

Research Article

A Novel Sol-Gel (TiO_2/ZrO_2) Carbon Paste Electrode to Detect Phenol and Derivatives of Phenol Utilizing Cyclic Voltammetry

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Abstract

This study investigated the detection of phenol and some of its derivatives (dopamine and catechol) using a novel class of TiO_2 and ZrO_2 sol-gel modified carbon paste sensors. The performances of the three different TiO_2 and ZrO_2 sol-gel modified carbon paste sensors were cross-compared as well as evaluated on the basis of the unmodified carbon electrode's performance. It was found that the TiO_2/ZrO_2 sol-gel mixture modified carbon paste electrode offered the best analytical response toward phenol and its derivative. In addition to cyclic voltammetric analysis, Environmental Scanning Electron Microscopy (ESEM) and Atomic Force Microscopy (AFM) studies were also conducted to investigate the morphologies of the sol-gel modified sensors' surfaces.

INTRODUCTION

Phenol and phenol derivatives are commonly found in industrial wastewater and chemical products. These compounds are known to be harmful to aquatic life, even at a low dose exposure, as numerous studies have been conducted to investigate the toxicity of phenolic compounds in aqueous environment [1-7]. Due to the level of toxicity of these compounds, it is urgent that reliable analytical methods must be developed to detect their presence and quantify their concentrations in aqueous solution. Asides from electrochemistry, current analytical techniques often employed to quantify phenolic compounds are gas chromatography (GC/GC-MS) [8-10] and liquid chromatography (HPLC) [11-13]. As the development of novel sensors to quantify toxic substances has become a vital part in modern day electrochemical research, the use of electrochemical sensor in quantifying organic substances in aqueous environment has gained a lot of attention due to several advantages. Such advantages include: high level of sensitivity, simplicity of operation, rapid data acquisition, and reasonable cost management.

In the past, oxide based sol-gels (TiO_2 and ZrO_2) have been

shown to be suitable modification agents on carbon-based electrochemical sensor in detecting neurotransmitters due to their favorable electro-catalytic interaction with these compounds [14-17]. Our current study, which is an expansion from past studies, focused on the use of a newly synthesized TiO_2/ZrO_2 sol-gel composite modified carbon paste electrode in detection of phenol and phenol derivatives (catechol and dopamine) via cyclic voltammetry (CV). Our research goal is not only to synthesize a novel sensor capable of quantifying phenol and phenol derivatives, but also to create an electrode with desirable electrochemical/physical and economical characteristics, which include: selectivity, enhanced sensitivity, high stability, physically rigid, non-toxic, and low production cost. In addition to CV analysis, surface morphology of the new sol-gel composite sensor will be investigated utilizing scanning electron microscopy (SEM) and atomic force microscopy (AFM).

EXPERIMENTAL

Reagents

Pyrocatechol (Sigma-Aldrich), Dopamine (3-Hydroxytyramine HCl) (United States Biochemical Corporation) were dissolved in

0.1 M Sulfuric Acid to prepare 5 mM solution. Phenol solution, 5 mM, was prepared in phosphate buffer ($\text{pH} \sim 7$), and 0.1 M NaOH solution was used to adjust pH level.

Safety/Hazards

All solution preparations and synthesis were carried out under a fume hood. Protective garment and gloves were worn at all times.

Apparatus

All CV measurements were performed on Bioanalytical Systems (BAS) Instrumentation in a three-electrode compartment cell (auxiliary Platinum electrode, Ag/AgCl reference electrode). Morphological characterization of the electrode surface was studied by an environmental scanning microscope (ESEM, Philips XL 30 ESEM-FEG) and an atomic force microscope (AFM, Veeco Dimension AFM, USA) in tapping mode.

Synthesis of ZrO_2 , TiO_2 and Sol-Gel Mixture ($\text{TiO}_2/\text{ZrO}_2$)

Titanium (IV) isopropoxide (97%, Sigma-Aldrich), zirconium (IV) propoxide (70 wt% in 1-propanol, Sigma-Aldrich), de-ionized water, acetylacetone (Sigma-Aldrich) and ethanol (99.5%, Sigma-Aldrich) were used. The molar ratio of zirconium (IV) propoxide (and/or titanium (IV) isopropoxide): water: acetylacetone: ethanol was 2:4:1:62. All chemicals were used as received.

Construction of Bare Electrode

A 0.5 mm O.D., 12.5 cm long copper wire was inserted into a capillary tube (Sutter Instrument, 0.69 mm I.D., 1.2 mm O.D., 10 cm long, borosilicate glass both ends open) as the wire was exposed by 2.5 cm only on one end of the tube; the wire functioned as an electrical contact component. 0.7g of graphite powder (Alfa Aesar, 99.0%, 7-10 μm) was added 0.3g of silicon oil (Xiameter PMX-200 Silicon fluid 100cs, Sigma-Aldrich) with magnetic chip in a vial. This carbon paste mixture was placed on stir pan for 5 minutes in order to homogenize the carbon paste. Previously made capillary tube with copper wire core was dipped firmly into the graphite packing. The electrode was smoothed on a piece of transparent paper to obtain a uniform surface prior to each use.

Construction of Sol-gel Modified Electrodes

Solutions of ZrO_2 , TiO_2 , and sol-gel mixture ($\text{TiO}_2/\text{ZrO}_2$), prepared at molar ratio mentioned previously, were stirred vigorously. The bare carbon electrodes (described above) were dipped into sol-gel solutions (ZrO_2 , or TiO_2 , or $\text{TiO}_2/\text{ZrO}_2$) coating for 3 seconds. After 5 minutes of drying time, the coating process was repeated four more times. Then the electrode was heated at 230°C for 20 minutes and cooled down naturally under room temperature conditions.

RESULTS AND DISCUSSION

In this work, ZrO_2 , TiO_2 , and sol-gel mixture ($\text{TiO}_2/\text{ZrO}_2$) were used to modify the carbon paste electrode surface to study the electron transfer of catechol and dopamine (phenol derivatives) and phenol in order to establish a new type of electrochemical sensor.

Detection of phenol derivatives (dopamine and catechol)

Figure 1 depicted the cyclic voltammograms of dopamine (5 mM) obtained with four different working electrodes, bare carbon paste electrode, TiO_2 sol-gel modified carbon paste electrode, ZrO_2 sol-gel modified carbon paste electrode, and $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode. From these CVs, a significant enhancement in sensitivity toward dopamine was observed for the modified electrodes compared to that of the bare electrode. The cathodic peaks current obtained with the TiO_2 sol-gel and ZrO_2 sol-gel modified carbon paste electrode were almost three folds higher than that of the bare electrode; four folds enhancements in sensitivity was observed with the $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode. In addition, the anodic branch also exhibited similar sensitivity improvement (except for the TiO_2 sol-gel modified carbon paste electrode as the anodic branch was not well-defined for this particular electrode). Furthermore, redox process of dopamine appeared to be more reversible when the ZrO_2 sol-gel and $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrodes were used as the potential separations decreased significantly. **Table 1** summarized the redox potentials and redox peak current magnitudes for the four working electrodes. Overall, when comparing the performances of the four working electrodes, it was observed that the $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode gave the best response for dopamine detection, in term of both redox couple reversibility and electro-analytical sensitivity.

In addition to cyclic voltammetric analysis of dopamine individually, simultaneous detection of dopamine and catechol utilizing the four working electrodes was also investigated.

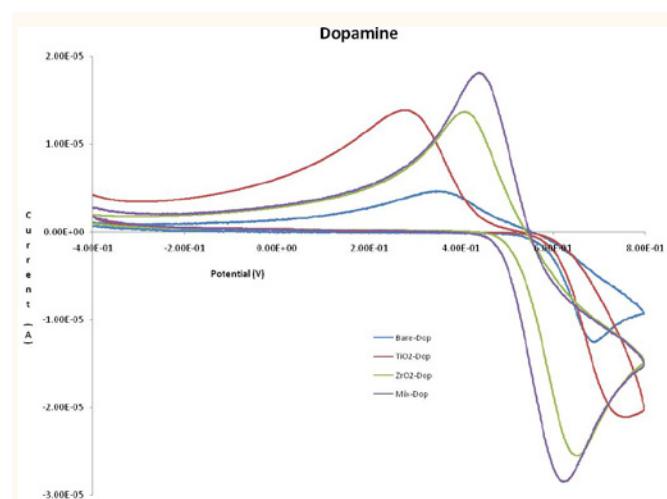


Figure 1 CV analysis of 5mM dopamine in 0.1 M Sulfuric acid utilizing: Bare, TiO_2 sol-gel, ZrO_2 sol-gel, $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste electrodes

Table 1: Cyclic voltammetric data for dopamine detection.

	E_{pa} (V)	E_{pc} (V)	ΔE (V)	I_{pa} (A)	I_{pc} (A)
Bare	0.69	0.342	0.348	6.00E-06	4.60E-06
TiO_2 only	NA	0.27	NA	NA	1.28E-05
ZrO_2 only	0.655	0.398	0.257	1.50E-05	1.37E-05
$\text{TiO}_2/\text{ZrO}_2$	0.629	0.443	0.186	1.75E-05	1.80E-05

Figure 2 illustrated the cyclic voltammograms of dopamine and catechol (both at 5 mM) simultaneous detection using the four working electrodes. It is observed that, with respect to anodic peak current magnitude, the sensitivity toward dopamine was enhanced by two folds when utilizing the TiO_2 sol-gel and ZrO_2 sol-gel modified carbon paste electrodes, and four and one-half folds when the $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode was used, compared to that of the bare electrode. Similar sensitivity enhancement pattern was also observed for the cathodic branch. In addition, when the ZrO_2 sol-gel and $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrodes were used, oxidation and reduction peaks for catechol were also observed, which were not seen when the bare or TiO_2 sol-gel electrodes were utilized. This illustrated the potential for simultaneous detection of catechol and dopamine using the ZrO_2 sol-gel and $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode, without prior separation of dihydroxybenzenes. **Table 2** summarized the redox potentials and redox peak current magnitudes for the four working electrodes. Overall, in term of electro-analytical sensitivity, the $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode offered the best response for dopamine and catechol detection.

Detection of phenol

In the past, cyclic voltammetric analysis has shown that phenol redox was an irreversible process [18]. The CV data obtained for phenol in our study supported this previous finding as only the anodic peak was observed. Cyclic voltammograms of phenol (5 mM) obtained with the four different working electrodes were illustrated in (**Figure 3**). It was observed that phenol was undetectable using the bare electrode, while the anodic peak, indicating the oxidation of phenol, was well-defined when the sol-gel modified electrodes were used. **Table 3** provided the oxidation potentials of phenol as well as anodic peak current magnitudes for the different working electrodes. Overall, the TiO_2 sol-gel and ZrO_2 sol-gel modified carbon paste electrodes gave similar response in term of phenol sensitivity, while the $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode provided

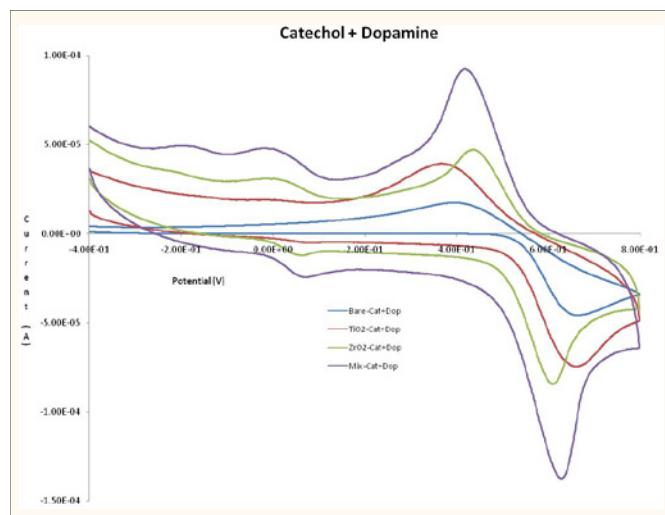


Figure 2 Simultaneous CV analysis of 5 mM dopamine and 5 mM catechol in 0.1 M Sulfuric acid utilizing: Bare, TiO_2 sol-gel, ZrO_2 sol-gel, $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste electrodes.

Table 2: Cyclic voltammetric data for simultaneous dopamine and catechol detection.

Dopamine	E_{pa} (V)	E_{pc} (V)	ΔE (V)	I_{pa} (A)	I_{pc} (A)
Bare	0.667	0.388	0.279	2.80E-05	1.74E-05
TiO_2 only	0.665	0.353	0.312	4.40E-05	3.00E-05
ZrO_2 only	0.614	0.423	0.191	5.00E-05	3.50E-05
$\text{TiO}_2/\text{ZrO}_2$	0.634	0.407	0.227	8.40E-05	7.70E-05

Catechol	E_{pa} (V)	E_{pc} (V)	ΔE (V)	I_{pa} (A)	I_{pc} (A)
Bare	NA	NA	NA	NA	NA
TiO_2 only	NA	NA	NA	NA	NA
ZrO_2 only	0.065	0	0.065	8.00E-06	1.00E-05
$\text{TiO}_2/\text{ZrO}_2$	0.071	-0.025	0.096	9.50E-06	1.20E-05

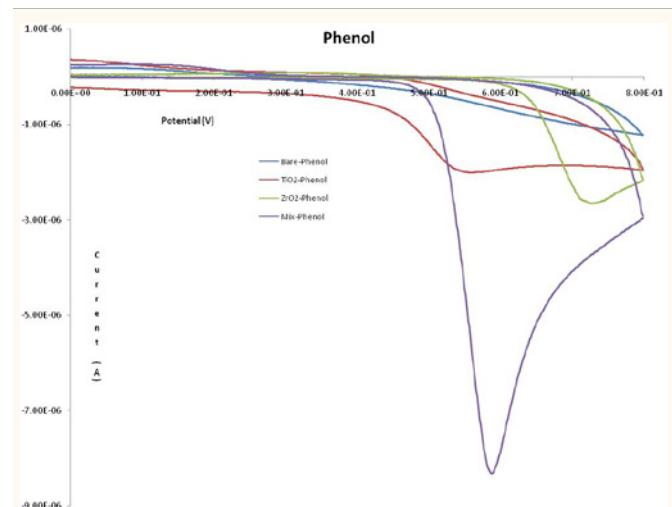


Figure 3 CV analysis of 5 mM phenol in 0.1 M phosphate buffer (pH ~ 7) utilizing: Bare, TiO_2 sol-gel, ZrO_2 sol-gel, $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste electrodes.

Table 3: Cyclic voltammetric data for phenol detection.

	E_{pa} (V)	I_{pa} (A)
Bare	NA	NA
TiO_2 only	0.731	1.00E-06
ZrO_2 only	0.554	1.10E-06
$\text{TiO}_2/\text{ZrO}_2$	0.592	6.80E-06

the best response toward phenol, almost seven times better than that of the TiO_2 sol-gel modified carbon paste electrodes.

ESEM and AFM analysis

In (**Figure 4a**) and (**Figure 4b**) showed the ESEM images of the ZrO_2 sol-gel modified carbon paste surface and $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste surface, respectively. A small amount of nano structures were observed at the ZrO_2 sol-gel modified carbon paste surface; however, the $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste surface exhibited much more developed nano substructure morphology. Such nano structures have been found to enhance the electro-catalytic activity of the sensor

toward organic molecules such as phenol and derivatives of phenol. ESEM images further confirmed our cyclic voltammetric analysis results, which indicate that the $\text{TiO}_2/\text{ZrO}_2$ mixture sol-gel modified carbon paste electrode offered the best sensitivity toward phenol and its derivatives. In addition, AFM image (tapping mode) of the $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste surface was also obtained (Figure 5). From this image, it was observed that nanoparticles, which we hypothesized to function as nucleation site for oxidation-reduction process, appeared to be in a uniformly dispersed stage. This further explained the electro-analytical sensitivity enhancement of the TiO_2 and ZrO_2 sol-gel modified carbon paste sensors surface.

CONCLUSION

In this study, we demonstrated the successful development

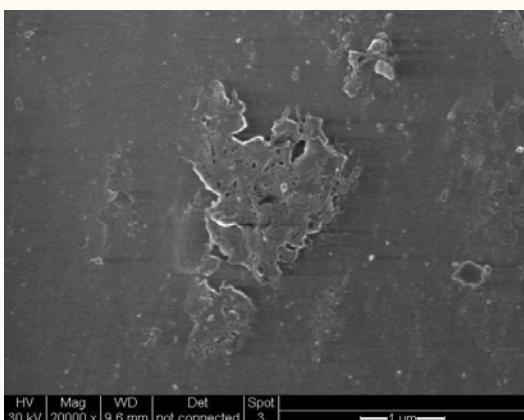


Figure 4a ESEM image of ZrO_2 sol-gel modified carbon paste surface.

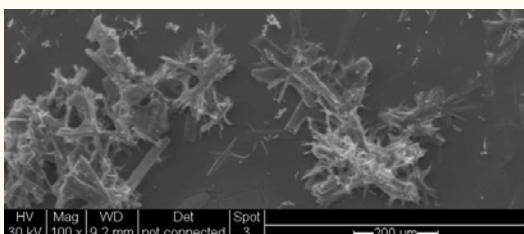


Figure 4b ESEM image of $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste surface.

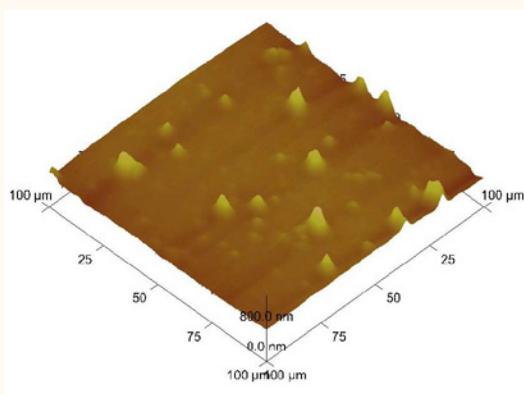


Figure 5 AFM image of $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste surface.

of a new class of sol-gel sensor in detection of phenol and its derivatives. Of the three different sol-gel modified electrodes investigated, the $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste electrode gave the best analytical response toward phenol and its derivatives (catechol and dopamine). Future studies will involve estimating detection limits and linear detection range for phenol and its derivatives utilizing the $\text{TiO}_2/\text{ZrO}_2$ sol-gel modified carbon paste electrode, as well as determination of electrokinetic parameters via CV analysis.

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REFERENCES

- Park JS, Brown MT, Han T. Phenol toxicity to the aquatic macrophyte *Lemna paucicostata*. *Aquat Toxicol*. 2012; 106-107: 182-8.
- Nweke CO, Okpokwasili GC. Inhibition of β -galactosidase and α -glucosidase synthesis in petroleum refinery effluent bacteria by zinc and cadmium. *Journal of Environmental Chemistry and Ecotoxicology*. 2010; 2: 20-27.
- Paisio CE, Agostini E, González PS, Bertuzzi ML. Lethal and teratogenic effects of phenol on *Bufo arenarum* embryos. *J Hazard Mater*. 2009; 167: 64-8.
- Sannadurgappa D, Ravindranath NH, Aladkatti RH. Toxicity, bioaccumulation and metabolism of phenol in the freshwater fish *Oreochromis mossambicus*. *J Basic Clin Physiol Pharmacol*. 2007; 18: 65-77.
- Huang H, Wang X, Shao Y, Chen D, Dai X, Wang L, et al. QSAR for prediction of joint toxicity of substituted phenols to tadpoles (*Rana japonica*). *Bull Environ Contam Toxicol*. 2003; 71: 1124-1130.
- Wu RSS, Lam PKS, Zhou BS. A phototaxis inhibition assay using barnacle larvae. *Environmental Toxicology and Water Quality*. 1997; 12: 231-236.
- Kahru, Kurvet M, Kulm I. Toxicity of phenolic wastewater to luminescent bacteria *Photobacterium phosphoreum* and activated sludges. *Water Science and Technology*. 1996; 33: 139-146.
- Feshin DB, Brodskii ES, Mir-Kadyrova Ya E, Kalinkevich GA. Determination of phenols in aqueous solutions by chromatography-mass spectrometry as isopropyl hydroxycarbonyl derivatives. *Journal of Analytical Chemistry*. 2013; 68: 272-274.
- Kronholm J, Revilla-Ruiz P, Porras SP, Hartonen K, Carabias-Martínez R, Riekkola ML, et al. Comparison of gas chromatography-mass spectrometry and capillary electrophoresis in analysis of phenolic compounds extracted from solid matrices with pressurized hot water. *J Chromatogr A*. 2004; 1022: 9-16.
- Lanças FM, Olivares IR, Alves PM. Development, validation and application of a method to analyze phenols in water samples by solid phase micro extraction-gas chromatography-flame ionization detector. *J Environ Sci Health B*. 2007; 42: 491-8.
- Valente IM, Santos CM, Moreira MM, Rodrigues JA. New application of the QuEChERS methodology for the determination of volatile phenols in beverages by liquid chromatography. *J Chromatogr A*. 2013; 1271: 27-32.
- Mahugo Santana C, Sosa Ferrera Z, Santana Rodríguez JJ. A new and fast extraction method for the determination of priority phenols from marine sediments by liquid chromatography. *J Chromatogr Sci*. 2005; 43: 282-8.

13. Huang C, Zhou G, Peng H, Gao Z. Simultaneous determination of N,N-dimethylaniline and phenol in wastewater by high-performance liquid chromatography with chemiluminescence detection. *Anal Sci.* 2005; 21: 565-7.
14. Chen Y, Lunsford SK, Song Y, Ju H, Falaras P, Likodimos V, et al. Synthesis, Characterization and Electrochemical Properties of Mesoporous Zirconia Nanomaterials Prepared by Self-assembling Sol-gel Method with Tween 20 as a template. *Chemical Engineering Journal.* 2011; 170: 518-524.
15. Chen Y, Lunsford SK, Dionysiou DD. Photocatalytic Activity and electrochemical Response of Titania Film with Macro/Mesoporous Texture. *Thin Solid Films.* 2008; 516: 7930-7936.
16. Lunsford SK, Nguyen PK, Dagher J, Kingdom R. Sonogel carbon zirconium dioxide (ZrO_2) electrode sensor to detect dopamine. *Chemical Educator.* 2009; 14: 204-207.
17. Chen Y, Lunsford SK, Dionysiou DD. Characterization and Electrochemical Response of Sonogel Carbon Electrode Modified with Nanostructured Zirconium Dioxide Film. *Sensors and Actuators B.* 2009; 137: 291-296.
18. Yi H, Wu K, Hu S, Cui D. Adsorption stripping voltammetry of phenol at Nafion-modified glassy carbon electrode in the presence of surfactants. *Talanta.* 2001; 55: 1205-10.

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