Green synthesis of carbon quantum dots embedded onto titanium dioxide nanowires for enhancing photocurrent

Yin-Cheng Yen, Chia-Chi Lin, Ping-Yu Chen, Wen-Yin Ko, Tzu-Rung Tien and Kuan-Jiuh Lin

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Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History
RSOS-161051.R0 (Original submission)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Is it clear how to access all supporting data?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No
Recommendation?
Major revision is needed (please make suggestions in comments)

Comments to the Author(s)
Lin et al reported a simple electrochemical way to prepare carbon QDs and the application in building a carbon QDs/TiO2 hybrids photoelectrode for water oxidation. It was observed that the anodic photocurrent was evidently enhanced in comparison with that without carbon dots, which showed the importance of carbon dots in the effective separation of excited charger-carriers in the light irradiation. In general, the results are technique sound and supported by the experimental along with proper discussions. However, to improve the quality of the manuscript, I would like to recommend its publication in Royal Society Open Science with a major revision as listed as follows:

(1) The experimental details of how to deposit carbon QDs on TiO2 nanowires should be given. Moreover, it is better to show a scheme to make the presentation more vivid.
(2) The HRTEM image of carbon QDs is of low quality. It is difficult to see any dots of uniform distribution. Moreover, the crystallinity of carbon QDs is interesting, for instance, the graphitic lattice was observed in the HRTEM images?
(3) It is suggested to compare the proposed technique with previous electrochemical way (e.g. ref. 7: Angewandte Chemie International Edition. 2010, 49, 4430) to prepare carbon QDs. How about the stability and PL quantum yield?
(4) 0 V vs. AgAgCl in a three electrode system does not mean the absolute biased potential between working electrode and counter electrode in practical applications is zero. Thus, it is suggested to show the influence of the biased potential on the photocurrent via a LSV curve under a chopped light (cf. Lou et al., ACS Appl. Mater. Interfaces 2016, 8, 22287) along with proper discussion of the results.
(5) To given readers a more comprehensive research background, the progress of preparation of carbon dots, including the surface passivation and doping (e.g. Zhou et al., ACS Nano 2015, 9, 12480) should be included in the introduction.

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Is it clear how to access all supporting data?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Major revision is needed (please make suggestions in comments)
Comments to the Author(s)
The authors reported the development of carbon quantum dots-decorated TiO2 nanowires for water photooxidation. The work is interesting and I believe that it will receive wide readerships especially in the field of photocatalysis, energy and materials science. This work could be considered for the publication in Royal Society Open Science after appropriate revisions from the authors to further improve the quality of the manuscript. Specific comments are shown below:

1. I would suggest the authors to make modification to the present title. It should be “titanium dioxide” instead of “titanium”, since both show different meanings.

2. There is a lack of recent important works on the carbon dots provided in the introduction. More emphasis on the recent works should be paid.

(2) Nano Research, 2015, 8 (2), 355–381

3. The authors should introduce TiO2 as the semiconductor photocatalysts in the introduction. Relevant important works on TiO2 should be given merits for wider readerships.

(1) Nanoscale, 2014, 6 (4), 1946-2008
(2) Nanotechnology, 2016, 27, 435405
(4) Nanotechnology, 2017, 28 084002
(5) Nano Research, 2014, 7 (10), 1528-1547
(6) Nanoscale, 2013, 5, 3601-3614

4. FTIR spectra of carbon quantum dots (CQDs) and the CQD/TiO2 hybrid should be provided in the revised manuscript.

5. XPS analysis for the studied samples (CQD and CQD/TiO2) should be conducted for examining the chemical status and environment of each element, i.e. C, O, and Ti.

6. I would suggest the authors to provide the HRTEM image of CQD/TiO2 to show the lattice spacing of both CQD and TiO2 to prove the formation of heterojunction structure in the nanocomposite.

7. The authors have performed the EIS Nyquist plot analysis. Fitting to the EIS Nyquist plots is essential. A table summarizing the resistivity value of each element should be provided. Please provide the discussion on this section.

8. Based on the transient photocurrent analysis, the photocurrent of CQD/TiO2 was greater than that of TiO2 nanowires. I would suggest the authors to perform steady state PL analysis to study the charge carrier trapping and recombination process.

9. Since the manuscript title mentions the photooxidation of H2O, the evolution rate of O2 should be studied and determined for both TiO2 nanowires and CQD/TiO2 samples. This piece of information should be included in the revised manuscript.

After taking into account all the aforementioned comments, this work could be considered for the publication in Royal Society Open Science.

Decision letter (RSOS-161051)

08-Feb-2017

Dear Professor Lin,

Title: Green synthesis of carbon quantum dots embedded onto titanium nanowires for photo-driven water oxidation
Manuscript ID: RSOS-161051
Thank you for your submission to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The editor assigned to your manuscript has now received comments from reviewers. We would like you to revise your paper in accordance with the referee and Subject Editor suggestions which can be found below (not including confidential reports to the Editor). Please note this decision does not guarantee eventual acceptance.

Please submit your revised paper within three weeks (i.e. by the 03-Mar-2017). If we do not hear from you within this time then it will be assumed that the paper has been withdrawn. In exceptional circumstances, extensions may be possible if agreed with the Editorial Office in advance. We do not allow multiple rounds of revision so we urge you to make every effort to fully address all of the comments at this stage. If deemed necessary by the Editors, your manuscript will be sent back to one or more of the original reviewers for assessment. If the original reviewers are not available we may invite new reviewers.

To revise your manuscript, log into http://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under "Manuscripts with Decisions." Under "Actions," click on "Create a Revision." Your manuscript number has been appended to denote a revision. Revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you must respond to the comments made by the referees and upload a file "Response to Referees" in "Section 6 - File Upload". Please use this to document how you have responded to the comments, and the adjustments you have made. In order to expedite the processing of the revised manuscript, please be as specific as possible in your response.

Once again, thank you for submitting your manuscript to Royal Society Open Science and I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Yours sincerely,
Dr Siobhán Hackett
Publishing Editor
Royal Society of Chemistry
Email: chemistryopenscience@rsc.org
Tel: +44 (0) 1223 432114

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Professor Hisanori Shinohara.

******************************************************************************

RSC Subject Editor: Professor Anthony Stace

Comments to the Author:
Although the decision for the paper is "Accept with minor revision", you will see that both referees recommended that quite major revision is required in order to make the paper acceptable for publication. In particular, there are extensive suggestions regarding the provision of more detail on the experiments and/or additional experiments that may be required. Both authors have also highlighted background material that may help with the interpretation of results. Please provide a covering letter detailing all of the changes that are made to the paper in response to the referees comments.
RSC Associate Editor: Professor Hisanori Shinohara
Comments to the Author:
Two reviewers recommended major revisions of the present manuscript and I agree with their comments. The manuscript could be accepted after the major revisions according to the reviewers' comments.

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Reviewers' Comments to Author:
Reviewer: 1

Comments to the Author(s)
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(5) To given readers a more comprehensive research background, the progress of preparation of carbon dots, including the surface passivation and doping (e.g. Zhou et al., ACS Nano 2015, 9, 12480) should be included in the introduction.

Reviewer: 2

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(2) Nano Research, 2015, 8 (2), 355–381
3. The authors should introduce TiO2 as the semiconductor photocatalysts in the introduction. Relevant important works on TiO2 should be given merits for wider readerships.

4. FTIR spectra of carbon quantum dots (CQDs) and the CQD/TiO2 hybrid should be provided in the revised manuscript.

5. XPS analysis for the studied samples (CQD and CQD/TiO2) should be conducted for examining the chemical status and environment of each element, i.e. C, O, and Ti.

6. I would suggest the authors to provide the HRTEM image of CQD/TiO2 to show the lattice spacing of both CQD and TiO2 to prove the formation of heterojunction structure in the nanocomposite.

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After taking into account all the aforementioned comments, this work could be considered for the publication in Royal Society Open Science.

Author's Response to Decision Letter for (RSOS-161051)

See Appendix A.

Decision letter (RSOS-161051.R1)

11-Apr-2017

Dear Professor Lin:

Title: Green Synthesis of Carbon Quantum Dots Embedded onto Titanium Dioxide Nanowires for Enhancing Photocurrent

Manuscript ID: RSOS-161051.R1
It is a pleasure to accept your manuscript in its current form for publication in Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The comments of the reviewer(s) who reviewed your manuscript are included at the end of this email.

Thank you for your fine contribution. On behalf of the Editors of Royal Society Open Science and the Royal Society of Chemistry, I look forward to your continued contributions to the Journal.

Yours sincerely,

On behalf of the Subject Editor Dr Anthony Stace and the Associate Editor Professor Hisanori Shinohara.

*******

RSC Associate Editor
Comments to the Author:
(There are no comments.)

*******
Dear editor and reviewers:

Thank you for your decision letter on Feb. 08, 2017 concerning the manuscript of RSOS-161051. The manuscript has been revised according to the all of comments. The major corrections are as follows:

Reviewer: 1

(1) The experimental details of how to deposit carbon QDs on TiO$_2$ nanowires should be given. Moreover, it is better to show a scheme to make the presentation more vivid.
→ The experimental details of fabrication of CQDs/TiO$_2$ NW was added in manuscript (the description is on page 3, line 28—31). Furthermore, a scheme of the three electrode system for preparation of CQDs/TiO$_2$ NW was provided in supporting information, figure S1, please go through it.

(2) The HRTEM image of carbon QDs is of low quality. It is difficult to see any dots of uniform distribution. Moreover, the crystallinity of carbon QDs is interesting, for instance, the graphitic lattice was observed in the HRTEM images?
→ The resolution of TEM image was adjusted to 300 dpi* 300dpi and 300 ppi* 300 ppi by Photoshop. From HRTEM images, as shown in figure 1d and 1e, the size distribution of CQDs is from 0.5-4 nm and it presents the average lattice spacing of CQDs as 0.323 nm, corresponding to (002) planes of graphite.

![Figure 1. (d) and (e) HRTEM images of CQDs.](image-url)
(3) It is suggested to compare the proposed technique with previous electrochemical way (e.g. ref. 7: Angewandte Chemie International Edition. 2010, 49, 4430) to prepare carbon QDs. How about the stability and PL quantum yield? (Reminder: ref. 7 in previous manuscript is the ref. 31 in new one.)

→ In this manuscript, the significantly different between this work and previous report is the usage of ultra-pure water as electrolyte. It does not need chemicals (strong acid or base, solvents), surface passive agents and post-treatment (the detail description is on page 2, line 26—34). The luminescence properties and appearance of as-prepared CQDs solution remains unchanged after storing for 10 month in air at room temperature (figure S2). Therefore, it exhibits good stability. Usually, the quantum yield of CQDs is related lower than semiconductor QDs. Therefore, we do not further investigate PL quantum yield of CQD solution.

Figure S2. PL spectra of CQD solution on 2016.06 and 2017.03.
(4) 0 V vs. AgAgCl in a three electrode system does not mean the absolute biased potential between working electrode and counter electrode in practical applications is zero. Thus, it is suggested to show the influence of the biased potential on the photocurrent via a LSV curve under a chopped light (cf. Lou et al., ACS Appl. Mater. Interfaces 2016, 8, 22287) along with proper discussion of the results. 

→ Sorry about the description of parameters for measuring is not clear and definite. Actually, the LSV curve and I-t curve were measured in every experiment. The 0V vs. AgAgCl was a voltage which was select for comparing photocurrent. It does not mean that the experiment was perform on absolute biased potential is zero. Both LSV curve and I-t curve were provide with proper discussion in revised manuscript.

Measurements of linear sweep voltammogram (LSV) and photocurrent density versus elapsed time ($I-t$) of CQDs/TiO$_2$ NW and as-prepared TiO$_2$ NW devices were carried out under AM 1.5G sunlight illumination, as shown in figure 5a and 5b. It is important to note that a photocurrent density of 160 μA/cm$^2$ at 0 V vs.Ag/AgCl for CQDs/TiO$_2$ NW was remarkably obtained and a net enhancement ratio of 6.4 was achieved as compared with as-prepared TiO$_2$ electrode (25 μA/cm$^2$). From figure 5b, both of two photoanode devices represented a good reproducibility and stability as the illumination was continually turned on and off. Furthermore, the sharp spike in the photocurrent during the on/off illumination cycles demonstrates the predominant transport of photo generated electron in the CQDs/TiO$_2$ NW.

Figure 5. (a) LSV curve and (b) $I-t$ curve of TiO$_2$ NW and CQDs/TiO$_2$ NW under AM 1.5G sunlight illumination.

(5) To given readers a more comprehensive research background, the progress of preparation of carbon dots, including the surface passivation and doping (e.g. Zhou et al., ACS Nano 2015, 9, 12480) should be included in the introduction.

→ Thank you for your suggestion. The progress of preparation of carbon dots were described in the introduction, please go through it. (the description is on page 2, line
Reviewer: 2

1. I would suggest the authors to make modification to the present title. It should be “titanium dioxide” instead of “titanium”, since both show different meanings. → Thank you for your reminder. We’ve modified it.

2. There is a lack of recent important works on the carbon dots provided in the introduction. More emphasis on the recent works should be paid.
   (2) Nano Research, 2015, 8 (2), 355–381
   → Thank you for your suggestion. The introduction was revised as your suggestion and the references were cite in manuscript, please go through it.

3. The authors should introduce TiO$_2$ as the semiconductor photocatalysts in the introduction. Relevant important works on TiO$_2$ should be given merits for wider readerships.
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   (6) Nanoscale, 2013, 5, 3601-3614
   → Thank you for your suggestion. The introduction was revised as your suggestion and the references were cite in manuscript, please go through it.

4. FTIR spectra of carbon quantum dots (CQDs) and the CQD/TiO$_2$ hybrid should be provided in the revised manuscript.
   → FTIR spectra was record by FTIR spectrometer (BRUKER/Vertex 70V). Few drops of CQD solution were dried on FTO for measuring FTIR spectra. However, it is difficult to obtain observable signal of CQDs which may due to technical problem or sample preparation.
Instead of CQD’s sample, the FTIR spectra of TiO$_2$ NW and CQDs/TiO$_2$ NW were received as shown in figure 3c. As shown in figure 3c, the peak for Ti-O-Ti and Ti-O was present in the range of 600-800 and 1024 cm$^{-1}$, respectively. The characteristic transmittance peaks of the CQD/TiO$_2$ at 1648 cm$^{-1}$ associated with the C=O stretching vibration, indicate the existence of CQDs in the composites. Moreover, the broad peak at 3369 cm$^{-1}$ was attributed to vibrations of surface adsorbed water.

**Figure 3.** (c) FTIR spectra of TiO$_2$ NW and CQDs/TiO$_2$ NW.
5. XPS analysis for the studied samples (CQD and CQD/TiO$_2$) should be conducted for examining the chemical status and environment of each element, i.e. C, O, and Ti. XPS of CQD/TiO$_2$ was conducted by ULVAC-PHI, PHI 5000 VersaProbe/Scanning ESCA Microprobe. Fitting of the XPS data was accomplished using XPSPEAK41 software. XPS was carried out to investigate the components and surface properties of CQD/TiO$_2$ composite which show in figure 4. The full survey spectrum of figure 4a indicates the presence of titanium (Ti 2p), carbon (C 1s), and oxygen (O 1s) in the CQD/TiO$_2$ composites. The Ti 2p spectra were deconvoluted and resolved into four spin orbit components at 2p3/2 binding energies 457.6, 458.14 eV and their corresponding 2p1/2 components (463.21, 464.0 eV) which are assigned as Ti$^{3+}$ (TiOOH/ coordinatively unsaturated) and Ti$^{4+}$ (TiO$_2$), respectively. The large ratio of Ti$^{3+}$ suggested due to the increase electron content of lattice surface of TiO$_2$ within the voltage-driven reduction process. The peaks at 284.24, 285.44 and 287.99 eV for C 1s spectrum are ascribed to C–C bond with sp$^2$ orbital, C–O and C=O bonds, respectively. The main peak of O 1s spectrum at 529.06, 530.49 and 531.49 eV is attributed to Ti=O, C=O and C–OH, respectively.

6. I would suggest the authors to provide the HRTEM image of CQD/TiO$_2$ to show the lattice spacing of both CQD and TiO$_2$ to prove the formation of heterojunction.
structure in the nanocomposite.

It was observed that TiO$_2$ NWs have a diameter of 30 nm and the dark dots in the TEM image represent the CQDs. Moreover, the distance between the adjacent lattice fringes is 0.325 nm and 0.223 nm, which can be assigned to the interplane distance of the rutile TiO$_2$ (110) plane and (101) planes of graphite (JCPDS card: No 65-6212) (figure S3).

![HRTEM images of CQDs/TiO$_2$ NW.](image)

Figure S3. HRTEM images of CQDs/TiO$_2$ NW.

7. The authors have performed the EIS Nyquist plot analysis. Fitting to the EIS Nyquist plots is essential. A table summarizing the resistivity value of each element should be provided. Please provide the discussion on this section.

→ EIS spectra show that both of photoanodes revealed an obviously semicircle of Nyquist plot at the high frequencies and a Warburg type line at low frequencies under illumination. The equivalent circuit modes applied to fit the experimental EIS data of the as-prepared TiO$_2$ NW and CQD/TiO$_2$ composite electrode was shown in the inset of figure 5c. The fitting results of all parameters of the equivalent circuit were listed in Table 1. It should be noted that a larger charge transfer resistance (Rct) for TiO$_2$ electrode (520.6 Ω) was observed as compared with that of the CQD/TiO$_2$ electrode.
(337.9 Ω). In addition, the Warburg resistance for CQD/TiO$_2$ electrode (1273 Ω) is apparent smaller than that of TiO$_2$ electrode (4921 Ω). This illustrated that better electronic and ionic conduction of CQD/TiO$_2$ which is attributed to the decomposing of toxic H$_2$O$_2$ on the photo anode.

Figure 5. (c) Nyquist plot of TiO$_2$ NW and CQDs/TiO$_2$ NW under AM 1.5G sunlight illumination.

Table 1. EIS fitting parameters of as prepared TiO$_2$ NW and CQDs/TiO$_2$ NW.

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameters</th>
<th>TiO$_2$ NW</th>
<th>CQDs/TiO$_2$ NW</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic series resistance</td>
<td>Rs</td>
<td>216.9</td>
<td>304.9</td>
<td>Ω</td>
</tr>
<tr>
<td>Charge transfer resistance at electrode/electrolyte interface</td>
<td>Ret</td>
<td>520.6</td>
<td>337.9</td>
<td>Ω</td>
</tr>
<tr>
<td>CPE for capacitance of electrode</td>
<td>CPE</td>
<td>1.89 × 10$^{-5}$</td>
<td>1.90 × 10$^{-6}$</td>
<td>F$^{sp^{-1}}$</td>
</tr>
<tr>
<td>Warburg impedance</td>
<td>Rw</td>
<td>4921</td>
<td>1273</td>
<td>Ω</td>
</tr>
</tbody>
</table>

8. Based on the transient photocurrent analysis, the photocurrent of CQD/TiO$_2$ was greater than that of TiO$_2$ nanowires. I would suggest the authors to perform steady state PL analysis to study the charge carrier trapping and recombination process.

→ Thank you for your suggestion. It will be an interested study for giving kinetic information of CQDs/TiO$_2$ NW. However, we lack the experimental instrument to carry out the measurement. Instead of steady state PL analysis, EIS analysis was respect to investigate charge/electron transport properties.

9. Since the manuscript title mentions the photooxidation of H$_2$O, the evolution rate of
O₂ should be studied and determined for both TiO₂ nanowires and CQD/TiO₂ samples. This piece of information should be included in the revised manuscript.

→ The evolution rate of H₂/O₂ is one of data that we hope to measure in this research. But, we lack equipment to carry out. Therefore, we are still looking for cooperation to do it in this moment. We think the title of origin one is not appropriate due to we can’t provide the information of photo oxidation of water. So, the title was revised into “Green Synthesis of Carbon Quantum Dots Embedded onto Titanium Dioxide Nanowires for Enhancing Photocurrent”.