

# The preparation and characterization of nanostructured $\text{TiO}_2\text{-ZrO}_2$ mixed oxide electrode for efficient dye-sensitized solar cells

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## Abstract

The preparation of nanostructured mixed metal oxide based on a sol–gel method with surfactant-assisted mechanism, and its application for dye-sensitized solar cell (DSSC) are reported. The mixed zirconia ( $\text{ZrO}_2$ ) and titania ( $\text{TiO}_2$ ) mesoporous powder possessed larger surface area than the corresponding titania. For the UV action spectra of unsensitized photochemical cell, the mixed zirconia/titania electrode can absorb UV light below 380 nm, corresponding to band gap ( $E_g$ ) around 3.27 eV, which is higher than that of pure component of titania ( $E_g = 3.2$  eV). Both of these improved properties, i.e., BET surface area and band gap, contributed to the improvement on a short-circuit photocurrent up to 11%, an open-circuit voltage up to 4%, and a solar energy conversion efficiency up to 17%, for the DSSC fabricated by mesoporous zirconia/titania mixed system when compared to the cell that was fabricated only by nanostructured  $\text{TiO}_2$ . The cell fabricated by 5  $\mu\text{m}$  thick mixed  $\text{TiO}_2\text{-ZrO}_2$  electrode gave the short-circuit photocurrent about 13  $\text{mA}/\text{cm}^2$ , open-circuit voltage about 600 mV and the conversion efficiency 5.4%.

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**Keywords:** Mixed metal oxide; Surfactant-assisted method; Photoelectrochemical; Dye-sensitized solar cell

## 1. Introduction

Mesoporous film-based dye-sensitized solar cells (DSSCs) have recently received considerable attention as practical solar energy conversion devices [1,2]. DSSC is composed of a few micrometer-thick film consisting nanocrystalline oxide covered with monolayer of Ru-bipyridyl-based charge-transfer dye, a redox electrolyte and a platinum metal electrode. Such a high efficiency of DSSCs was achieved only when the nanoporous  $\text{TiO}_2$  electrodes which facilitate high optical density of a dye monolayer are applied. In general, an electrode with high surface area is of great significance since a higher amount of dye adsorbed on an electrode corresponds to a higher current density. During the past years,  $\text{TiO}_2$  electrodes consisting of nanosized semiconductor col-

loids have been sintered on a transparent conduction substrate. They resulted in a porous geometry and very large surface area. They are one of the most commonly used electrodes for the DSSCs. However, the resulting electrode geometry introduces special characteristics, some of which reduce the performance of the DSSCs [3].

Although dye-sensitization can be achieved with porous films of non- $\text{TiO}_2$  semiconductors with high band gap [4,5], it has never been reported to be as efficient as the  $\text{TiO}_2$  cells reported by Regan and Grätzel [1]. To increase the open-circuit photovoltage ( $V_{oc}$ ) of a cell, several research groups attempted to improve the properties of the electrode such as modifying the structure of  $\text{TiO}_2$  [6,7] or using a bilayer technique [8–11]. This bilayer technique required another metal oxide, which has more negative conduction band energy ( $E_c$ ), coated onto base nonporous electrode to reduce the recombination rate of photo-injected electron. Since the  $V_{oc}$  is in proportion to the difference in the electron

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energies between redox potential level and the level of  $E_c$  of an electrode [12], another possible way to increase the  $V_{oc}$  is the increase in the conduction band energy level of the material used in electrodes.

In this study, nanostructured mesoporous mixed metal oxide was synthesized by the surfactant-assisted [13] method using laurylamine hydrochloride (LAHC)/mixed metal alkoxides modified with acetylacetone (ACA) system. A mixture of  $ZrO_2$  and  $TiO_2$  was used as an electrode for DSSC. Many properties of these nanostructure mixed metal oxides were reported to be better than that of  $TiO_2$  [6]. These include the BET specific surface area, which can improve the amount of adsorbed dye molecules.

## 2. Experimental

### 2.1. Materials and methods

Tetra-isopropyl-orthotitanate (TIPT) and laurylamine hydrochloride (LAHC) (Tokyo Chemical Industry Co.), acetylacetone (ACA) and 2-propanol (Nacal Tesque Co.), and Zr-butoxide (ZrBt) (HOKKO Chemical Industry Co., Ltd.) were used as starting chemicals. All chemicals were of analytical grade and used as received. The *bis*(tetrabutylammonium) *cis*-di(thiocyanato) *bis*(2,2'-bipyridine-4,4'-carboxylic acid) ruthenium (II) (called N719) [9] (Solaronix SA Co.) was used as a dye. Conducting glass plates (Geomatec Co., Ltd.), with Indium doped tin oxide (ITO), sheet resistance  $5 \Omega/\square$ , were cleaned with acetone, rinsed with distilled water, and dried in  $80^\circ\text{C}$  oven.

Transmission electron microscopy (TEM, JEOL JEM-200CX at 200 kV) was employed to investigate the morphology of synthesized material. The crystal structure of mixed metal oxide was analyzed by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  radiation (RIGAKU-A2). BET surface area of synthesized samples was recorded using nitrogen adsorption desorption analysis (BELSORP 18 PLUS).

The film thickness was determined by an Alpha-Step 200 apparatus (Tencor Instruments) and the amount of adsorbed dye concentration was measured by using the solution of 0.1 M NaOH and ethanol (1:1 in volume fraction), in which the anchored dye from dyed-electrodes was desorbed. The absorption spectrum was analyzed by an UV-Vis spectrophotometer (SHIMADZU, model UV-2450).

### 2.2. Preparation of nanostructured mixed metal oxides electrode

The mesoporous  $TiO_2$  and  $ZrO_2$ , as a reference, were synthesized from TIPT and ACA at the same molar concentration ( $[\text{TIPT}]/[\text{ACA}] = 1$ ) and  $[\text{ZrBt}]/$

$[\text{ACA}] = 1$ , respectively. The  $ZrO_2$ -mixed mesoporous  $TiO_2$  ( $[\text{TiO}_2]:[\text{ZrO}_2] = 95:5$ ) was synthesized from TIPT, ZrBt, and ACA at the molar ratio of  $[\text{TIPT} + \text{ZrBt}]/[\text{ACA}] = 1$ . After the mixing, 0.1 M LAHC aqueous solution (pH 4–4.5) was added to each of these solutions, so as to attain  $[\text{TIPT}]/[\text{LAHC}] = 4$ ,  $[\text{ZrBt}]/[\text{LAHC}] = 1$ , and  $[\text{TIPT} + \text{ZrBt}]/[\text{LAHC}] = 4$ , and then the mixture was stirred at  $40^\circ\text{C}$  for 24 h until a clear yellow solution was obtained. The reaction bottles were then sealed and kept in an oven preheated at  $80^\circ\text{C}$  for 7 days to yield a gel. These gel samples were washed by 2-propanol to remove LAHC.

$TiO_2$  or  $TiO_2$ - $ZrO_2$  gels were coated on ITO glass plates ( $0.5\text{ cm} \times 0.5\text{ cm}$ ) by glass rod, using adhesive tapes (3 M) as spacers. After the films were dried in air, the coated conducting glasses were sintered at  $450^\circ\text{C}$  for 90 min and left to be cooled to  $80^\circ\text{C}$ . Then, these two electrodes were immersed in 50 wt% butanol and 50 wt% acetonitrile mixed solution of 0.3 mM N719 dye at least 24 h. After the dye adsorption, these electrodes were immediately fabricated into thin-layer, sandwich-type solar cells. The counterelectrodes, thin platinum layer sputtered on F-doped  $\text{SnO}_2$  film conducting glass plates, were kept in contact with these two dyed electrodes. In order to prevent a direct contact between the working and the counter electrodes which result in the  $V_{oc}$  reduction to less than 300 mV [9], a stripe of 25  $\mu\text{m}$  thick Surlyn (Dupont, Himilan 1702) was inserted as a spacer between them. The redox electrolyte comprising a 0.6 M dimethylpropyl-imidazolium iodide solution, a 0.1 M lithium iodide (LiI) solution, and a 0.05 M iodide ( $\text{I}_2$ ) solution in acetonitrile was introduced to the gap between the counter and working electrodes by the capillary force.

The photovoltaic properties of these sandwich-type cells were measured by using a potentiostat (Bunko Keiki model HCSSP-25) irradiated with simulated solar light, A.M. 1.5,  $100\text{ mW}/\text{cm}^2$  (Bunko Keiki, model CEP-2000).

## 3. Results and discussion

### 3.1. Characterization of synthesized $TiO_2$ and $TiO_2$ - $ZrO_2$ mixed oxide

Generally, when the sol-gel technique is used, surface area and particle size are largely affected by the sintering temperature [14]. Figs. 1(a) and (b) show TEM images and electron diffraction patterns of calcined powders at  $500^\circ\text{C}$  for 4 h of  $TiO_2$  and 95:5 mol%  $TiO_2$ - $ZrO_2$  mixed oxide, respectively. These TEM images show particle size distributions in the range of 10–25 nm for  $TiO_2$ -powder and 7–15 nm for  $TiO_2$ - $ZrO_2$  mixed oxide powder. The smaller particle size for the mixed oxide

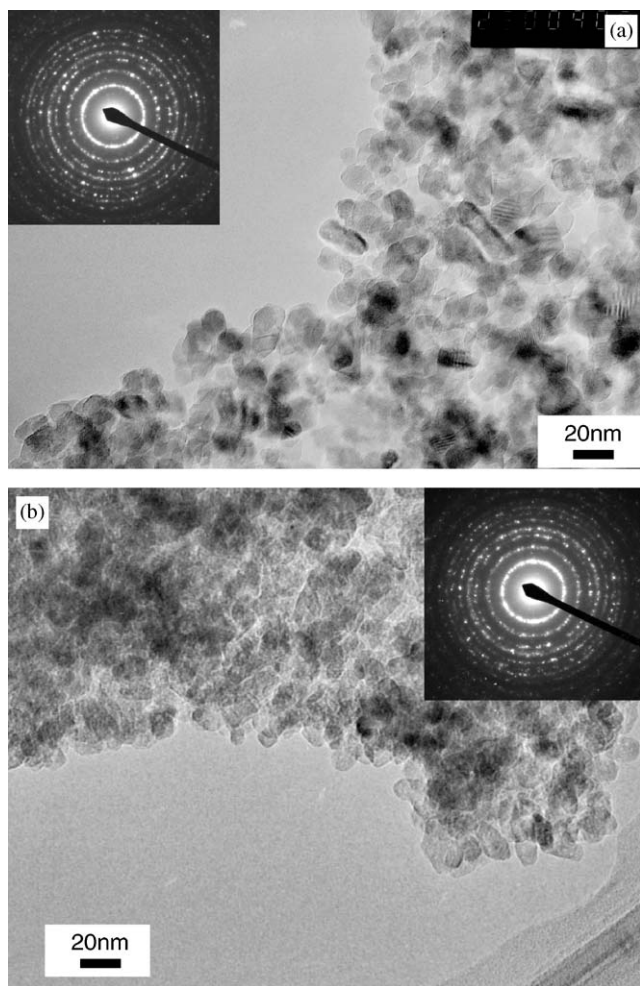


Fig. 1. TEM images and electron diffraction patterns of (a) synthesized  $\text{TiO}_2$  and (b) 95:5 mol%  $\text{TiO}_2$ - $\text{ZrO}_2$  mixed oxide.

could be attributed to an increase in the thermal stability and the resistance to sintering caused by the doped oxide.

From electron diffraction analysis, circular rings of electron diffraction patterns have been obtained as shown in insertion of Fig. 1(a) and (b). Both ED patterns show the Debye-Scherrer rings of anatase, which are in good agreement with the results from X-ray diffraction patterns, as shown in Fig. 2.

Fig. 2 illustrates the XRD patterns of calcined  $\text{TiO}_2$ , 95:5 mol%  $\text{TiO}_2$ - $\text{ZrO}_2$  mixed oxide, and  $\text{ZrO}_2$ . These results show that the prepared  $\text{TiO}_2$ -powder consists of anatase titania crystal; rutile phase could not be detected. The diffraction peaks from prepared  $\text{ZrO}_2$  can be assigned to the tetragonal structure. In case of 95:5 mol%  $\text{TiO}_2$ - $\text{ZrO}_2$  mixed oxide, there are no diffraction peaks of the  $\text{ZrO}_2$  structure. In other words, the structure of mixed oxide is an anatase type. This means that the addition of a small amount of  $\text{ZrO}_2$  did not change the structure of anatase- $\text{TiO}_2$  [15].

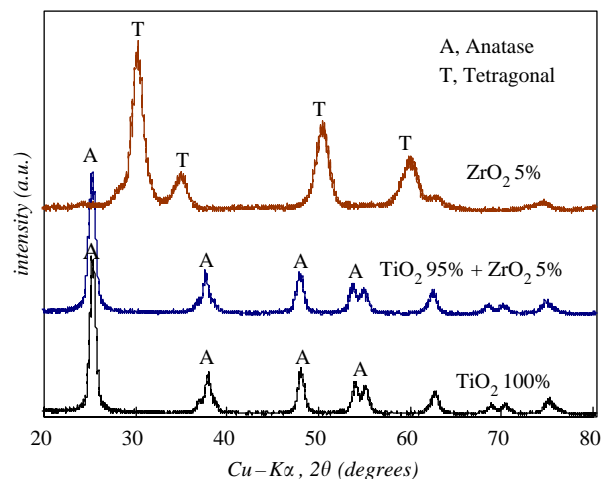


Fig. 2. XRD patterns of the sample powders of  $\text{TiO}_2$  100%, mixed  $\text{ZrO}_2$  5% and  $\text{TiO}_2$  95%, and  $\text{ZrO}_2$  100%. All samples calcined at  $500^\circ\text{C}$ , 4 h.

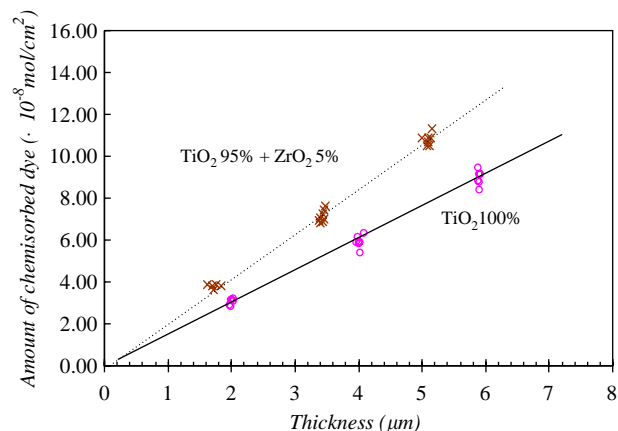


Fig. 3. Relationship between the amount of chemisorbed dye and the thickness of electrodes fabricated by  $\text{TiO}_2$  100% and mixed metal oxides ( $\text{ZrO}_2$  5% +  $\text{TiO}_2$  95%).

### 3.2. Dye-chemisorption and $I$ - $V$ characterization

The BET surface area of 95:5 mol%  $\text{TiO}_2$ - $\text{ZrO}_2$  mixed oxide is  $109 \text{ m}^2/\text{g}$ , that is about 35% higher than  $\text{TiO}_2$ , which has a surface area of  $80 \text{ m}^2/\text{g}$ . As shown in Fig. 3, the amount of chemisorbed dye on both types of films increases with the film thickness and the amount of absorbed dye for  $\text{TiO}_2$ - $\text{ZrO}_2$  film were approximately 30% higher than  $\text{TiO}_2$  film.

Fig. 4 shows the relationship between the short-circuit current density ( $J_{\text{sc}}$ ) and the film thickness. This figure illustrates that, for both of  $\text{TiO}_2$  and  $\text{TiO}_2$ - $\text{ZrO}_2$  film, the increasing of  $J_{\text{sc}}$  seems to get saturated with an increasing of thickness. This is probably due to the fact that, for the thicker films, electrons generated at a distance farther from the interface between the film and conducting glass are getting lost by recombination

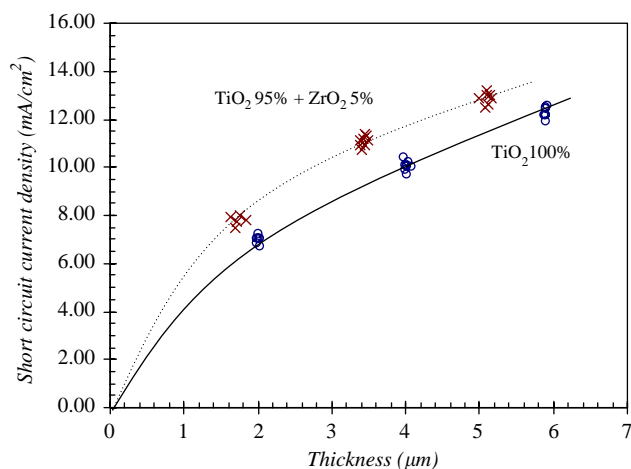


Fig. 4. Relationship between the short-circuit photocurrent density and the thickness of electrodes fabricated by TiO<sub>2</sub> 100% and mixed metal oxides (ZrO<sub>2</sub> 5% + TiO<sub>2</sub> 95%).

before they can reach the interface [16]. For the thickness in range of 2–6 μm, the average  $J_{sc}$  obtained from TiO<sub>2</sub>–ZrO<sub>2</sub> electrode is approximately 11% higher than that obtained from TiO<sub>2</sub> electrode.

The dependencies of open-circuit voltage ( $V_{oc}$ ) and fill factor ( $ff$ ) on the film thickness of TiO<sub>2</sub> and TiO<sub>2</sub>–ZrO<sub>2</sub> electrode were reported in Fig. 5. The results show no definite dependence of both  $V_{oc}$  and  $ff$  on the film thickness. The fill factor is found to be in the range of 0.65–0.68 and 0.70–0.73 for TiO<sub>2</sub> film and TiO<sub>2</sub>–ZrO<sub>2</sub> film, respectively. The  $V_{oc}$  that were obtained from TiO<sub>2</sub>–ZrO<sub>2</sub> electrode are in the range of 585–605 and 565–585 mV for the TiO<sub>2</sub> electrode. These results indicated that the average  $V_{oc}$  from TiO<sub>2</sub>–ZrO<sub>2</sub> electrode is about 4% higher when compared to that of TiO<sub>2</sub> electrode.

Fig. 6 shows the UV action spectra of un-sensitized photovoltaic cells. The band gap ( $E_g$ ) of an electrode containing 95:5 mol% TiO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide adsorbs UV light below  $\lambda_g \sim 380$  nm, corresponding to  $E_g$  around 3.27 eV, which is larger than that of a TiO<sub>2</sub> electrode ( $E_g \sim 3.2$  eV,  $\lambda_g \sim 387$  nm). The difference between the quasi-Fermi level (QFL) of electrons in the semiconductor under illumination and the potential of the redox couple ( $I^-/I_3^-$  in almost all cases) is the driving force of the electrons in the external circuit that determine the  $V_{oc}$  of the cell [17]. As the QFL could increase up to  $E_c$ , the maximum achievable  $V_{oc}$  is of the order of the difference between the energies of the bottom of the semiconductor conduction band and the electrolyte redox potential [18]. It could be seen that  $E_c$  of ZrO<sub>2</sub> is approximately  $-1.0$  eV, which is more negative than that of TiO<sub>2</sub> ( $-0.3$  eV). So, a larger  $E_g$  of TiO<sub>2</sub>–ZrO<sub>2</sub> electrode could result in a more negative value of  $E_c$  than that of TiO<sub>2</sub> electrode. This could be responsible

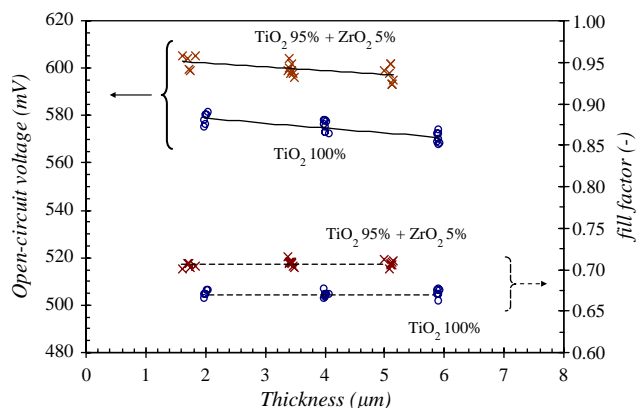


Fig. 5. Dependencies of open-circuit voltage and fill factor on the thickness of electrodes fabricated by TiO<sub>2</sub> 100% and mixed metal oxides (ZrO<sub>2</sub> 5% + TiO<sub>2</sub> 95%).

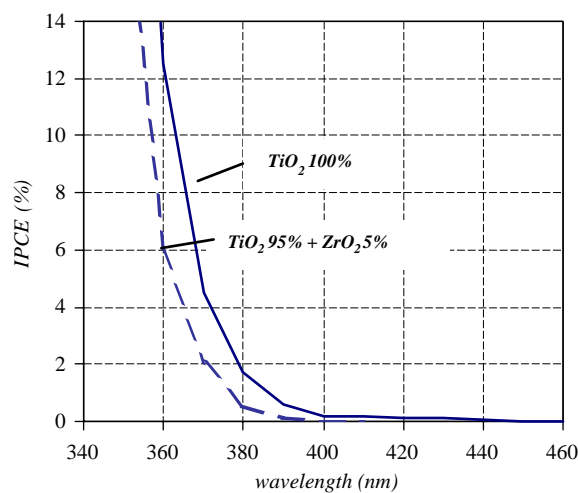


Fig. 6. UV action spectra of un-sensitized photovoltaic cells. The comparison between IPCE plotted as function of excitation wavelength of cells fabricated by synthesized TiO<sub>2</sub> and those of 95:5 mol% TiO<sub>2</sub>–ZrO<sub>2</sub> mixed oxides.

for a higher  $V_{oc}$  of the cell fabricated from TiO<sub>2</sub>–ZrO<sub>2</sub> electrode.

Fig. 7 shows the relationship between the solar energy conversion efficiency ( $E_{ff}$ ) and the film thickness. By the increase in  $J_{sc}$ ,  $V_{oc}$ , and  $ff$ , the electrode fabricated by a 95:5 mol% TiO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide as described above exhibits an efficiency approximately 17% higher than that of TiO<sub>2</sub> electrode.

#### 4. Conclusions

This work represents an alternative method to improve the efficiency of DSSCs. The TiO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide system based on sol-gel method of surfactant-assisted mechanism was synthesized. By adding small amount of other metal oxides, in this case, ZrO<sub>2</sub>, into

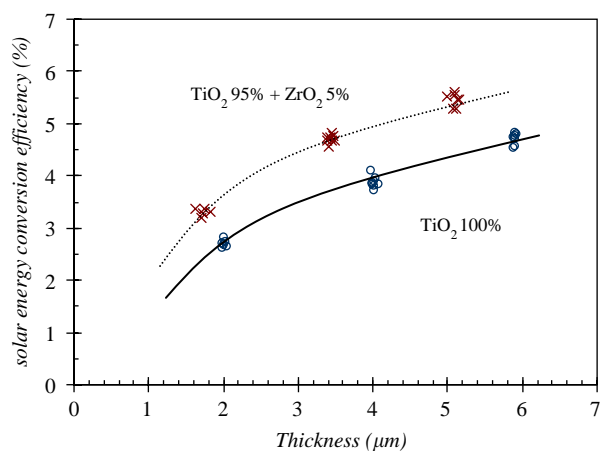


Fig. 7. Relationship between the solar energy efficiency and the thickness of electrodes fabricated by TiO<sub>2</sub> 100% and mixed metal oxides (ZrO<sub>2</sub> 5% + TiO<sub>2</sub> 95%).

nanostructured TiO<sub>2</sub>, the structure of TiO<sub>2</sub>–ZrO<sub>2</sub> mixed oxide still maintains an anatase type of TiO<sub>2</sub>. The addition of 5% ZrO<sub>2</sub> can adjust both of band gap and BET surface area which lead to the increase in  $V_{oc}$  ( $\Delta$  4%) and  $J_{sc}$  ( $\Delta$  11%), respectively, when compared to the cell that was fabricated by TiO<sub>2</sub> electrode. These increases enhanced the solar energy conversion efficiency up to  $\Delta$  17%.

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