Titanium dioxide (TiO$_2$) is one of the most abundant compounds in our planet. It is cheap, non-toxic, highly chemically and thermally stable semiconductor material. Titanium dioxide nanoparticles (TiO$_2$-NPs) show high visible light transparency combined with high UV light absorption. However, altering the particle size and crystalline structure of TiO$_2$-NPs influences the absorption range, adsorption of dye molecules and electron transfer rate at the surface. Unfortunately, TiO$_2$-NPs suffer high electron/hole recombination rates. Therefore, an ordered superstructure consisting of nanoparticles on the scale of nanometers to several micrometers is proposed titanium dioxide mesocrystals (TiO$_2$-MCs).

In this work, we represent a new and facile way to fabricate TiO$_2$-MCs with spherical structure by sol-gel method. We were able to fabricate spherical TiO$_2$-MCs with narrow size distribution by controlling the hydrolysis conditions. The effect of air annealing on the morphology, size shrinkage, and phase transition of the nanoparticles was studied by scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. Also, the fabricated TiO$_2$-MCs showed exceptional photoactivity compared to their Degussa p-25 nanoparticles counterparts upon their use in water splitting cells.

Keywords: TiO$_2$, Water Splitting, Mesocrystals, Nanoparticles, Solar fuel.

**Introduction**

Titanium dioxide nanoparticles (TNPs) acquired a great attention along the running decade as a cheap and efficient semi-conductor for many emerging applications such as photonic band material, gas sensing, photocatalysts and dye-sensitized solar cells (DSSCs) [1-4]. Moreover, enhanced solar energy conversion efficiency would provide enormous economic advantages [5–10].

It’s known that photoactivity of (TNPs) varies greatly with its morphology [11] which can be controlled easily by varying the conditions and method of preparation. TNPs size can affect their properties such as specifics surface area, life time of the exciton (e-h pair), conductivity, and surface to bulk defects [12]. Sol-gel method has been extensively used for synthesis of TNPs due to its simple preparation technique that can be done at low temperatures as well as its low preparation cost. Due to the high reactivity of the alkoxides that are usually used as precursors for TNPs synthesis with water, HCl or KCl has been reported to reduce the reactivity of the alkoxides in addition to size control [13, 14].

Spherical TiO$_2$ NPs are of great interest to be used in solar energy conversion devices because it is required to obtain maximum photon absorption by introducing higher exposed surface area and allow infiltration of electrolyte molecules into the mesoporous TiO$_2$. In addition, spherical particles minimize grain boundaries so that it facilitates electron transport, harvesting and minimizes recombination [1]. However, tailoring of TiO$_2$...
NPs or design of mesoscopic TiO$_2$ structure for photoanodes have scarcely been attempted thus far, in spite of their importance in determining the performance of the photocatalytic cell [15]. Spherical particles can be synthesized from controlled hydrolysis of titanium precursors with the aid of capping agents [2]. Hydrofluoric acid has been studied widely as a capping agent for synthesis of TiO$_2$ spherical particles with an increased percentage of reactive anatase 001 facet [15] as mentioned by yang et al. [16] that 001 facet can be stabilized and produced with high percentage by F ions terminated surfaces.

With the development of new class of solid materials in order to solve the problem of charge recombination, Mesocrystals; a new class of solid materials, which can be formed through a controllable orientation of nanocrystals, have received great attention for their unique characteristics such as single crystal-like behavior, high pore volume, high crystallinity, and the perfect alignment of their subunits [17]. Having these mesocrystals is a promising alternative to single and poly crystalline materials for many applications especially in solar energy conversion and photocatalysis [18-22]. It is worth mentioning that the long-range ordered materials can significantly reduce the recombination of the e-h pairs due to the anisotropic electron flow along the interparticles [18]. A lot of work has been done for the preparation of TiO$_2$ mesocrystals[19-23]. TiO$_2$ mesocrystals was firstly reported by O’Brien’s group through topotactic conversion of NH$_4$TiOF$_3$ mesocrystals [24, 25]. Lie et al. reported aformation of TiO$_2$ mesocrystals by anisotropic dissolution of NH$_4$TiOF$_3$ mesocrystals [26]. Also, TiO$_2$ sheets with controlled size were achieved in surfactant free aqueous solution of NH$_4$F and TiCl$_4$ [27].

Doping of TiO$_2$ nanoparticles with transition metals like Fe, Ni, Cr and Co can greatly enhance the system efficiency such as hydrogen production via photocon version process. Amongst them cobalt won the most attention and was extensively studied as it is proved that incorporation of Co leads to a redshift in absorption hence, a decrease in energy bandgap [28, 29]. It has also been observed that cobalt-doped TiO$_2$ growth conditions are more likely to be O-poor [30, 31]. O-poor conditions lead to roughly equal concentrations of substitutional and interstitial Co, n-type behavior resulting from thermal excitation of electrons from interstitial Co into the conduction band.

Tailoring the morphology of TiO$_2$MCs by sol-gel methods haven’t been discussed widely so far. From the previous work done by Hegazy and Prouzet [32], Hegazy et al. [33]; as well as Ahmed et al. [34], it has been concluded that the proposed synthesis way of TiO$_2$ resulted in highly ordered-template free small size of the nanoparticles with high specific surface area that enhances the efficiency of solar cells and the photocurrent density for water splitting applications. However, in this work we present a facile synthesis of TiO$_2$ MCs with submicron particles via surfactant free sol-gel method. We have followed the same recipe presented by Hegazy and Prouzet [32] except for replacing the HCl by HF. In addition, we also aim to increase the crystallinity of the mesocrystals by adding an oxidizing agent (K$_2$S$_2$O$_8$) through the synthesis process. Moreover, we managed to decrease the bandgap by in situ doping the TiO$_2$MCs with Co. The obtained results show the success of preparation of TiO$_2$ MCs with homogenous spherical shapes in the range of 1-2μmcovered byuniform plates. This synthesis resulted in bandgap narrowing and increased photocurrent density (4.2 mA/cm$^2$), upon the use of the material in water splitting systems.

**Materials and Methods**

Titanium n-propoxide (Ti(O-n-Pr)$_3$, Aldrich) was used as the titanium source. Hydrochloric acid (HCl, 37 wt%), Formamide (FA: H$_2$N-CHO), and Commercial P25 (Degussa P25) were purchased from Sigma-Aldrich. Potassium persulphate (K2S2O8) was used as the oxidizing agent. Hydrofluoric acid (HF 40%) was purchased from Al-Gomhoreya-Egypt. Cobalt(II) nitrate hexahydrate from Sigma-Aldrich was used as a doping agent. All the chemicals were used as received without any further purification. Fluorine-doped Tin Oxide (FTO) glass, 2.2 mm thick with a sheet resistance of 7 Ω cm$^2$ was purchased from Solaronix.

**Preparation of titanium mesocrystals**

The preparation method of the TiO$_2$ mesocrystals was inspired by the proposed method detailed in Hegazy and Prouzet [31]. However, the HCl was replaced by HF. In a typical synthesis, 3ml HF was added to 5gm (Ti(O-n-Pr)$_3$ in an iced bath drop by drop. 2.4ml of DI H$_2$O and 2.8ml formamide mixed together and added very slowly to the previous solution. The clear solution was kept at 80°C and left for aging overnight. This was the blank sample used.
form comparison and was termed as HF_RT. The sample was calcined at 400°C and termed as HF_400. In the case of doping with Co, 0.25gm Cobalt(II) nitrate hexahydrate was dissolved in the mixture of formamide and water and added slowly to the mixture of (Ti(O-n-Pr)_4) and HF and calcined at 400°C (HF_CoO_400). This sample to enhance the crystallinity of the previous solution 0.6 gm of 0.1 M K_2S_2O_8 was added to part of the formamide and water solution and added in the same way as the Co solution one, then annealed at 400°C (HF_CoO_K2S2O8).

The morphological analysis of the particles was performed using a Zeiss SEM Ultra 60 field emission scanning electron microscope (FESEM). The crystal structure of the prepared samples was detected by XRD on PANalyticalX’Pert PRO diffractometer. The UV–Vis absorption spectra of diluted samples in 50/50 (Ethanol:DI water) were collected using a Varian Cary 500 UV–Vis spectrophotometer, using quartz cuvette (Transparency 170–2700 nm) and 1 cm² optical path length. The Photoelectrochemical analysis was performed in 1.0 M KOH aqueous solution of diluted samples in 50/50 (Ethanol:DI water) of transparency 170–2700 nm) and 1 cm² optical path length. The working electrode using Bio-Logic SP 200 as a counter electrode and the titania sample as AgCl electrode as reference electrode, platinum in a three-electrode cell configuration with Ag/AgCl. Photoelectrochemical analysis was performed in 1.0 M KOH aqueous solution equipped with AM 1.5 G filter. Figure 1a shows the formation of nonporous intermediate NH_TiOF_3 at low temperature (<200 °C). At 200 °C, the same formamide and water solution was added in the same way as the Co solution one, then annealed at 400°C (HF_CoO_K2S2O8).

Results and Discussions

The TiO_2 mesocrystals were obtained through a facile synthesis with aid of HF. Figure 1a shows a formation of nonporous intermediate NH_TiOF_3 at low temperature (<200 °C). At 200 °C, the TiO_2 anataseappears follows the reaction from precursors of Ti^4+, F^-, NH^4+, and H_2O. At 400 °C NH_TiOF_3 is topotactically transformed into porousanatase TMCs with the dominant facets[35] as explained by the following equations (1-5)[36].

\[
\begin{align*}
Ti^4+ + 4F^- + NH^4+ + H_2O &\rightarrow NH_TiOF_3 
\end{align*}
\]

\[
\begin{align*}
NH_TiOF_3 + H_2O &\rightarrow TiO_2 \downarrow + NH_3 \uparrow + 2HF^- (<200°C) \quad (37)
\end{align*}
\]

\[
\begin{align*}
NH_TiOF_3 + HTiOF_3 &\rightarrow HN_3 \uparrow + 2HF^- (<200°C) \quad (38)
\end{align*}
\]

\[
\begin{align*}
2HTiOF_3 &\rightarrow 2TiO_2 \downarrow + 2HF \quad (300–400°C) \quad (39)
\end{align*}
\]

\[
\begin{align*}
TiO_2 + H_2O &\rightarrow TiO_2 \downarrow + 2HF \quad (400–500°C) \quad (40)
\end{align*}
\]

X-ray diffraction patterns show a mixture of anatase and brookite phases as in Fig. 1b. Where peaks of 2θ= 25.3, 48.05 are assigned for {101} and {200} facets of anatase phase [40], while peaks of 2θ= 30.7, 54.7, 63.9 are assigned for {121}, {230} and {521} facets of brookite [41]. Cobalt oxide (CoO) appeared at 2θ=36.2 and 37.4 for its {311} and {222} facets respectively [30]. Crystal size calculated by measuring FWHM by gaussian fitting of XRD peaks and substituting in Scherrer equation:

\[
L = \frac{0.9λ}{A \cosθ}
\]

Where λ is full width at half maximum (FWHM) in radian, L is crystallite size, λ is the wavelength of X-ray beam (0.154 nm), and θ is the incident angle for the peak center. Particle size HF_CoO and HF_CoO_K2S2O8 were calculated to be 7.8 nm.

From the Raman spectrum (Fig. 2), we can see clearly the characteristic E_g peak of brookite at 154 cm^-1 followed by E_g band at 204.17 cm^-1 for HF_CoO sample while at 203.3 cm^-1 for HF_CoO_K2S2O8 sample. Two B_1g modes B_1g at 393.3 cm^-1 and 505.5 cm^-1, respectively for HF_CoO sample, while B_1g peak is shifted to 388.13 cm^-1 in HF_CoO_K2S2O8. Finally, E_g peaks situated at 620.8 cm^-1 and 628.48 cm^-1 for HF_CoO_K2S2O8 and HF_CoO samples, respectively. The blue shift observed in E_g and E_g and the red shift in B_1g, B_2g and E_g modes can be explained due to crystal size going from larger to smaller sizes according to Ahmed et al. [34].

The SEM images for the undoped sample of TiO_2 MCs presents (Fig.1a) both semispherical and quasi-square shape TiO_2 of small size ranging from 50-200nm. Low and high-magnification SEM images of TiO_2-MCs were prepared with in situ doping of CoO and further treated by oxidizing agent, respectively show also both spherical and plate sheet shapes of large size between 2-3 µm. The high magnification of Fig. 3b confirms porous structure of tiny nanoparticles of size 15-20nm.

Figure 4 depicts the UV-Vis absorption spectrum of the doped TiO_2 mesocrystals and further treated with potassium persulfate. It is found that there is a decrease in the bandgap to reach 2.9eV. This bandgap narrowing can be related to the doing of Co oxide as well as the defect states that could be created by the mesocrystalinity of the particles.

Taking the bandgap narrowing and small crystalline subunit cells into consideration,
Fig. 1. XRD diffraction patterns for a) Samples prepared at RT (HF_RT), at 200oC (HF_200), and at 400oC (HF_400) b) TiO₂ MCs in situ doped with Co (HF_CoO) and treated with Oxidizing agent (K₂S₂O₈) at 400°C compared to the undoped and untreated one (HF_400).

Fig. 2. Raman spectra for both TiO₂MCs doped with CoO (HF_CoO) and treated with K₂S₂O₈ (HF_CoO_0.1M K₂S₂O₈).

Fig. 3. FE-SEM images for (a) HF_400 (b) HF_CoO_400 (inset HMSEM for the spherical particles) (c) HF_CoO_K₂S₂O₈_400 (inset is high magnification image).

we tested the mesocrystalline doped Co Oxide and treated with the oxidizing agent sample as photoanode in solar water splitting cells. Figure 5 shows higher performance toward the visible-light-driven photocatalytic water splitting, resulting in a photocurrent of 4.27 mA/cm$^2$, which is much higher than that obtained for the commercial Degussa P25. In addition, the sample showed more negative onset potential than P25, the light contribution toward the minimum potential needed for water splitting process to take place, which can highly lead to better charge kinetics and lower consumption of applied potential.

### Conclusions

TiO$_2$ mesocrystals were successfully prepared via a facile sol gel synthesis route. The size of the mesocrystals was found to be in the range of 2-3µm with 15-20nm subunit size. This superstructure doped with Co-Oxide and further treated with oxidizing agent to enhance the sample crystallinity shows mixture phases of anatase and brookite that was induced by the doping of metals (Co). In addition, the sample exhibits a band gap narrowing of 2.9 eV and a perfect performance in photoelectrochemical water splitting application with photocurrent of 4.2eV compared to its counterpart (P25).

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**Fig. 4.** Absorption spectrum of TiO$_2$MCs(HF$\_CoO\_K2S2O8$) (inset is Tauc plot).

**Fig. 5.** The photoelectrochemical characteristics in 1M KOH aqueous solutions under AM 1.5 illumination for HF$\_CoO\_K2S2O8$ and Degussa P25.
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References


الاداء الامثل لبلورات اكسيد التيتانيوم المتناهية الصغر لانتاج الوقود الشمسي

أيات حجازي
قسم الطاقة الشمسى - المركز القومي للبحوث - الجيزة - مصر.

أكسيد التيتانيوم هو واحد من أكثر المركبات وفرة في كوكبنا. و يعتبر ثاني اكسيد التيتانيوم مادة شبة موصلة حيث يتميز بأنه رخيص، غير سام، مستقر كيميائيا و حراريا. نتيجة لهذه المميزات فقد تم استخدام اكسي التيتانيوم بكثرة كقطب ضوئي للانتاجي، حيث يعتبر وقود غير تقليدي حيث يعد انتاجه على وقود مصدر طاقة متغير (الشمس). تظهر جسيمات ثاني اكسيد التيتانيوم النانومترية شفافية عالية للضوء المرئي، حسب اعتماد اتصال ضوئي عالي للثقوب فebile-second (الثقوب). و مع ذلك فإن نوى انتر متين في جسيمات التيتانيوم النانومترية ضروري من ارتفاع معدل الربط بين الإلكترونات و الفجوة. و تم معالجة هذه المشكلة بت testim بلورات اكسيد التيتانيوم بطريقة تجعل البلورات المكونة من جسيمات متانوية الصغر تعزز انتقال الضوء بشكل منتظم لدرجة عالية. في هذا البحث تم تحضير جزيئات اكسيد التيتانيوم الكروية بتخفيف الطوارئ و مثبتة بتوزيع ضيق للحجم من خلال التحكم في ظروف التحلل المائي خلال التحضير بطريقة المحلول الغرواني حيث يتم تحضير المحلول تدريجيا تكوين نظام ثمانية الطور يشبه الالواح بتكون كل من الطور السائل و المواد البلورية، تتراوح اشكالها من الجزيئات المنفصلة الي شبكات البوليمرات المستمرة. تم دراسة تدفق الهواء على البلورات و تأثير التشكل و توفيرو المحلول في الطوارئ التيتانيوم، و حبوب الانتشار السينتيمترية، و طيف رامان. كما اظهرت هذه البلورات شناط ضوئية انشطة الناتجة من تطورهم التجارية.

"ديجوسا"25 عند استخدامها في انتاج الوقود الشمسي.