

# FTIR Study of Chemical Modification of Tellurium Oxide Nanoparticles by Dicarboxyl Amino Acids

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**Abstract:** The modification and modulation of dicarboxylic amino acids on tellurium oxide nanoparticles (TeO<sub>2</sub>NPs) were investigated by Fourier transform infrared spectroscopy. The TeO<sub>2</sub>NPs prepared in aspartic acid (Asp) or glutamic acid (Glu) were spheres with main size distribution of 30-80 nm. TeO<sub>2</sub>NPs were bound with Asp and Glu through a bidentate chelating mode and a bidentate bridging mode by the carboxyl group, respectively.

## Introduction

Tellurium dioxide (TeO<sub>2</sub>) materials have many important applications because of high physical and chemical stability, excellent optical crystal with elastic behavior, high refractive index, good non-linear optical properties [1-3]. In recent years, they have been widely used in the field of host matrix such as photoinduced non-linear optical investigations [3], optical filters [4] and so on. Furthermore, TeO<sub>2</sub> nano-materials have attracted great interest in the fields of up-conversion luminescent materials [5, 6], biomedical research [7, 8] and sensors [9, 10].

In our previous work, TeO<sub>2</sub>NPs were prepared and modified with monocarboxylic acids gallic acid and acetum [11]. However, the modification mechanism is still unclear. Dicarboxylic amino acids, such as aspartic acid (Asp) and glutamic acid (Glu), have more modified sites, so they were the ideal acids to prepare and modify TeO<sub>2</sub>NPs. In this work, TeO<sub>2</sub>NPs were prepared in Asp and Glu through the hydrolysis reaction of sodium tellurite. Herein, the Asp and Glu served as catalyzers for the hydrolysis as well as modifiers for the hydrolysate (TeO<sub>2</sub>). Furthermore, according to Fourier transform infrared spectra, the possible binding mode between dicarboxylic amino acids and TeO<sub>2</sub> would be discussed.

## Experimental Details

### Chemicals.

Chemicals were all analytical grade. Sodium tellurite (Na<sub>2</sub>TeO<sub>3</sub>) was purchased from Aladdin reagent Co. (China). Gallic acid (GA), acetum (HAc), aspartic acid (Asp) and glutamic acid (Glu) were purchased from Sinopharm Chemical Reagent Co. (China). Water was purified using a Milli-Q-system (Millipore, Bedford, MA, USA).

### Preparation of TeO<sub>2</sub>NPs Sol

At room temperatures, 1.0 mL 10 mmol/L Na<sub>2</sub>TeO<sub>3</sub> were added into 2.0 mL 10 mmol/L Glu or Asp. Then the mixture solution was diluted to 10 mL with Milli-Q water. The color of the solutions

changed from colorless to milky, the TeO<sub>2</sub>NPs sol was obtained. After a few days, the TeO<sub>2</sub>NPs precipitated at the bottom.

### Characterization

Transmission electron microscopy (TEM; TECNAL-10, PHILIPS) technique and Zeta sizer (Nano-ZS; Malvern Instruments) were used to observe the morphology and size of the samples. The samples were also followed by FTIR spectroscopy and the FTIR spectra were recorded in the range of 400–2000 cm<sup>-1</sup> frequency.

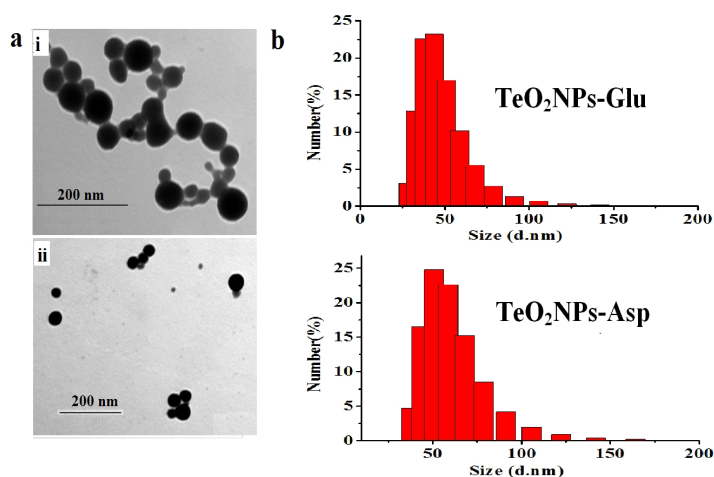
## Results and Discussion

### Preparation Mechanism of TeO<sub>2</sub>NPs

In the beginning, TeO<sub>2</sub> primary particles were formed by hydrolysis reaction of Na<sub>2</sub>TeO<sub>3</sub> in acidic solution. Meanwhile, the acid molecules started to modify TeO<sub>2</sub> by adsorbing to the surface of the primary particles and prevented the growth of TeO<sub>2</sub> particles. The colorless transparent solution changed to milky sol and TeO<sub>2</sub>NPs were obtained. Whereafter, the color of TeO<sub>2</sub>NPs-Asp (Glu) sol became clearer and clearer for days because the TeO<sub>2</sub>NPs aggregated and precipitated gradually.

### Morphology and Size of the TeO<sub>2</sub>NPs

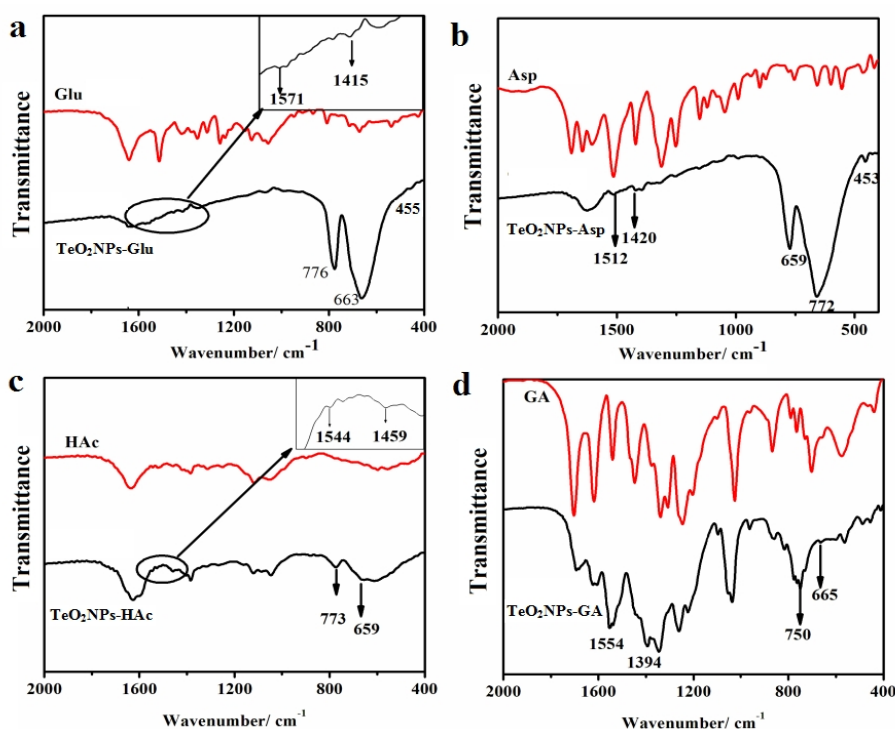
As shown in Fig.1, TeO<sub>2</sub>NPs prepared in Glu and Asp were spheres with the diameter range 30-120 nm (main range 30-80 nm). The results showed that the size of TeO<sub>2</sub>NPs was smaller than previous report [11], indicating that the dicarboxylic amino acid could prevent the growth of TeO<sub>2</sub>NPs more effectively than monocarboxylic acids.



**Fig. 1** TEM micrographs (a) and Size distribution (b) of TeO<sub>2</sub>-Glu (i) and TeO<sub>2</sub>-Asp (ii)

### FTIR Analysis of TeO<sub>2</sub>NPs

The binding modes of a carboxyl group with TeO<sub>2</sub> may be in several ways, including simple adsorption (electrostatic attraction and hydrogen bonding) and chemical adsorption (ester linkage, bridging, and chelating) [12]. Furthermore, the binding mode could be characterized by the separation  $\Delta\nu_{a-s}$  between the carboxylate anion asymmetric ( $\nu_{as}$ ) and symmetric ( $\nu_s$ ) stretching bands. Generally, the band separation was 350-500 cm<sup>-1</sup> for monodentate binding, 150-180 cm<sup>-1</sup> for bidentate bridging, and 60-100 cm<sup>-1</sup> for bidentate chelating [12].



**Fig. 2** FT-IR spectra of TeO<sub>2</sub>NPs prepared in different acids

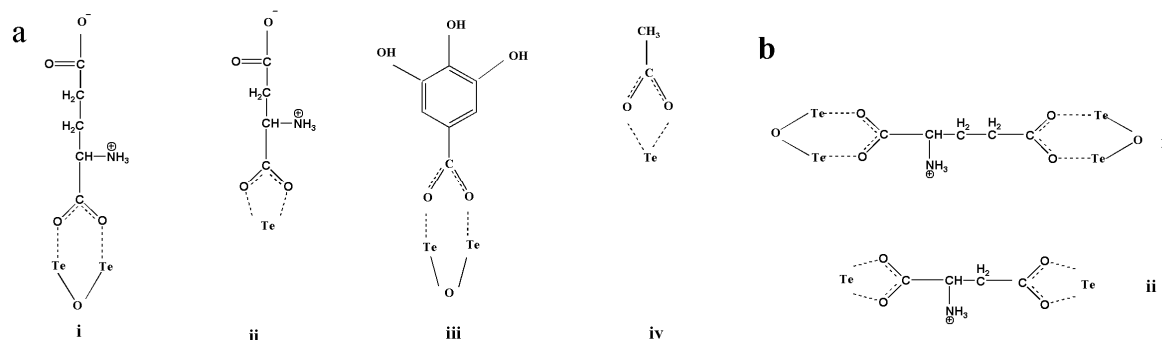
The detailed FTIR spectra are presented in Fig.2. The most sensitive bands for the chemical reaction between the carboxyl groups and Na<sub>2</sub>TeO<sub>3</sub> located in the ranges 1500–1800 cm<sup>-1</sup>, 1200–1450 cm<sup>-1</sup>, which assigned to the stretching vibrations of carbon-oxygen bonds. The shifts of these bands were clearly related to the type of coordination of the carboxyl groups. Hence, the values of  $\Delta\nu_{a-s}$  in table 1 showed that TeO<sub>2</sub>NPs was bound with the carboxyl group through the bidentate bridging for Glu and GA or through bidentate chelating for Asp and HAc.

**Table 1** Principal IR Bands Position of TeO<sub>2</sub>NPs-acid Systems

System	band of infrared absorption spectra (cm <sup>-1</sup> )						$\Delta\nu_{a-s}$
	$\delta_{\text{Te-O-Te}}$	$\nu_{\text{Te-O}}$ in (TeO <sub>4</sub> )	$\nu_{\text{Te-O}}$ in (TeO <sub>3</sub> )	$\nu_s(\text{COO}^-)$	$\nu_{as}(\text{COO}^-)$	$\delta_{\text{-OH}}$ in (-COOH)	
TeO <sub>2</sub> [13,14]	450-50	620-665	730-765	—	—	—	—
	6						
TeO <sub>2</sub> NPs-Glu	455	663	776	1415	1571	1644	156
TeO <sub>2</sub> NPs-Asp	453	659	772	1420	1512	1625	92
TeO <sub>2</sub> NPs-GA	455	655	750	1380	1542	1649	162
TeO <sub>2</sub> NPs-HA		659	773	1459	1546		87

On the basis of FTIR, the modifications of TeO<sub>2</sub> by different carboxylic acids are depicted in Fig. 3. The Glu and Asp bound to TeO<sub>2</sub>NPs with one carboxyl group (Fig. 3a i and ii) or two carboxyl groups (Fig. 3b). Compared with GA and HAc, Asp and Glu had more modified sites which could effectively inhibit growth of TeO<sub>2</sub>NPs. Therefore, the size of TeO<sub>2</sub>NPs modified by Asp and Glu was smaller than that modified by GA and HAc. However, the stability of TeO<sub>2</sub>NPs-Asp sol and TeO<sub>2</sub>NPs-Glu sol was slightly lower than that of TeO<sub>2</sub>NPs-GA sol because the double bidentate bridging (chelating) structure could not form a stable conjugated system. Meanwhile, the benzene ring played a vital role to form conjugate structure with the bidentate

bridging structure in TeO<sub>2</sub>NPs-GA (Fig. 3a iii). HAC had no other auxiliary modified groups except one carboxyl group (Fig. 3a iv), so the TeO<sub>2</sub>NPs-HAc sol showed the worst stability.



**Fig.3** (a) Binding modes of carboxyl group with TeO<sub>2</sub>: i) TeO<sub>2</sub>NPs-Glu, ii) TeO<sub>2</sub>NPs-Asp, iii) TeO<sub>2</sub>NPs-GA, iv) TeO<sub>2</sub>NPs-HAc; (b) Binding modes of double carboxyl group with TeO<sub>2</sub>: i) TeO<sub>2</sub>NPs-Glu, ii) TeO<sub>2</sub>NPs-Asp

## Conclusion

The TeO<sub>2</sub>NPs were successfully prepared with the modifiers of dicarboxylic amino acids, Asp and Glu. The FTIR analyses proved that the Glu and Asp bound to TeO<sub>2</sub>NPs with carboxyl groups by forming bidentate bridging and bidentate chelating, respectively.

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