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Electrochemical Determination of Adenine by Zn/Au-doped Sol-Gel Silicate Matrix

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A B S T R A C T

Zn-Au@SiO_2 was synthesized by simple and cost-effective sol-gel method. The obtained Zn-Au@SiO_2 was examined by high resolution-scanning electron microscopy (HR-SEM) with energy dispersive X-ray (EDX) analysis. Zn-Au@SiO_2 was modified by glassy carbon electrode (GCE) can be used as efficient electrochemical sensing of guanine. The role of Au, Si and Zn) in the electrochemical sensing has been discussed.

Key words: Zinc oxide, Nanocomposite, Adenine, Cyclic voltammetry, Sensing

Carbon materials touch every part of our daily lives. The advantage of demanding properties of novel carbon derived materials to develop a myriad of new applications for chemical sensing. A range of materials including platinum, gold, and various forms of carbon have thus been found useful for electrochemical detection [1–5]. Drug and biomolecule investigation have played a very important role in drug quality control, and such has been found to have a enormous impact on public health. Therefore, a simple, selective, fast, sensitive and accurate way for the determination of active biological and pharmaceutical compounds is very important [6–9]. Zinc oxide nanoparticles (ZnO NPs) represent a recent topic of research due to their large excitation energy, wide band gap and high surface-to-volume ratio. There is increased demand for the usage of ZnO NPs in many devices such as biosensors, solar cells, batteries, photodetectors and nanolasers [10–18].

Adenine is a component of DNA, and most of the recent electro analytical protocols for DNA detection are based on this electro active species [18]. Recently, due to the merits of strong adsorption ability (isoelectric point of about 9.5) and fast electron transfer kinetics, ZnO is also considered as a very promising sensing material with high catalytic efficiency [19–22]. ZnO NPs are also a definite asset towards the development of electrochemical sensing platforms for single-molecule detection [23–27]. However, guanine exhibit slow direct electron transfer and irreversible absorption on the electrode surface, which lead to low sensitivity for DNA detection. Over the past years, significant efforts have been paid on the development of chemical modified electrodes to improve the electrochemical sensing performance for guanine [28–33]. Here, in this paper Zn-Au@SiO_2 was synthesized by a simple and cost-effective sol-gel method. The obtained material was characterized by HR-SEM with EDX analysis. Zn-Au@SiO_2 modified GCE was used on electrochemical sensing of guanine and the results are discussed.

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MATERILAS AND METHODS

Chemicals

Chloro auric acid, Zinc acetate dihydrate, Tetraethyl orthosilicate, anhydrous ethanol (C_2H_5OH), sodium hydroxide (NaOH), potassium chloride (KCl) and guanine ($C_5H_5N_5O$) were the guaranteed reagents of Sigma Aldrich and used as such. Conductivity water is used as a solvent throughout the experiment.

Characterization methods

High-resolution scanning electron microscopy and elementary dispersive X-ray analysis experiments were carried out on a FEI Quanta FEG 200 instrument with EDX analyzer facility at 25 °C. The sample was prepared by placing a small quantity of prepared nanocomposites on a carbon coated copper grid and allowing the solvent to evaporate.

Electrochemical investigations

Cyclic voltammograms (CVs) were performed by using a CHI 604C electrochemical analyzer (CHI Instruments Inc., Austin, TX). A conventional three-electrode cell was used, including an Ag/AgCl (saturated KCl) electrode as the reference electrode, a Pt wire served as a counter electrode, and glassy carbon coated with synthesized Zn-Au@SiO_2 as a working electrode. GCE was sequentially polished before the experiments with 1.5, 0.35 mm alpha alumina powder and 0.08 mm gamma alumina powder/water slurry on microcloths pads. To fabricate a working electrode, 0.8 g of the prepared Zn-Au@SiO_2 was suspended in 4 mL of conductivity water and

sonicated for 60 min. 5 drops of this solution was pipetted onto the surface of the GCE and dried for 20 min at room temperature. GCE was coated with 6% Nafion 118 solution was then placed onto the GCE and dried for 15 min to form a membrane on the top. The Nafion membrane helps the loaded material to stick on the electrode surface. All electrocatalytic solutions were deaerated with high purity nitrogen before the CV measurements.

RESULTS AND DISCUSSION

Surface morphology and elemental analysis

(Fig 1a) shows the HR-SEM image of Zn-Au@SiO_2 nanoparticles. The HR-SEM images revealed that individual spherical size particles were composed by an aggregation. Au/Zn@Si Zn-Au@SiO_2 O_2 shows the average particle size of 50 nm. Nanoparticles smaller than 50 nm have markedly altered properties and are often referred to as "quantum dots" because of their size controls the separation (or quantization) of energy level within them [34]. EDX analysis confirms Zn, Au, Si and O are present in Zn-Au@SiO_2 (Fig 1b)

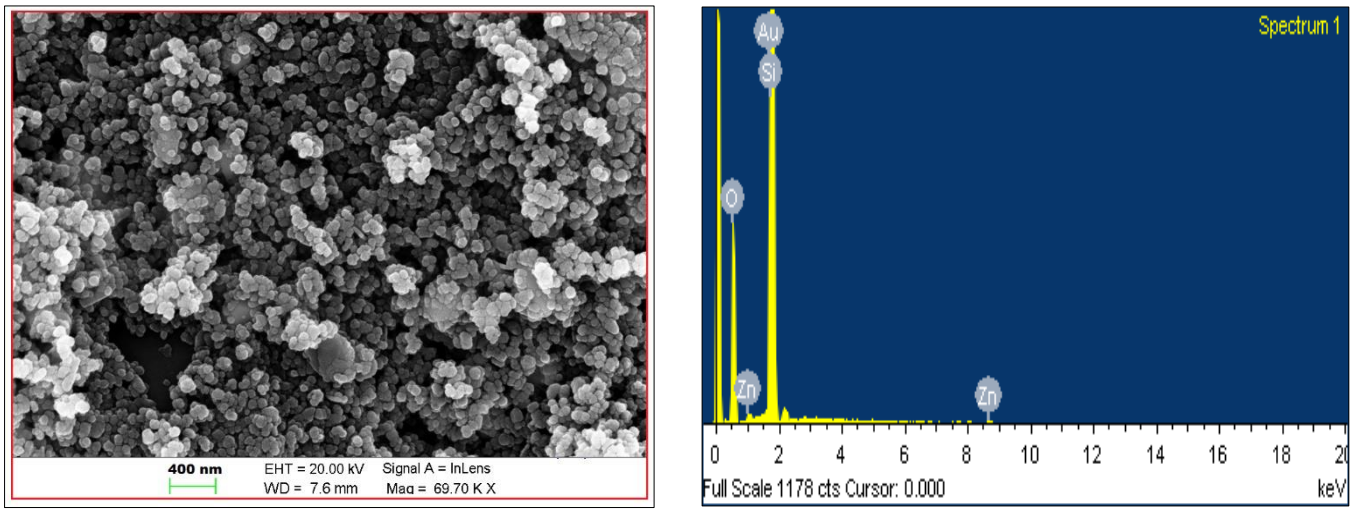

Fig 1 (a) SEM image of Zn-Au@SiO_2 nanoparticles and (b) EDX analysis of Zn-Au@SiO_2

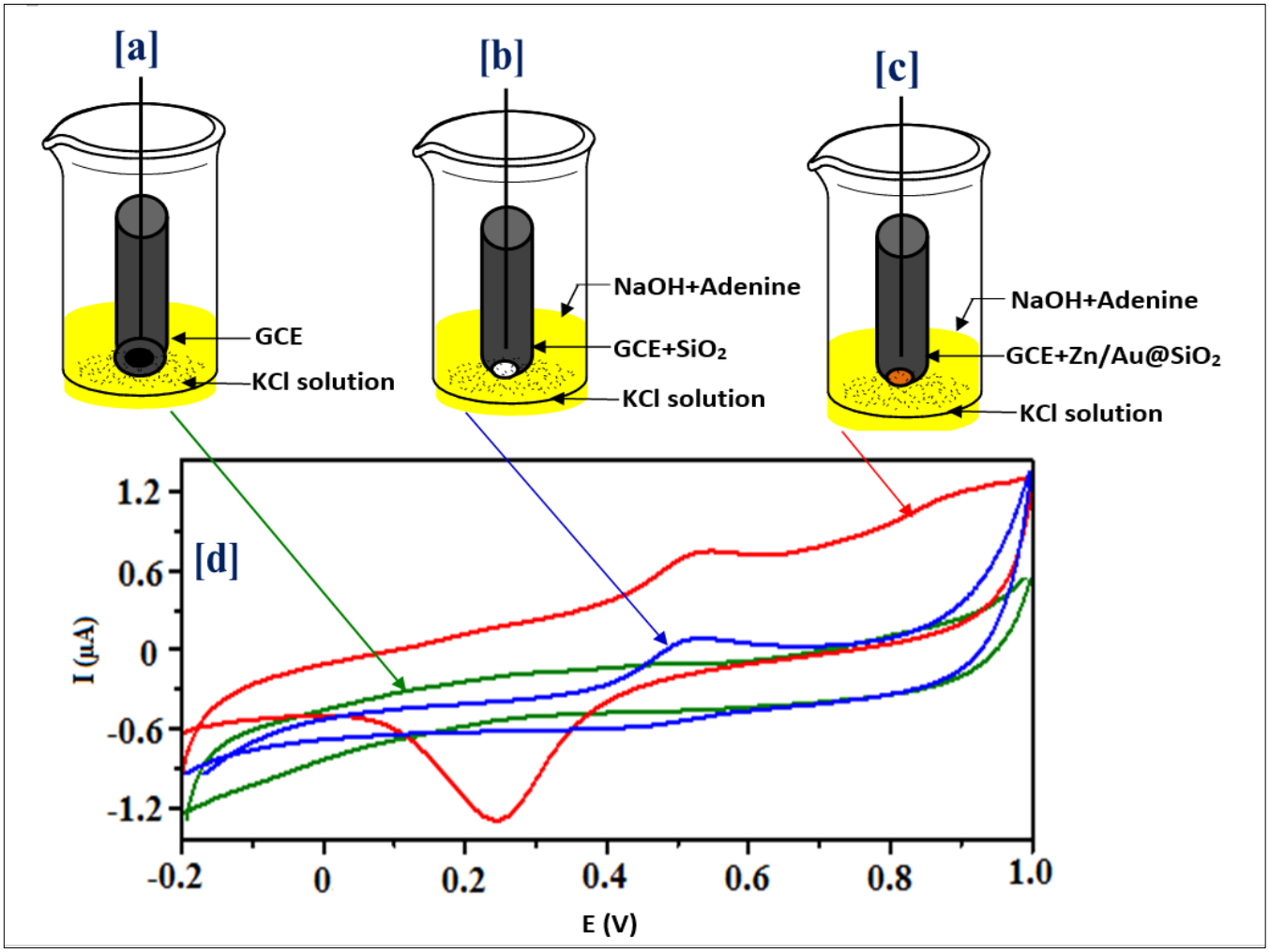

Fig 2 CVs of uncoated GCE with 0.2 M KCl solution (green curve), SiO_2 coated GCE in 0.2 M KCl with 0.002 M Adenine solution (blue curve) and Zn-Au@SiO_2coated GCE in 0.2 M KCl with 0.002 M Adenine solution (red curve).

Cyclic voltammetry studies

(Fig 2) shows the modified electrodes in 0.2 M KCl as a supporting electrolyte. (Fig 2a) shows uncoated GCE in 0.2M KCl, (Fig 2b) shows SiO_2 coated GCE in 0.2 M KCl with 4 mL of 0.002 M Adenine/NaOH solution and (Fig 2c) shows Zn-Au@SiO_2 coated GCE in 0.2 M KCl with 4 mL of 0.002 M Adenine/NaOH solution. (Fig 2d) shows the CVs of different modified electrodes in 0.2 M KCl as a supporting electrolyte at a scan rate of 0.02 V/s. This figure represents CVs of uncoated GCE in 0.2M KCl (green curve), SiO_2 coated GCE in 0.1 M KCl with 2 mL of 0.002M Adenine/NaOH (blue curve) and Au/Zn@SiO_2 coated GCE in 0.1 M KCl with 2 mL of 0.002M AdenineNaOH (red curve). The ΔEp value observed of Zn-Au@SiO_2/GCE (15 mV) reveals the kinetic hindrance exerted on the electron transfer process. Red curve shows the sensing of guanine by the Zn-Au@SiO_2/GCE electrode as an enhanced anodic and cathodic current and the (Epa) peak potential of 0.547 V and 0.245 V. Where as in the SiO_2 modified GCE electrode (blue curve) enhanced anodic current and the (Epa) peak potential of 0.527 V, there is no significant cathodic peak was observed. SiO_2 modified GCE was electrochemically oxidized and bismuth were released from Zn-Au@SiO_2. Au and Zn was deposited on the GCE at the reduction potential [36]. In contrast with the Au and Zn in Au/Zn@SiO_2 modified electrode exhibited a couple of redox peaks, which can be clearly seen in (Fig 2d). Interestingly, Zn-Au@SiO_2which was uniform in size (Fig 1a) uniformly distributed over the electrode surface. These resulted in an increase in the electrode surface area, indicating that the Zn-Au@SiO_2modified GCE had larger adsorption/desorption than the SiO_2 modified electrode. These results indicated that the Zn-Au@SiO_2showed higher electro-sensing activity than SiO_2.

CONCLUSION

Au/Zn@SiO_2 was synthesized by simple sol-gel method. Au/Zn@SiO_2 was characterized by HR-SEM with EDX analysis. The HR-SEM showed the size as 30 nm. The spherical particles uniform in size uniformly distributed over the GCE surface and an increases the electrode surface area. Cyclic voltammogramic method showed that the modified Au/Zn@SiO_2/GCE had a higher electrochemical response than the SiO_2 modified electrode in the sensing of guanine. Good selectivity and high sensitivity of the Au/Zn@SiO_2 as a promising candidate for electroanalytical and biomedical application for detecting the DNA bases.

Conflict of interest

The authors declare no competing financial interest.

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