times \pi \times \sin(\theta)/\lambda$.

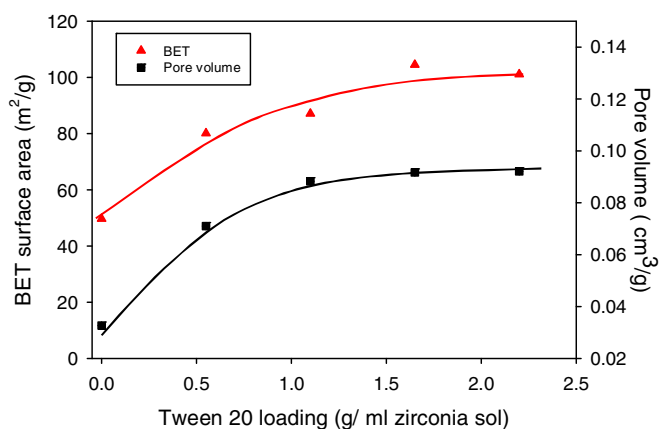


Fig. 4. Effect of Tween 20 loading on the BET surface area and pore volume of ZrO₂ nanomaterials.

angle of $\sim 0.70^\circ$ with an average inter-particle distance of ~ 12.6 nm among the mesoporous nanocrystals, while there was almost no peak for the ZrO₂ sample prepared without Tween 20. Therefore, Tween 20 can improve the formation of mesoporous crystal structure of ZrO₂ nanomaterials.

3.4. Texture of the mesoporous ZrO₂ nanomaterials

It was found that increasing Tween 20 loading in the sol can remarkably increase BET surface area and pore volume of ZrO₂ nanocrystals (see Fig. 4). When Tween 20 loading reaches 1.10 g/ml zirconia sol, the BET surface area and pore volume of ZrO₂ nanoparticles reach 87.1 m²/g and 0.0883 cm³/g, respectively. Fig. 5 shows the pore size distribution (PSD) and nitrogen adsorption–desorption isotherms of the ZrO₂ sample prepared with Tween 20 loading of 1.10 g/ml zirconia sol. A type-IV isotherm, characteristic of mesoporous structure (the BDDT classification) [15,36], was obtained. The shape of the hysteresis loop is of a type H2, suggesting the existence of spherical pores [36]. BJH adsorption average pore diameter was 3.8 nm with a relatively narrow pore size distribution, ranging from 2.5 to 15 nm. The smaller pore size may be attributed to the smaller micelle size of Tween 20 surfactant in the sol during the evaporation self-assembling sol–gel process. In order to obtain more information associated with the characteristic of mesoporous ZrO₂ nanomaterials, HRTEM analysis

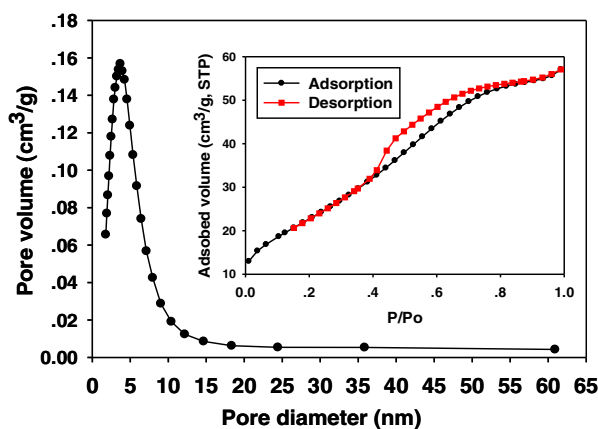


Fig. 5. Pore size distribution curve of ZrO₂ material (500 °C calcination). Inserted graph: nitrogen adsorption and desorption isotherm of ZrO₂ material (Tween 20 loading of 1.10 g/ml in the zirconia sol).

was also performed. As an example, Fig. 6(a) and (b) shows particle morphology, pore structure and lattice space of ZrO₂ nanoparticles prepared with Tween 20 loading of 1.10 g/ml zirconia sol. Interconnected nanoparticles with size of 4–10 nm are observed (Fig. 6(a)). SAED pattern of the images shown in the inserted graph of Fig. 6(a) indicates that, after calcination at 500 °C, the particles have been completely crystallized, since only diffraction spots and not amorphous diffraction rings are observed. Therefore, an interconnected crystal network has been formed in the mesoporous ZrO₂ film. Fig. 6(b) proves the presence of mesopores with pore wall of particles with a lattice space of 0.295 nm, corresponding to the (1 0 1) inter-plane distance of the ZrO₂ tetragonal phase [34]. Therefore, tetragonal phase can be formed in mesoporous ZrO₂ nanomaterials after 500 °C calcination.

3.5. The mechanism on the mesopore formation of ZrO₂ nanomaterials

In the employed zirconia sol, there are Zr(OR)_(4-x)(acetyl)_x new precursors ($x = 0$ to 4, acetyl: acetylacetone) due to the complexation of Zr(OR)₄ with acetylacetone [37]. When Tween 20 is added into the zirconia sol, hydrogen bonds can be formed between Tween 20 and water in the sol, due to Tween 20's high hydrophilicity (hydrophilic/lipophilic balance HLB = 16). During ageing and dry-

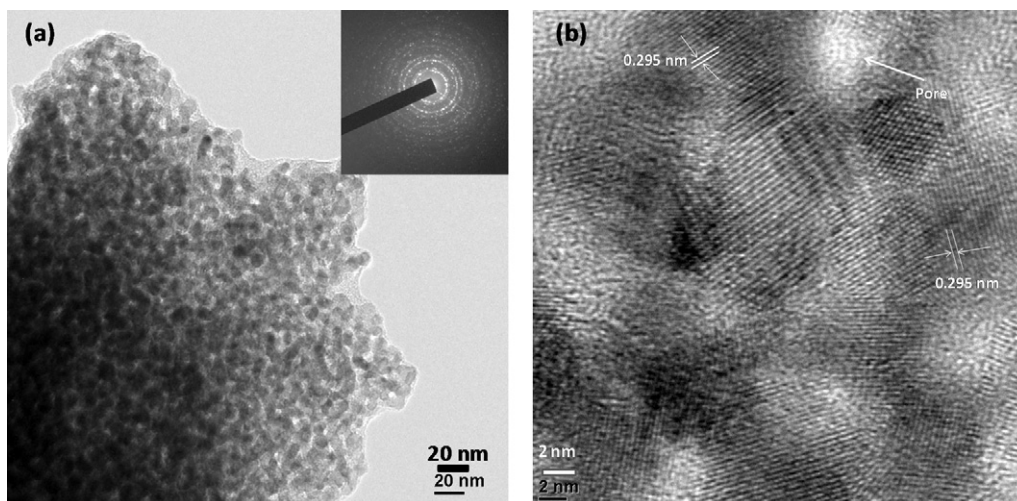
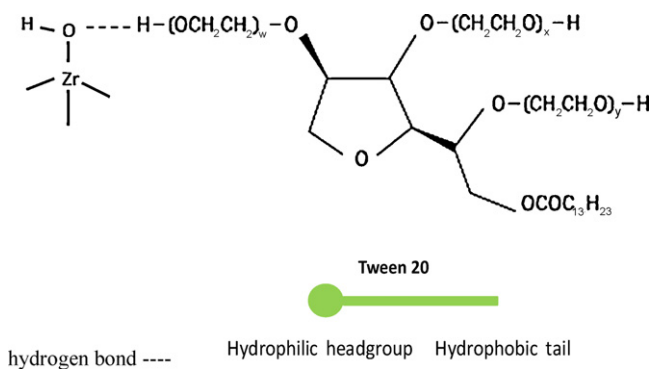
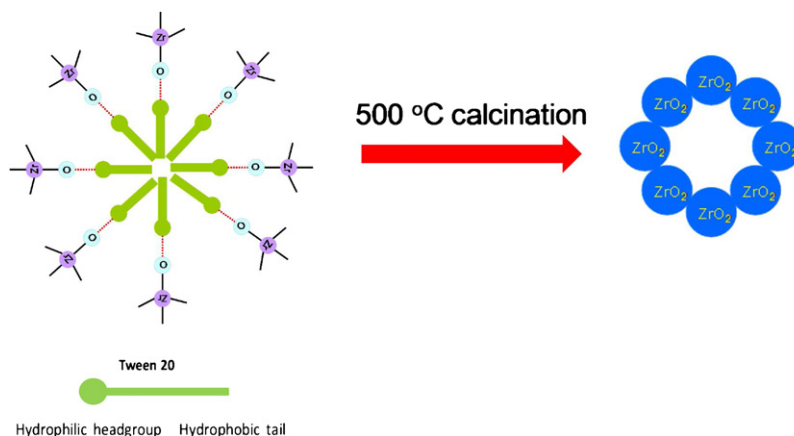


Fig. 6. HRTEM images of ZrO₂ particles prepared with Tween 20 1.10 g/ml in the zirconia sol. (a) Low magnification (inserted graph: SAED pattern of image) and (b) high resolution image.



Scheme 1. Molecular structure of $-\text{Zr}-\text{O}-\text{H}-\text{---}-\text{Tween}20$ copolymer.

ing periods, a large number of Tween 20 micelles can be formed as a result of the solvent evaporation. At the same time, hydrolysis and condensation reactions of the new precursors take place, which lead to the formation of zirconium-based organic–inorganic hybrid copolymer networks (see proposed **Scheme 1**). High calcination temperature (i.e., $500\text{ }^\circ\text{C}$) eliminates Tween 20 micelles and other organic content (i.e., ethanol) and leads to the formation of mesoporous ZrO_2 inorganic crystalline framework, while pore size is determined by the Tween 20 micelle size in correlation with its molecular size. Thus, the assembly of mesoporous structure of ZrO_2 film is mainly due to the existence of hydrogen



Scheme 2. The mechanism on the mesopore formation.

bonding between Tween 20 and Acetyl-Zr–O–H organic–inorganic network (see **Scheme 2**). Therefore, S^0I^0 assembly pathway (where S^0 is the nonionic surfactant and I^0 is the inorganic framework [38]) is suitable for such a Tween 20 modified sol–gel system.

3.6. Electrochemical performance of the electrode modified by mesoporous ZrO_2 film

Former work has demonstrated that zirconia is a promising metal oxide for the detection of neurotransmitters (i.e., catechol and dopamine) [25]. Considering the fact that catechol is another toxic compound, which belongs to a phenolic chemical of environmental concern in water and wastewater [39], in this study, the electrochemical behavior of catechol at the sono-gel carbon electrode modified by mesoporous ZrO_2 film (M- ZrO_2 film) was investigated by cyclic voltammetry. **Fig. 7**(a) and (b) shows the electrochemical responses to catechol and ascorbic acid (a common interferent [6,25]) for the three types of electrodes: (i) the bare carbon electrode, (ii) the modified electrode with ZrO_2 film prepared without Tween 20 [25] and (iii) the modified electrode with mesoporous ZrO_2 film prepared with Tween 20 with 1.10 g/ml zirconia sol (M- ZrO_2 film). Enhanced peak currents for catechol and ascorbic acid can be observed when employing the M- ZrO_2 film as electrode material. In addition, the electrode modified by M- ZrO_2 film exhibits good reversibility, good repeatability, stability, and good selectivity (highly resolved oxidation peaks of catechol and ascorbic acid) [23–25] at the anodic peak potentials (E_{pa} equal

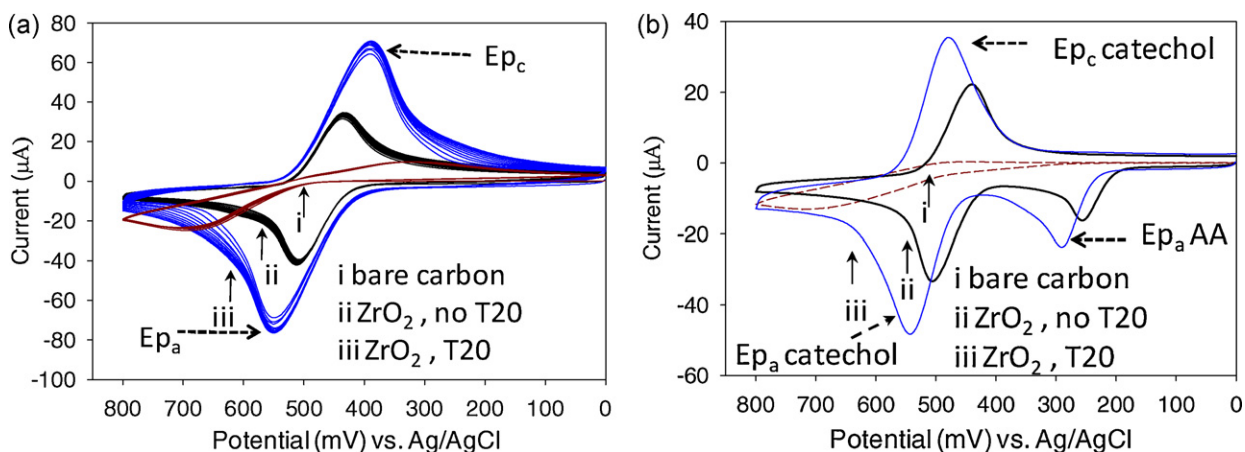


Fig. 7. (a) Cyclic voltammograms of 5.0 mM catechol (20 segments) and (b) cyclic voltammograms of 5.0 mM catechol and 5 mM ascorbic acid (2 segments). Scan rate 100 mV/s; electrolyte 0.1 M sulfuric acid.

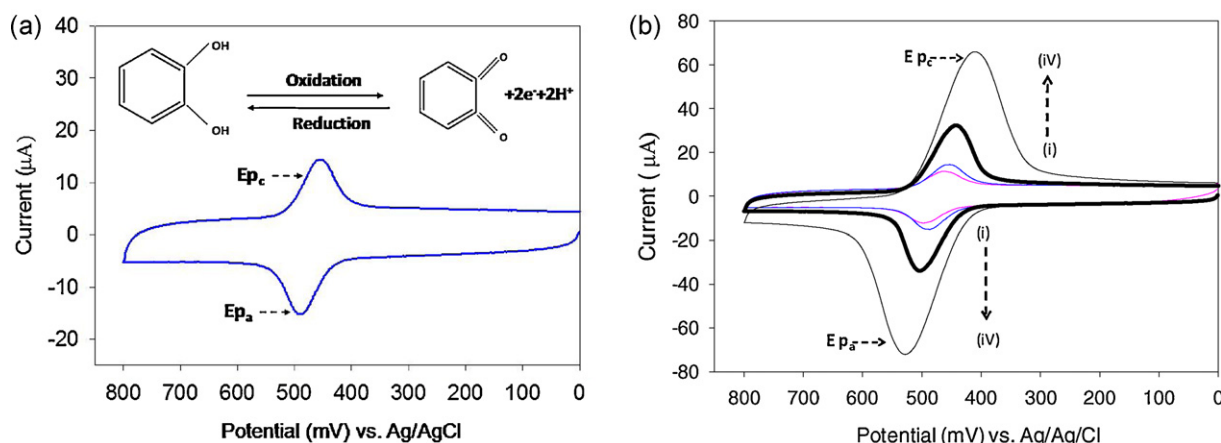


Fig. 8. (a) Cyclic voltammogram of 1.0 mM catechol on the sono-gel carbon electrode modified by ZrO_2 film (Tween 20 loading of 1.10 g/ml zirconia sol), and (b) cyclic voltammograms of catechol with concentration of (i) 0.5 mM, (ii) 1.0 mM, (iii) 2.5 mM, and (iv) 5.0 mM. Scan rate 100 mV/s; electrolyte 0.1 M sulfuric acid.

to 545 mV and 290 mV, respectively). Fig. 8(a) shows typical electrochemical response of 1.0 mM catechol in 0.1 M H_2SO_4 solution (pH=0.7). There are reversible waves displaying that the ratio of peak current at reduction (i_{pc}) and at oxidation (i_{pa}) is near unity ($i_{pc}/i_{pa} \approx 1$). The cathodic peak potential (E_{pc}) and the anodic peak potential (E_{pa}) for catechol were 454.2 mV and 489.3 mV, respectively. As a result, a smaller peak separation ($\Delta E_p = 35.0$ mV) of 1.0 mM catechol was observed using such a modified electrode with M- ZrO_2 film, indicating a fast charge-transfer rate and a good reversibility. According to the Nernst Equation, for a reversible redox couple, $\Delta E_p = E_{pa} - E_{pc} = 59 \text{ mV}/n$ (n is the number of electrons transferred). Therefore, based on a completely two electron reversible electrode reaction of $\Delta E_p = 29.5$ mV, a two electron redox reaction of catechol took place at such an electrode surface. From Fig. 8(b), it can be inferred that the peak separation (ΔE_p) increased as catechol concentration increases. Therefore, increased amounts of reactants or products attaching on the surface of M- ZrO_2 film may function as a resistance “layer” for blocking the normal electron transfer of diffusing species in the electrode. Fig. 9 shows the calibration curves of catechol solution using the electrode modified by mesoporous ZrO_2 film (M- ZrO_2 film). A good linearity of the calibration curve with a broad concentration range (from 0.13 mM to 5.0 mM) can be observed. Although the Tween 20 loading has not been optimized, the detection limit was found to reach

as low as 0.13 mM, a comparable result to that obtained by the sono-gel carbon electrode modified by a mesoporous TiO_2 film [6]. The good electrochemical response of M- ZrO_2 film is considered to be due to the improved structural properties permitting enhanced adsorption of catechol on its surface as well as to a fast electron transfer facilitated by its interconnected crystal network. The good electrochemical response of M- ZrO_2 film is considered to be due to the improved structural properties for enhanced adsorption of catechol on its surface and a fast electron transfer facilitated by its interconnected crystal network. Therefore, it can be concluded that mesoporous ZrO_2 film prepared by such a surfactant self-assembling sol-gel method is a promising electrode material on the detection of catechol in water. Our preliminary results have also shown a good electrochemical response to dopamine at such an electrode (the results are not shown in this paper). More work is needed on the optimization of the preparation parameters as well as to investigate electrochemical behavior of other important neurotransmitters, such as dopamine, in the clinical and pharmaceutical fields. Such studies are currently on-going in our groups. Since such a preparation method is suitable for the synthesis of mesoporous ZrO_2 nano particles and films with tailor design properties for electrochemical sensor applications, we anticipate that it can be further modified or applied for the synthesis of ZrO_2 nanomaterials with specific morphology for many other applications.

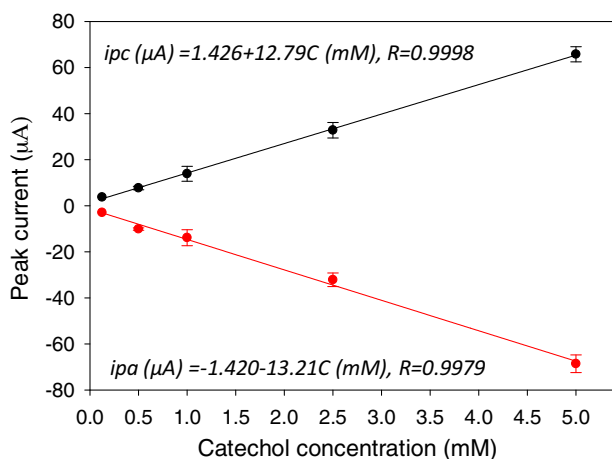


Fig. 9. Calibration curve of the sono-gel carbon electrode modified by ZrO_2 film (Tween 20 loading of 1.10 g/ml in the zirconia sol). Scan rate 100 mV/s; electrolyte 0.1 M sulfuric acid.

4. Conclusions

Our results have demonstrated that the self-assembling sol-gel route employing the complexation of zirconium alkoxide precursor with acetylacetone as a chelating agent and the environmentally friendly surfactant Tween 20 as a structure-directing agent is a promising method for the synthesis of mesoporous ZrO_2 nanoparticles and films. Tween 20 was proved to be a suitable structure directing agent in the formation of mesoporous structures of ZrO_2 nanoparticles and their derived films with high BET surface area and pore volume, decreased particle size, and good structural integrity. The improved structural properties of ZrO_2 films are considered to be responsible for the enhancement of catechol adsorption on the surface of ZrO_2 and fast electron transfer, which lead to very interesting electrochemical behavior for catechol detection, including high sensitivity and selectivity, excellent repeatability and stability, good reversibility and linearity over a wide range of catechol concentration.

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