



# Bare and cationic surfactants capped tungsten trioxide nanoparticles based hydrazine chemical sensors: A comparative study



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## ABSTRACT

Herein, we report the fabrication and characterization of electrochemical sensors based on bare- and cationic surfactants with different chain lengths and counter ions capped-tungsten trioxide ( $\text{WO}_3$ ) nanoparticles. Four different cationic surfactants, i.e., tetradecyltrimethyl ammonium bromide (TTAB), cetylpyridinium chloride (CPyC), cetylpyridinium bromide (CPyB) and hexadecyltrimethyl ammonium chloride (HTAC) were used for the capping of  $\text{WO}_3$  nanoparticles. The prepared bare and capped  $\text{WO}_3$  nanoparticles were characterized in terms of their morphological, structural and compositional properties which revealed that the prepared nanoparticles possess mono-dispersity, spherical shape and monoclinic crystal phases. Finally, the prepared nanoparticles were used to fabricate electrochemical sensors for the detection of hydrazine. Our report describes massive comparison of current responses, monitored through cyclic voltammetry for bare and surfactant capped- $\text{WO}_3$  nanoparticles (NPs). The sensitivity values of the fabricated amperometric sensors range from 3.38 to 10 ( $\mu\text{A}/\mu\text{M cm}^2$ ) with limits of detection ranging from 29 to 59  $\mu\text{M}$ .

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## 1. Introduction

Hydrazine and its derivative class of compounds possess multitudinous applications in diverse fields, to name a few, agriculture, chemical, pharmaceutical industry, corrosion inhibitors, antioxidants, photographic agents, blowing agents, aircrafts, fuel, etc. [1,2]. Hydrazine enters our biosphere from industrial or aerospace emissions and due to the toxic nature, the exposure of hydrazine or its derivatives can result in dizziness, temporary blindness, and irritation of eyes, nose, throat, etc. [3]. The environmental protection agency (EPA) has authenticated hydrazine as human carcinogen and dreadful to central nervous system, liver and brain [4–6]. Hence, a reliable and rational method for sensing and detection

of hydrazine and its derivatives is highly desired. Chromatographic technique, spectrophotometric titration and fluorescence are some of the fundamental procedures that are practiced to determine the presence of hydrazine or its derivatives [7–9]. But, all these techniques own some inevitable snags such as their irrational costs, protraction and often they require sample pre-treatments too. For practical purposes, electrochemical method has been regarded as a better method having advantages of time-efficiency, easy automation, portability, wide linear range, greater sensitivity and selectivity [10,11]. In literature, the use of conventional, unmodified as well as modified electrodes for detection and sensing of hydrazine has been reported [12,13]. However, none of these are free from flaws. The former has been reported to show inconspicuous electrochemical response due to poor rate of electron transfer on electrode surface. The latter has been related with reduced sensitivity, passiveness of chemically modified electrode with time or instability of electron mediators [14–16]. Hence, integration of electrode with high stability and tremendous efficiency is anticipated.

From this outlook, search for sensing materials with outstanding sensitivity remains pivotal. Semiconducting oxide nanoparticles stand as remarkable candidates as the sensing materials as

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supported by vast literature [17]. More specifically, n-type semiconductor i.e., tungsten trioxide ( $\text{WO}_3$ ) with wide band gap ranging from 2.4 to 2.8 eV forms an exceptionally potential sensing material [18]. It is further known to be an electrochromic, photochromic and gasochromic material [19,20]. Furthermore, its activity is commendable in the fields of catalysis, smart windows, optical displays, electrochemical sensing and photo-electrochemical splitting of water [21–23]. The efficiency of the nanomaterials in these applications strongly depend on morphology i.e., shape and size, orientation and arrangement of nanocrystals in some cases. Many authors have fabricated  $\text{WO}_3$  nanomaterials via sol–gel process, physical vapor deposition, chemical vapor deposition, electrochemical deposition, spray pyrolysis, vacuum evaporation, dip-coating, polymer-assisted deposition and hydrothermal process [24,25]. However, certain drawbacks are present in these acknowledged routes i.e., diminished yield, tedious procedures and heterogeneity in size distribution.

Herein, we report the synthesis of bare and cationic surfactants coated  $\text{WO}_3$  nanoparticles and their potential application in the fabrication of efficient electrochemical hydrazine chemical sensors. It was observed that the surfactant reduces the agglomeration of nanoparticles, tune the optoelectronic properties and act as stabilizing agent to prevent the unlimited growth of  $\text{WO}_3$  [26–28]. Keeping in view the importance as well as toxicity, hydrazine was selected for detection and sensing using sensitive, quick responding and easy-to-handle amperometric  $\text{WO}_3$ -based sensor. The modification of working electrode with functionally biocompatible, with higher catalytic activity and wide band gap  $\text{WO}_3$  nanoparticles helped greatly in lowering the potential of the analyte (i.e., hydrazine). Our work demonstrates the incredible capacity of capped (non-calcined) over bare (calcined or surfactant-free)  $\text{WO}_3$  NPs for electrochemical sensing employing cyclic voltammetry (CV) technique. This technique serves a consistent procedure in terms of reproducibility and sensitivity. The CV scans for bare and capped- $\text{WO}_3$  NPs displayed striking differences in terms of peak current responses and hence sensitivities of the fabricated sensors.

## 2. Experimental details

### 2.1. Chemicals and reagents

Cetylpyridinium bromide (CPyB) (purity >99%), cetylpyridinium chloride (CPyC), dodecylethyldimethyl ammonium bromide (DEDMAB), hexadecyltrimethyl ammonium bromide (HTAC), tetradecyl trimethyl ammonium bromide (TTAB), tungsten(VI) chloride ( $\text{WCl}_6$ , 99.9%), were obtained from Sigma–Aldrich. Sodium dihydrogen phosphate (>99%), disodium hydrogen phosphate (>99%) and ammonia solution (25%, v/v) was obtained from Merck. Acetone (98–100%) and ethanol (99.9%) were obtained from BDH and Changshu Yangyuan (China), respectively. All reagents were used as received without further purification. Deionized and double distilled water was used for solution preparation.

### 2.2. Bare and cationic surfactant capped $\text{WO}_3$ nanoparticles

The syntheses of the  $\text{WO}_3$  NPs using four different cationic surfactants (i.e., CPyB, CPyC, TTAB and HTAC) was carried out using the same procedure as established in our earlier report [29]. Briefly, in a typical reaction process, 7.0 mM surfactant solution (20 ml) was added to 0.25 M ml of aqueous ammonia solution (10 ml) under stirring (15 min). Consequently, 8.0 mM  $\text{WCl}_6$  was quickly injected into the resultant mixture under stirring and the obtained reaction mixture was kept at 30 °C under static conditions for 4 h. The subsequent product was aged for 3 days at room-temperature and were collected by centrifugation. The obtained powders were

washed sequentially with water and ethanol several times and dried at room-temperature which resulted the formation of surfactant capped dispersed  $\text{WO}_3$  nanoparticles. To obtain bare  $\text{WO}_3$  nanoparticles, the obtained material was calcined at 600 °C for 2 h.

### 2.3. Characterizations of $\text{WO}_3$ nanoparticles

The surface morphology and dimensional parameters of the synthesized  $\text{WO}_3$  nanoparticles were explored by employing TEM investigations. The chemical compositions and purity of the prepared  $\text{WO}_3$  nanoparticles were examined by Fourier transform infrared (FTIR) spectroscopy. The FTIR spectral data were recorded by PerkinElmer (RX1) FTIR spectrophotometer in the range 4400–350  $\text{cm}^{-1}$  by taking the samples in the form of KBr pellets using standard procedure.

### 2.4. Fabrication of $\text{WO}_3$ nanoparticles based electrochemical sensors for the detection of hydrazine

The construction of four different  $\text{WO}_3$ -based electrochemical sensors was accomplished for the detection of hydrazine. All of these were built on similar design and varied only in the type of cationic surfactant used during the synthesis of  $\text{WO}_3$  NPs [29]. To formulate the  $\text{WO}_3$ -based sensors, the gold electrode (Au; surface area = 3.14  $\text{mm}^2$ ) was refined with alumina slurry, sonicated in distilled water and dried out at room-temperature. The surface of gold electrode was modified using the slurry of butyl carbitol acetate (BCA) and  $\text{WO}_3$  NPs (synthesized from aqueous solutions of five different surfactants). The modified Au electrode was then dried at 60 ± 5 °C for 4–6 h to acquire a homogeneous and dried layer over whole electrode surface. For all the measurements, 0.1 M phosphate buffer (pH 7.0) was used. Electrochemical studies were performed at room-temperature using a  $\mu$ Autolab Type-III cyclic voltammeter having three-electrode configuration. In all the electrochemical investigations,  $\text{WO}_3$  NPs modified gold electrode was used as a working electrode, a Pt wire as a counter electrode and an Ag/AgCl (sat. KCl) as a reference electrode.

## 3. Results and discussion

### 3.1. Morphological and compositional properties of bare and surfactant capped- $\text{WO}_3$ nanoparticles

The general morphologies of the cationic surfactants capped and bare  $\text{WO}_3$  nanoparticles were examined by transmission electron microscopy (TEM). Figs. 1 and 2. exhibit the typical TEM images of cationic-surfactants capped and bare  $\text{WO}_3$  NPs. Interestingly, the capping on the surface of the NPs is pretty much evident from TEM analyses (Fig. 1) and on comparing the images of the capped  $\text{WO}_3$  NPs with those of bare NPs (Fig. 2), it can be safely concluded that the capped particles are well dispersed, far less aggregated, symmetrically spherical and very well separated having a narrow size distribution with the particle size in the range of 13–20 nm for TTAB, 6–10 nm for CPyC, 8–12 nm for CPyB and 10–15 nm for HTAC-capped  $\text{WO}_3$  NPs. In the presence of these capping agents, i.e., cationic surfactants, the interaction between the particles is reduced significantly, resulting in reduced agglomeration. This size variation is explainable on the basis of head group, chain length and counter ion. In the case of CPyB- and CPyC-synthesized NPs, bulkier pyridinium ring provides steric hindrance to the other molecules of surfactant, thus keeping them apart and hence cause reduction in extent of capping on NP surface. This leads to lesser restriction of sizes. Also, counter-ion effect contributes to the size variation as noticed in CPyC/CPyB or HTAC/TTAB, where in both the cases, the surfactant with bigger bromide ion as counter ion results in larger NPs which causes steric hindrance, leading to larger NPs.

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