NRC Publications Archive Archives des publications du CNRC

Characterization of CuO phase in SnO₂-CuO prepared by the modified Pechini method

Majid, Abdul; Tunney, James; Argue, Steve; Kingston, David; Post, Michael; Margeson, James; Gardner, Graeme J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1007/s10971-009-2108-x>

Journal of Sol-Gel Science Technology, 53, 2, pp. 390-398, 2009-11-24

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=b6580dc5-2535-4b31-bc83-fc272346d68c>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=b6580dc5-2535-4b31-bc83-fc272346d68c>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Characterization of CuO phase in SnO₂–CuO prepared by the modified Pechini method

Abdul Majid · James Tunney · Steve Argue ·
David Kingston · Michael Post · James Margeson ·
Graeme J. Gardner

Received: 18 June 2009 / Accepted: 31 October 2009 / Published online: 24 November 2009
© Springer Science+Business Media, LLC 2009

Abstract The modified Pechini method has been applied to the preparation of nano-structured SnO₂ and SnO₂:CuO. The sample characterization was carried out by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), infrared spectroscopy (IR) and nitrogen adsorption isotherms (BET). The CuO phase in SnO₂:CuO samples was successfully characterized by XRD, XPS and IR. The highest degree of crystallinity and subsequently the maximum intensity and area of CuO (002) diffraction peaks were observed for the samples prepared with templates. The morphology and microstructure of the hybrid were studied using SEM. The core level binding energies of Cu 2p, Sn 3d, and O 1s were measured in these samples. The appearance of a satellite peak in the Cu 2p spectra provided definitive evidence for the presence of Cu²⁺ ions in these samples. The influence of synthesis conditions such as solvent, precursor type, calcinations temperature and time on the detectability of CuO and the morphology and microstructure of the hybrid were also studied. The

calcinations conditions had a significant effect on the appearance and intensity of CuO diffraction peaks.

Keywords Perovskite · SnO₂ · SnO₂:CuO · CuO · Pechini method · XRD · XPS · SEM · IR

1 Introduction

Monitoring and control of toxic hydrogen sulphide (H₂S) gas is important in laboratories and industrial areas where it is used as a process gas or generated as a byproduct. Semiconductor tin oxide (SnO₂)-based gas sensors have been reported for the detection of SO_x and H₂S [1, 2]. These sensors work on the principle of change in electrical conductance on exposure to the detecting gas. Desirable characteristics of a gas sensor are, high sensitivity (defined as the ratio of conductance of the sensor in sample gas to that in air, fast response time (time taken to reach the 90% of the saturation conductance on exposure to gas, fast recovery time (time taken to reach the 10% of the initial conductance on removal of the gas), selectivity and long-term stability [3–5]. Sensors based on pure SnO₂ show good sensitivity but the selectivity has been reported to be poor as the sensors respond to many reducing gases in similar manner [6]. Doping with CuO has been shown to enhance the sensitivity and selectivity of SnO₂ toward H₂S [7, 8]. In comparison to pure SnO₂, SnO₂:CuO films show a high resistivity in air which drastically drops in the presence of hydrogen sulfide or other sulfur compounds [9]. This behavior has been attributed to the formation of p–n heterojunctions (p-CuO and n-SnO₂), which induces an electron depleted space charge layer at the surface of SnO₂ [3, 6, 9]. Upon exposure to H₂S, the p-type semi-

Issued as NRCC No. 51757.

A. Majid (✉) · J. Tunney · S. Argue · D. Kingston · M. Post
Institute for Chemical Process and Environmental Technology,
National Research Council of Canada, Ottawa, ON K1A 0R9,
Canada
e-mail: abdul.majid@nrc.gc.ca

J. Margeson
Institute for Research in Construction, National Research
Council of Canada, Ottawa, ON K1A 0R6, Canada

G. J. Gardner
Institute for National Measurement Standards, National
Research Council of Canada, Ottawa, ON K1A 0R6, Canada

conducting CuO particles are converted to CuS having metallic properties [10]. This transformation destroys the p–n junctions and results in a large drop in electrical resistance. Subsequent exposure to dry air brings the sulfide back to CuO and the p–n junctions are reconstructed.

In earlier reports, most of the studies on SnO₂:CuO have been carried out on thick films prepared by an impregnation technique where CuO is dispersed on prepared SnO₂ particles and thereby CuO and SnO₂ particles remain separate [11]. This results in slower response times. Thin film-based sensors are expected to have faster response times. In the case of thin films, the microstructure is expected to be different and may depend on preparation technique as the possibility of interaction between SnO₂ and CuO leading to homogeneous phase distribution exists and one may not expect CuO to be dispersed around SnO₂ grains [8, 11, 12].

In the preparation of tin dioxide and its doped derivatives, several routes have been developed. The material is usually prepared by the sol–gel route using inorganic hydrosols [13, 14] and tin alkoxides [15]. The major drawbacks associated with the latter procedure are the high cost of the alkoxides and their marked sensitivity to air and moisture. The sol–gel method based on the Pechini-type reaction has received considerable attention because of its relatively simple synthesis scheme. Recently, we reported detailed investigations on the application of the Pechini method for the preparation of SrFeO_x perovskite [16, 17]. In this investigation we have used this method for the synthesis of SnO₂:CuO hybrid for eventual sensor applications in the detection of H₂S. The aim of this study was to characterize the CuO phase in SnO₂:CuO, in view of the reported difficulty to detect CuO in the presence of SnO₂ at concentrations $\leq 5\%$ [8, 11, 18, 19]. The sample characterization was carried out by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), infrared spectroscopy (IR) and nitrogen adsorption isotherms (BET).

2 Experimental methods

2.1 Preparation of SnO₂/SnO₂:CuO

A modified Pechini method as reported previously [16, 17] was used to prepare both SnO₂ and SnO₂:CuO, using analytically pure (99.9%) tin chloride pentahydrate (SnCl₄·5H₂O), anhydrous tin(IV) chloride (SnCl₄) and tin(II) chloride dihydrate (SnCl₂·2H₂O) in both ethylene glycol and aqueous media. In some tests citric acid was added and dissolved by stirring so that an optimum molar ratio of citric acid (CA) to total metal ion (Sn + Cu) as determined previously [20] ($\sim 4:1$) was achieved. This ratio (Ra) is defined as $Ra = CA/(Sn \text{ or } Sn + Cu)$. For the

preparation of SnO₂:CuO samples, copper acetate solutions, corresponding to 0.6–5 w/w% Cu (based on tin) was added at this stage. For aqueous solutions, the pH of the resultant metal citrate solution was adjusted to a desired range by adding dilute ammonia solution drop-wise. The aqueous solution was heated to 80 °C on a hotplate while stirring with a magnetic stirrer to obtain a viscous solution. For solutions in ethylene glycol, the heating was carried out at 150 °C. For aqueous solutions, ethylene glycol was added in a molar ratio of ethylene glycol (EG) to citric acid of $EG/CA = 1.2$ [20]. In some cases, cetyltrimethylammonium bromide (CTMAB), a surfactant was added (~ 2 w/w% of Sn salt) just before the addition of EG in order to determine the influence of a structure directing agent [21–23]. Heating and stirring was continued until the solution started solidifying forming a gel-like porous mass. At this stage the temperature was raised to 180–200 °C to obtain a foamy dry mass. This was ground in an agate mortar using reagent grade acetone, followed by drying and ashing at 450 °C in a muffle furnace to completely remove the remaining organics and water. The resulting powder was used as a precursor for the preparation of crystalline SnO₂/SnO₂:CuO which upon calcinations at different temperatures in a programmable furnace (Lindberg/Blue 1,200 °C Box Furnace Model BF51732) yielded the SnO₂ or SnO₂:CuO product.

2.2 Measurements

The specific surface area S_p (m²/g) was estimated by N₂ adsorption–desorption porosimetry at 77 K via the BET method. The instrument employed was a Micromeritics ASAP2000 system. Prior to each measurement, the sample was evacuated overnight at 150 °C under a pressure $p = 10^{-6}$ torr. X-ray powder diffraction (XRD) data were collected between $20^\circ < 2\theta < 60^\circ$ with a scan rate of 1° min^{-1} at room temperature on a Bruker D8 diffractometer with a theta–theta geometry and a Cu–K α radiation ($\lambda = 1.54056 \text{ \AA}$). The average crystallite size was determined from a convolution based full pattern fitting using the Topas software package [24]. Peaks were fitted using a simplified integral breadth method to account for both strain and crystallite size effects [25]. Scanning electron micrographs (SEM) were obtained using a Hitachi field emission scanning electron microscope (FE-SEM) Model S-4800 fitted with an Oxford Inca energy dispersive spectrometer (EDS) for elemental analysis. It was operated at 1.2 keV and a current of 10 μA . The infrared spectra were recorded with a Bruker Tensor 27 FTIR instrument, using the KBr pellet technique.

XPS analyses were performed using the Kratos Axis Ultra equipped with a monochromated Al K α X-ray source. Analyses were carried out using an accelerating voltage of 14 kV and a current of 10 mA. Charge build-up was

compensated for using the Axis charge balancing system. The pressure in the analysis chamber during analysis was 2.0×10^{-9} torr.

Analyses consisted first of a survey scan performed at a pass energy of 160 eV to identify all the species present, followed by high resolutions scans at 40 eV of the species identified by the survey scan. Peak fitting was performed using Casa XPS (ver. 2.2.107) data processing software. Shirley background correction procedures were used as provided by Casa XPS. High resolution analyses were calibrated to adventitious C 1s signal, at 285 eV.

3 Results and discussion

3.1 X-ray diffraction

Figure 1A shows the X-ray diffraction (XRD) patterns of powder samples of CuO, SnO₂, SnO₂:CuO and a mechanical mixture containing 7 w/w% of CuO and 93 w/w% of SnO₂. The spectra for CuO and SnO₂ correspond to monoclinic and cassiterite structures (joint Committee on Powder Diffraction Standards, JCPDS, card nos. 05-0661 and 41-1445, respectively) without any indication of other crystalline byproducts. The X-ray diffraction spectra for the SnO₂:CuO samples annealed at 700 °C with 5% CuO loading shows monoclinic CuO along with the SnO₂ peaks, suggesting that CuO and SnO₂ are coexistent in the composites as separate phases.

Figure 1B demonstrates the effect of the calcination conditions on the appearance and intensity of CuO diffraction peaks in the XRD spectra of powder SnO₂:CuO samples. It was notable that the copper species in SnO₂:CuO samples calcined below 600 °C exhibited only SnO₂ diffraction peaks. This indicates very small grains or amorphous phase of CuO in the tin-oxide nanostructure. By raising the calcination temperature, the XRD spectrum shows sharper and more intensified CuO peaks, indicating an increase in the CuO grain size. However, increase in the calcination temperature beyond an optimum temperature leads to a decrease in the degree of crystallinity of the CuO phase. This may be attributed to the partial reduction of bivalent copper oxide into amorphous monovalent cuprous oxides according to [26]:

According to the results of powder X-ray diffraction analysis of SnO₂:CuO samples the highest degree of crystallinity and subsequently the maximum area of CuO (002) diffraction peaks was observed in the samples prepared with cetyltrimethyl ammonium bromide (CTMAB) as a template. Since, templating controls porosity [27], increased area of the CuO peak in the

Fig. 1 A XRD patterns of powder samples of : (a) CuO, (b) SnO₂, (c) a mechanical mixture of CuO and SnO₂ and (d) SnO₂:CuO; **B** The effect of calcination conditions on the area of CuO diffraction peaks in the XRD spectra of powder SnO₂:CuO samples

templated samples is probably related to the porosity of the samples. This relationship will be explored at a latter stage. For samples without template, the CuO peak was not as

Fig. 2 The effect of Cu loading on the area of XRD peak of CuO (002) in SnO₂:CuO samples calcined at 700 °C for 5 h

intense but still detectable for CuO loadings of as little as 1% as evidenced from the peak areas plotted in Fig. 2. This is contrary to the published work of several authors who could not detect the CuO phase in the XRD of SnO₂:CuO samples [11, 18, 19, 27, 28]. The peak intensity was stronger with increasing Cu loading suggesting that at a low Cu content, CuO was present in the form of nanoparticles while at a high Cu content, bulk CuO agglomerated particles were present.

The experimental conditions used for the preparation of SnO₂:CuO samples affected the optimum calcination conditions required for the appearance and intensity of CuO diffraction peaks in the XRD spectra of powder SnO₂:CuO samples. This included: the Sn salt used as a precursor, solvent, the use of a template and citric acid to metal ratio (CA:M). The data reported in Table 1 demonstrates the significance of these variables. The trend shown in Fig. 1B was typical of all cases, except when anhydrous SnCl₄ was used as a precursor in ethylene glycol. The optimum temperature to achieve the maximum degree of crystallinity

of crystalline phase of monoclinic CuO in these samples was found to be 700 °C. However, for the anhydrous SnCl₄ case, the degree of crystallinity of crystalline phase of monoclinic CuO and subsequently the areas of CuO diffraction peaks in the XRD spectra of powder SnO₂:CuO samples increased with temperature up to 900 °C, the maximum calcination temperature tested. Also, compared with water, the samples prepared in ethylene glycol without citric acid, had higher intensity as well as peak areas of CuO diffraction peaks.

3.2 Crystallite size and BET specific surface area

The data listed in Table 2, demonstrates the effect of the experimental conditions on the crystallite size and BET specific surface area of various samples. The presence of CuO in the system SnO₂:CuO contributed an increase in the crystallite sizes of both CuO and SnO₂ as well as a reduction of the total surface area of the samples. The increase in the grain size of CuO is due to the aggregation of fine grain CuO species on calcination and is in agreement with the appearance of the CuO diffraction peaks in the XRD pattern. This is most probably due to the surface diffusion of CuO on the SnO₂ particles [29]. The increase in the crystallite size of SnO₂ in the SnO₂:CuO samples is contrary to the published data that suggested a decrease in the growth rate of SnO₂ crystallites in the presence of dopants under the conditions of high temperature annealing [30].

The experimental conditions used, such as the solvent, Sn salt used as a precursor, use of citric acid and the calcination conditions all affected the crystallite size and BET specific surface area of the samples. Preparations were carried out in both water and ethylene glycol as a solvent. Compared with water, alcoholic solvents such as ethylene glycol are known to produce more stable sols with reproducible stoichiometries, when using metal chlorides as precursors [31]. It has been suggested that ethylene glycol prevents Cl[−] ions from accessing metal ions due to steric effects and hence increases the stability of the sol solution. Ethylene glycol functions not only as a complexation agent to form a polymer network but also as a spacer to modulate

Table 1 The effect of calcinations conditions on the CuO (002) XRD peak areas for SnO₂:CuO samples

Calcinations temperature (°C) and time (h)	Area of CuO (002) peak from XRD					
	SnCl ₄ ·5H ₂ O			SnCl ₂ ·2H ₂ O		Anhydrous SnCl ₄
	H ₂ O	EG ^a	EG	H ₂ O	EG ^a	EG
600–10 h	245	360	310	190	270	230
700–2 h				220		
700–5 h	426	675	515	1,080 ^b	270	280
900–1 h	216	420	200	195	460	355
900–2 h			200			435

^a No added citric acid; all other tests were carried out with a citric acid to metal ratio of 4:1; EG: Ethylene glycol

^b With CTMAB as a template

Table 2 The effect of experimental conditions on the crystallize size of SnO₂ and CuO

Experimental conditions					CS (nm)		SSA (m ² /g)
Sample	Solvent	Sn-salt	CA: Metal	Calcination conditions ^a	CuO	SnO ₂	
CuO	H ₂ O	–	4	600 °C–10 h	36		10
SnO ₂	H ₂ O	SnCl ₂ ·2H ₂ O	4	700 °C–3 h		23 ± 2	19 ± 3
	EG	SnCl ₂ ·2H ₂ O	4	700 °C–3 h		28 ± 1	11 ± 3
SnO ₂ :CuO	H ₂ O	SnCl ₂ ·2H ₂ O	4	800 °C–1 h	193	39	7
	H ₂ O ^b	SnCl ₂ ·2H ₂ O	4	700 °C–5 h	115	59	8
SnO ₂	H ₂ O	SnCl ₄ ·5H ₂ O	4	700 °C–5 h		18 ± 1	39 ± 1
SnO ₂ :CuO	H ₂ O	SnCl ₄ ·5H ₂ O	4	700 °C–5 h	85	52	8
	EG	SnCl ₄ ·5H ₂ O	4	700 °C–5 h		28	12
SnO ₂ :CuO	EG	SnCl ₄ ·5H ₂ O	4	700 °C–5 h	126	67	10
	EG	SnCl ₄ ·5H ₂ O	0	700 °C–5 h	181	24	11
	EG	SnCl ₄ -Anhydrous	0	900 °C–1 h	157	26	11
	EG	SnCl ₄ -Anhydrous	4	900 °C–1 h	97	69	7

EG ethylene glycol, CA citric acid, CS crystallite size, SSA BET specific surface area

^a For maximum (I_{max}) of CuO (002) peak intensity for SnO₂:CuO samples with 5% added Cu

^b With Cetyl-trimethylammonium bromide (CTMAB)

the distance between metal ions, preventing metal oxide particles from aggregation during earlier stages of organics removal.

In general, when compared with water the samples prepared in ethylene glycol had higher crystallite sizes for both CuO and SnO₂ and lower BET specific surface areas. The effect of Sn salt used as a precursor, was more pronounced for CuO compared with SnO₂. SnCl₂·2H₂O used as a precursor produced the largest CuO particles in water, while anhydrous SnCl₄ produced the smallest CuO particles in ethylene glycol. Citric acid also had a significant effect on the crystallize size of both CuO and SnO₂ in SnO₂:CuO samples. The increase in the crystallite size of SnO₂ in the samples prepared in ethylene glycol in the presence of citric acid was the highest. The samples prepared without citric acid had crystallite sizes of SnO₂ comparable to undoped SnO₂ samples. The crystallize size of CuO in these samples was much reduced in the presence of citric acid compared with the samples prepared without citric acid.

3.3 FTIR

Figure 3 shows FTIR spectra of polycrystalline SnO₂:CuO containing 5 w/w% Cu. For comparison, IR spectra for pure CuO, pure SnO₂ and a mechanical mixture of the two powders containing 7 w/w % of CuO are also shown. For pure SnO₂ and CuO all relevant IR bands were found to lie within the reported spectral ranges [31–36]. The IR spectrum of the mechanical mixture is a sum of the IR

spectra of the components. The IR spectrum of SnO₂:CuO sample is seen to consist of peaks corresponding to those of pure SnO₂ and a single merged peak for CuO. It is assumed that the broad CuO band in the spectrum of SnO₂:CuO sample overlaps wide shoulder at 530 cm^{−1} for SnO₂ whose presence is predicted from the strong transmittance located at 620 and 670 cm^{−1}. Note that the SnO₂ typical band located at 620 cm^{−1} in the spectrum of pure SnO₂ did not change its shape, position or relative intensity in the IR spectrum of SnO₂:CuO. However, a weak shoulder located at 670 cm^{−1} in the spectrum of pure SnO₂ has changed to a more easily distinguishable strong band in the spectrum of SnO₂:CuO sample. The position, relative intensity and width of the IR bands of microcrystalline polar solids are strongly affected by the shape and the state of aggregation of the particles [37, 38]. This suggests that the shape and the state of aggregation of CuO and SnO₂ particles could be different in the SnO₂:CuO samples compared with the pure component samples.

3.4 XPS

The CuO, SnO₂ and SnO₂:CuO samples prepared using modified Pechini method were investigated by X-ray photoelectron spectroscopy (XPS). The binding energies of Sn 3d, O 1s, and Cu 2p core levels in these samples were measured and compared to the corresponding binding energies in SnO₂, CuO and Cu₂O powders. These binding energies are listed in Table 3. The binding energies of the

Fig. 3 FTIR spectra of: (a) SnO₂, (b) CuO, (c) mechanical mixture of SnO₂ and CuO, (d) SnO₂:CuO

Sn 3d are consistent with those of Sn⁴⁺ ions in SnO₂ [39, 40]. The pure SnO₂ sample had Sn 3d_{5/2} and O 1s signals at 486.7 and 530.5 eV, respectively, irrespective of the treatments. On the other hand, the as-prepared SnO₂:CuO samples had these signals at 486.5 and 530.3 eV, respectively, which were 0.2 eV lower than those of the pure SnO₂ sample. The agglomeration of SnO₂ on the addition of dopants has been reported to result in a decrease in the

binding energy of SnO₂ [41]. The decrease in the binding energy (BE) of Sn 3d_{5/2} in SnO₂:CuO has also been ascribed to the presence of a CuO surface layer [7], suggesting that CuO is dispersed as fine particles on the surface of SnO₂ particles. Copper is known [42] to be primarily distributed as CuO_x segregations on the SnO₂ grain surface and have only a slight effect on the Sn–O bond energy.

The binding energies for the Cu 2p_{3/2} and Cu 2p_{1/2} lines in the SnO₂:CuO occur at approximately 933 eV and 953 eV, respectively. Two well defined satellite peaks associated with the Cu 2p_{3/2} lines at 940.6 and 943.3 eV were also observed. The shake-up satellites are associated with Cu(II), [41, 43, 44]. Moreover, the Cu 2p peaks were broader with a shoulder. It is, therefore, more realistic to assume the presence of two separate contributions to the main Cu 2p peaks. The broadened Cu 2p_{3/2} peaks were correspondingly decomposed into two distinct peaks separated by approximately 2 eV, with the lower energy peak being associated with Cu⁺ and the higher one with Cu²⁺ [45]. This is shown in Fig. 4. The relative Cu²⁺ content estimated from the spectral analysis was found to vary from 60 to 10%. Also, the Cu 2p peaks for SnO₂:CuO

Fig. 4 A typical high resolution Cu 2p_{3/2} spectrum for SnO₂:CuO samples and the resulting peak from a least-squares fit (dashed lines)

Table 3 The binding energies (eV) of Cu2p, Sn3d and O 1s

Sample ID	Binding energy (eV)				
	Cu2p _{3/2}	Cu2p _{1/2}	ΔECu2p	Sn3d _{5/2}	O 1s
SnO ₂				486.7 ± 0.1	530.5 ± 0.1
CuO	933.8 ± 0.1	953.6 ± 0.1	19.8		529.3 ± 0.1
Cu ₂ O	931.8 ± 0.3	951.5 ± 0.3	19.7		530.9 ± 0.4
SnO ₂ :CuO	934.2 ± 0.2;	953.9 ± 0.2;	19.7	486.5 ± 0.1	530.3 ± 0.1;
	932.6 ± 0.2	952 ± 0.2	19.4		531.6 ± 0.2; 533 ± 0.3

Fig. 5 Relationship between CuO(002) peak area from XRD and the ratio of Cu^{2+} to total Cu ($\text{Cu}^{2+} + \text{Cu}^+$) from XPS data

samples shift by 0.4 eV towards higher energies from its value for CuO.

The O 1s peaks for $\text{SnO}_2:\text{CuO}$ samples shift by 0.2 eV towards lower energies from its value for SnO_2 . It shifts 2.3 and 2.1 eV towards higher energies from its value for CuO and Cu_2O , respectively. Given that oxide ion polarizability is closely related to O 1s binding energy in the XPS spectra of oxides, decreased O 1s binding energy means increased oxygen ion polarizability (increased basicity) and a

stronger electron donor ability of the oxide ion and vice versa [46].

3.5 Relationship between XRD and XPS data

The relative Cu^{2+} content can be estimated from the XPS spectral analysis by using the area under the Cu^{2+} peak plus the area under the satellite peaks [47]. Defining

Concentration of $\text{Cu}^+ \propto$ area under peak at B.E of $932.6 \pm 0.2 \text{ eV} = A1$

Concentration of $\text{Cu}^{2+} \propto$ area under peak at B.E of $934.2 \pm 0.2 \text{ eV}$ plus area under satellite peaks = A2, then

$$\text{Cu}^{2+}/(\text{Cu}^{2+} + \text{Cu}^+) = A2/(A1 + A2)$$

This data was plotted against CuO (002) peak area from XRD and is shown in Fig. 5. The data was fitted to a linear plot with a correlation coefficient of 0.994. The existence of an excellent correlation between the ratio of Cu^{2+} to total Cu from XPS and the CuO (002) peak area from XRD, suggests that CuO (002) peak is indeed from the Cu^{2+} (CuO).

3.6 SEM

Figures 6 and 7 show some typical SEM images of the examined solids. SEM analyses indicated that there were large differences in microstructure between various samples. Some samples had much smaller grains with a

Fig. 6 SEM micrographs of powdered samples. **a–d** SnO_2 , Citric acid to metal ratios: **a** 1, **b** 3, **c**, **d** 4, calcinations temperatures: **a–c** 600°C –10 h, **d** 700°C –5 h with template; **e** CuO, **f** mechanical mixture of SnO_2 and CuO

Fig. 7 SEM micrographs of powdered samples of $\text{SnO}_2\text{:CuO}$, **a** 0.6% Cu; **b–e** 5% Cu, **b** 600 °C–4 h, **c** 600 °C–14 h, **d** 700 °C 5 h, **e** 700 °C with template

uniform distribution, but others had obvious bulk particles with irregular sizes and shapes. Figure 6a–d represent pure SnO_2 and Fig. 6e represents pure CuO . As can be seen SnO_2 phase consists of particulate structure and CuO phase shows the large cluster of irregular plates and slabs of varying sizes.

Figure 6a–c illustrate the effect of the ratio of citric acid: metal (R_a). With smaller amounts of citric acid (Fig. 6a, $R_a = 1$), smaller spherical particles agglomerate into balls of various sizes. Increasing R_a ratio results in uniformly sized spherical particles of ~ 20 nm. Figure 6d demonstrates the effect of a templating agent that results in a mixture of long rods, broken slabs and rocks.

The SEM analysis of the mechanical mixture of SnO_2 and CuO (Fig. 6f) clearly indicated the presence of two phases. As seen from the microgram, the particular structure for SnO_2 and platlets for CuO can be distinguished. Also, SnO_2 particles appear to be stuck together presumably by the CuO acting as a binding agent.

SEM micrographs of the as prepared samples of $\text{SnO}_2\text{:CuO}$ samples are shown in Fig. 7a–e. As against the SEM micrograph of the mechanical mixture of SnO_2 and CuO (Fig. 6f), no separate phase of CuO could be discerned on SnO_2 by SEM in these samples. However, except for small amount of Cu (0.6%, Fig. 7a) the grain sizes increase and the connectivity of the intergrains improves in the presence of Cu, meaning that CuO appears to work as a sintering aid. Also, as seen from Fig. 7b–d, the grain size further increases with the increase in calcination temperature. The effect of the templating agent appears to be

similar to pure SnO_2 , except that the grain size is bigger in the presence of Cu.

4 Conclusions

Modified Pechini method was successfully applied to the preparation of nano-structured SnO_2 and $\text{SnO}_2\text{:CuO}$. The CuO phase in the $\text{SnO}_2\text{:CuO}$ samples was easily detectable by XRD, IR and XPS. The highest degree of crystallinity and subsequently the maximum intensity and area of CuO (002) diffraction peaks were observed for the samples prepared with templates. The calcinations conditions had a significant effect on the appearance and intensity of CuO diffraction peaks. The experimental conditions such as: precursor type, solvent, use of a template and citric acid to metal ratio all affected the optimum calcinations conditions required for the appearance and intensity as well as area of CuO diffraction peaks.

Compared with water, the samples prepared in ethylene glycol had higher crystallite sizes for both CuO and SnO_2 and lower BET surface areas.

Acknowledgments The authors are grateful to Gordon Chan for some technical assistance.

References

1. Alcántara R, Fernández-Madrigal FJ, Pérez-Vicente C, Tirado JL, Jumas JC, Olivier-Fourcade J (2000) *Chem Mater* 12:3044

2. Batta N, Cinquegrani L, Mgno E, Tgliante A, Pizzini S (1992) *Sens Actuators B6*:253
3. Maekawa T, Tamaki J, Miura N, Yamazoe N (1994) *J Mater Chem* 4:1259
4. Ihokura K, Watson J (1994) The stannic oxide gas sensor. CRC Press, Boca Raton
5. Lantto V, Mizsei J (1991) *Sens Actuators B5*:21
6. Zhou X, Cao Q, Huang H, Yang P, Hu Y (2003) *Mater Sci Eng B00*:1
7. Tamaki J, Maekawa T, Miura N, Yamazoe N (1992) *Sens Actuators B9*:197
8. Rumyantseva MN, Labeau M, Senateur JP, Delabouglise G, Boulova MN, Gaskov AM (1996) *Mater Sci Eng B41*:228
9. Choe Y-S (2001) *Sens Actuators B77*:200
10. Esfandyarpour B, Mohajerzadeh S, Khodadadi AA, Robertson MD (2004) *IEEE Sens J* 4:449
11. Katti VR, Debnath AK, Muthe KP, Kaur M, Dua AK, Gadkari SC, Gupta SK, Sahni VC (2003) *Sens Actuators B96*:245
12. Vasiliev RB, Rumyantseva MN, Podguzova SE, Ryzhikov AS, Ryabova LI, Gaskov AM (1999) *Mater Sci Eng B57*:241
13. Santilli CV, Pulcinelli SH, Brito GES, Briois V (1999) *J Phys Chem B103*:2660
14. Davis SR, Chadwick AV, Wright JD (1998) *J Mater Chem* 8:2065
15. Mehrota RC (1990) *J Non-Cryst Solids* 121:1
16. Majid A, Tunney J, Argue S, Post M (2004) *J Sol Gel Sci Technol* 32:323
17. Majid A, Tunney J, Argue S, Wang D, Post M, Margeson J (2005) *J Alloys Compd* 398:48
18. Choi WK, Cho JS, Song SK, Jung HJ, Koh SK, Yoon KH, Lee CM, Sung MC, Jeong K (1997) *Thin Solid Films* 304:85
19. Ghimbeu CM, van Landschoot RC, Schoonman J, Lumberras M (2007) *J Eur Ceram Soc* 27:207
20. Majid A, Tunney J, Post M, Margeson J (2006) *J Sol Gel Sci Technol* 38:271
21. Sanchez C, Soler-Illia G, Ribot F, Grosso D (2003) *Chimie* 6:1131
22. Schuth F (2001) *Chem Mater* 13:3184
23. Peng Z, Mahone KA, Liu M (2000) *J Mater Sci Lett* 19:1473
24. Bruker AXS (2000) Topas V2.0: general profile and structure analysis software for powder diffraction data, user manual. Bruker AXS, Karlsruhe
25. Balzar D (1999) Defect and microstructure analysis from diffraction. In: Snyder RL, Bunge HJ, Fiala J (eds) *International union of crystallography monographs on crystallography* no. 10. Oxford University Press, New York, p 94
26. Shaheen WM, Selim MM (1998) *Thermochimica Acta* 322:117
27. Rumyantseva M, Labeau M, Delabouglise G, Ryabova L, Kutsenoka I, Gaskov A (1997) *J Mater Chem* 7:1785
28. Francisco MSP, Nascente PAP, Mastelaro VR, Florentino AO (2001) *J Vac Sci Technol A* 19:1150
29. Rumyantseva MN, Safonova OS, Boulova MN, Ryabova LI, Gaskov AM (2003) *Russ Chem Bull Int Ed* 52:1217
30. Fang G, Liu Z, Zhang Z, Hu Y, Ashur IA, Yao KL (1996) *Phys Status Solidi A Appl Res* 156:15
31. Zhang G, Liu M (1999) *J Mater Sci* 34:3213
32. Bordoni S, Castellani F, Cavani F, Trifiro F (1994) *J Chem Soc Faraday Trans* 90(19):2981
33. Song KC, Kang Y (2000) *Mater Lett* 42:283
34. Scarlat O, Susana-Mihaiu O, Zaharescu M (2002) *J Eur Ceram Soc* 22:1839
35. Mihaiu S, Scarlat O, Aldica G, Zaharescu M (2001) *J Eur Ceram Soc* 21:1801
36. Zhang YC, Tang JY, Wang GL, Zhang M, Hu XY (2006) *J Crystal Growth* 294:278
37. Ocena J, Serna CJ (1991) *Spectrochim Acta* 47A:765
38. Dieguez A, Romano-Rodriguez A, Morante JR, Weimar U, Schweizer-Berberich M, Gopel W (1996) *Sens Actuators B31*:1
39. Poznyak SK, Kulak AI (2000) *Electrochim Acta* 45:1595
40. Choe Y-S, Chung JH, Kim DS, Baik HK (1999) *Surf Coat Technol* 112:267
41. Espinós JP, Morales J, Barranco A, Caballero A, Holgado JP, González-Elipe AR (2002) *J Phys Chem B106*:6921
42. Shannon RD, Prewitt CT (1969) *Acta Cryst B25*:925
43. Shimizu K, Maeshima H, Yoshida H, Satsuma A, Hattori T (2000) *Phys Chem Chem Phys* 2:2435
44. Indovina V, Occhiuzzi M, Pietrogiammi D, Tuti S (1999) *J Phys Chem B* 103:9967
45. Khattak GD, Salim MA, Wenger LE, Gilani AH (2000) *J Non-Crystalline Solids* 262:66
46. Dimitrov V, Komatsu T (2002) *J Solid State Chem* 163:100
47. Salim MA, Khattak GD, Tabet N, Wenger LE (2003) *J Electrocatal Relat Phenom* 128:75