

Electronic Supplementary Information for

Chitosan-*grafted*-poly(aniline-*co*-anthranilic acid) as a water  
soluble binder to form 3D structures for Si anodes

Eunsoo Kim,<sup>a,b†</sup> Rajeev K.K.,<sup>a,b†</sup> Jaebin Nam,<sup>a,b</sup> Junyoung Mun,<sup>c</sup> and Tae-Hyun Kim<sup>a,b\*</sup>

<sup>a</sup>Organic Material Synthesis Lab. Department of Chemistry, Incheon National University, 119  
Academy-ro, Songdo-dong, Yeonsu-gu, Incheon 22012, Korea.

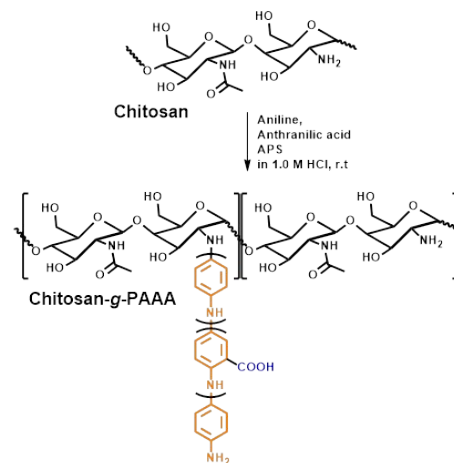
<sup>b</sup>Research Institute of Basic Sciences, Incheon National University.

<sup>c</sup>Department of Energy and Chemical Engineering, Incheon National University.

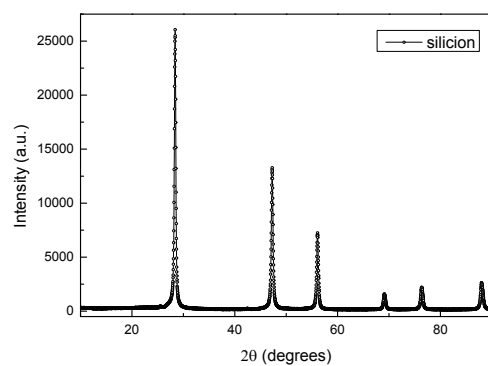
† These authors contributed equally to this work.

**Corresponding Author**

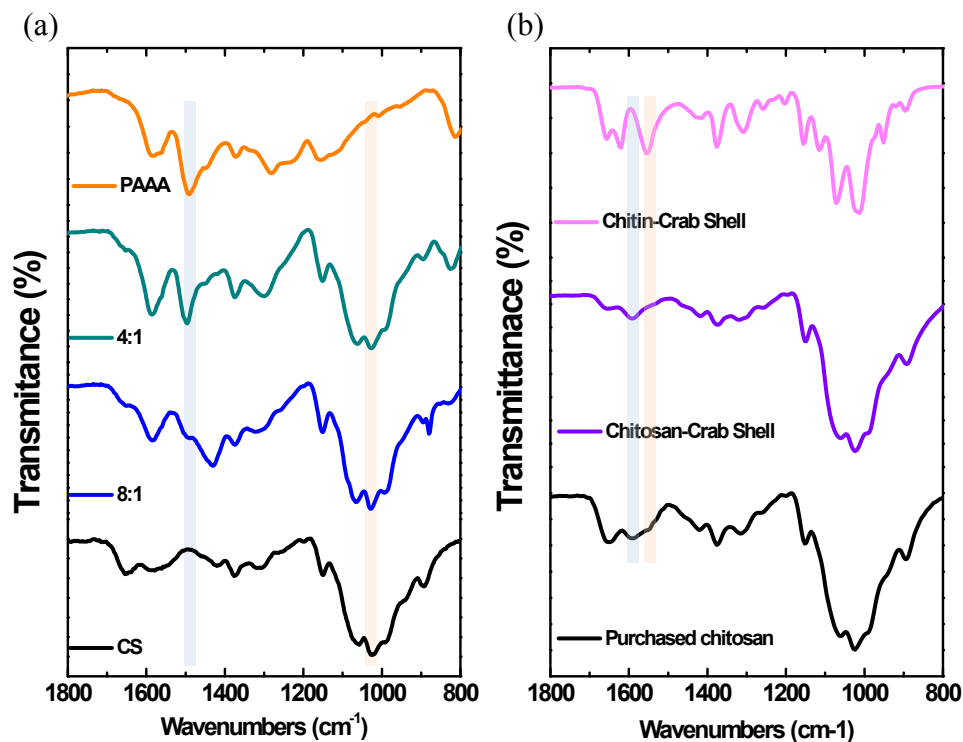
\*Tel: +82-32-835-8232; Fax: +82-32-835-0762; E-mail: [tkim@inu.ac.kr](mailto:tkim@inu.ac.kr) (T.-H. Kim)



**Scheme S1.** Synthetic procedure for the chitosan-*grafted*-PAAA (CS-*g*-PAAA).



**Figure S1.** XRD pattern of silicon powder used.



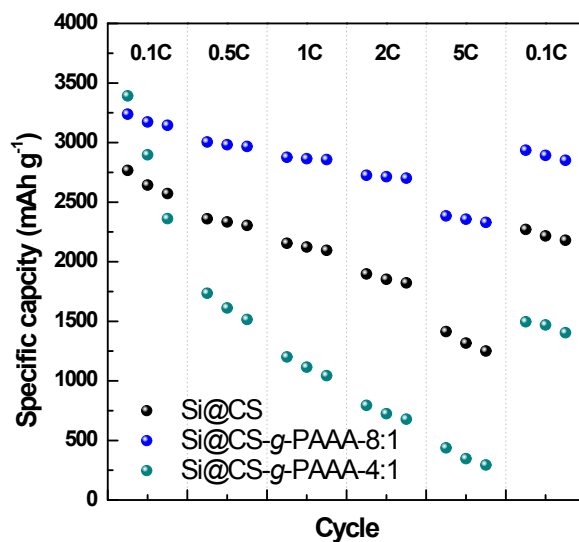
**Figure S2.** IR spectra of (a) CS (black line), CS-g-PAAA-8:1 (blue line), CS-g-PAAA-4:1 (dark cyan line) series and PAAA (orange line) and (b) commercially available CS (black line), CS from crab shell (violet line) and chitin extracted from crab shell (pink line).

**Table S1.** Main peaks of the IR spectra of CS, CS-g-PAAA and PAAA.

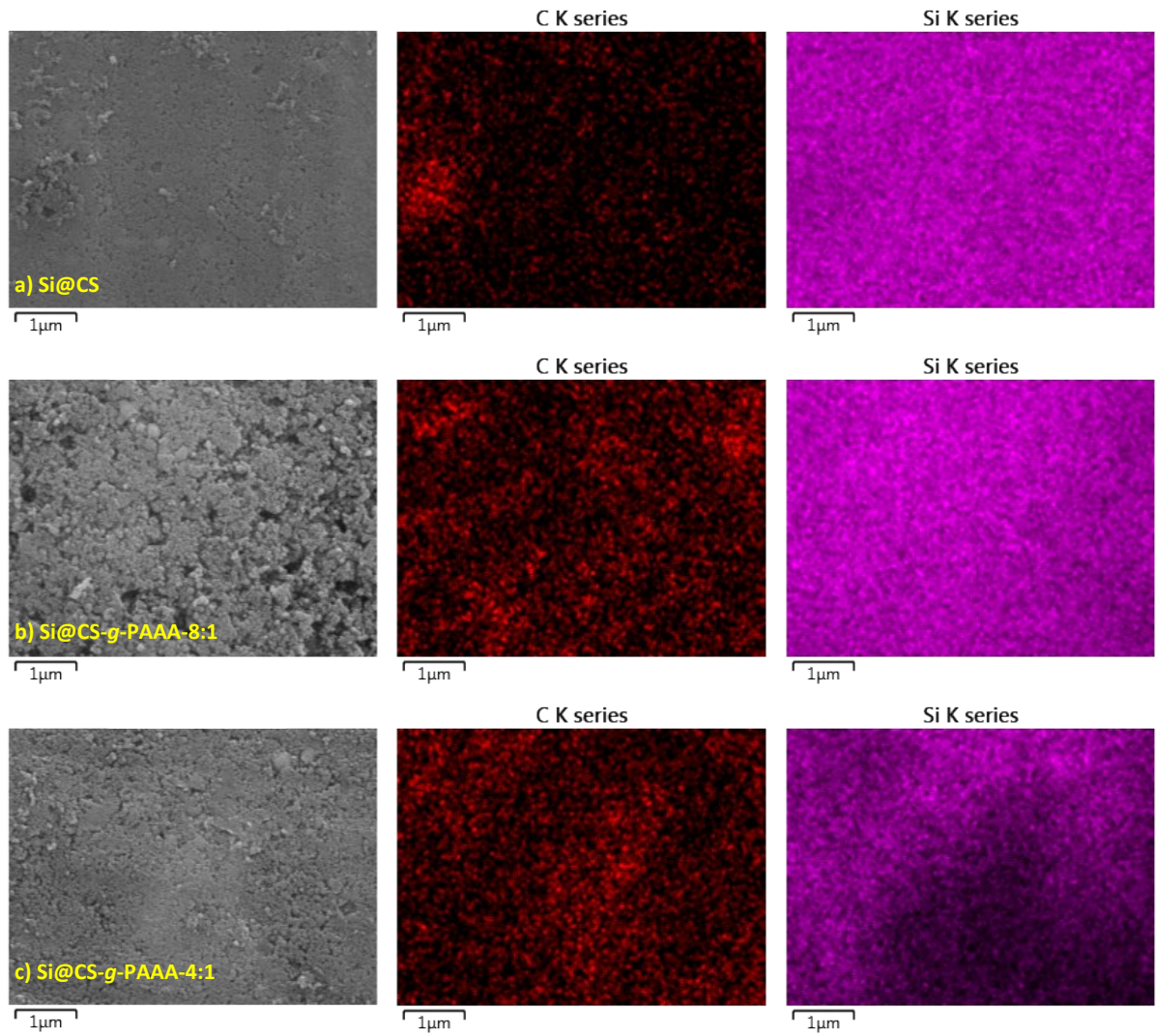
Assignment	Wavenumber (cm <sup>-1</sup> )		
	Chitosan	CS-g-PAAA	PAAA
Amide C=O stretch	1654	1652	-
Amide N-H bend	1592	1584-1600	-
Quinoid C=C stretch	-	1492-1506	1584
Benzenoid C=C stretch	-	1140-1150	1492
Glycosidic C-O-C stretch	1150	-	-
Aromatic C-H in-plane bend	-	1140	1140
Carbonyl C-O stretch	1058, 1026	1058, 1026	-

**Table S2.** TGA data (remaining mass % and degradation %) of PAAA and CS-g-PAAA series and HCl treated chitosan.

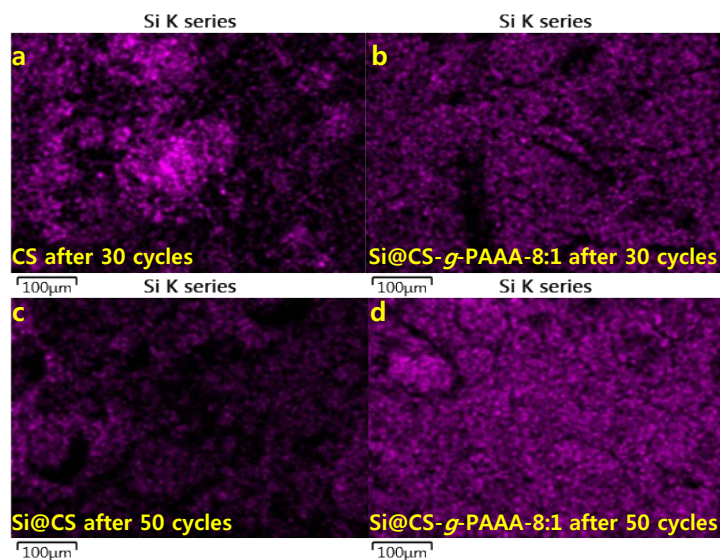
Binder	Remaining mass %			180 °C - 320 °C Degradation%
	180 °C	320 °C	700°C	
PAAA	97.21	90.13	44.67	7.283
CS-g-PAAA-4:1	92.85	56.97	36.35	35.41
CS-g-PAAA-8:1	92.54	51.78	34.45	44.05
HCl treated CS	90.10	46.75	28.05	48.11



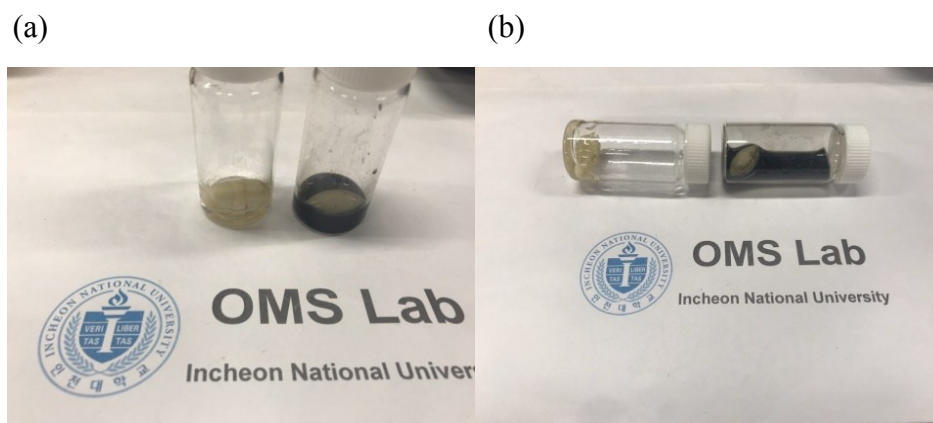
**Figure S3.** Rate capabilities of Si@CS, Si@CS-g-PAAA-8:1 and Si@CS-g-PAAA-4:1 electrodes at current densities varying between 0.1 C and 5 C.



**Figure S4.** SEM-EDS mapping images of (a) Si@CS, (b) Si@CS-g-PAAA-8:1 and (c) Si@CS-g-PAAA-4:1 electrodes.



**Figure S5.** SEM-EDS mapping images of (a) Si@CS and (b) Si@CS-g-PAAA-8:1 after 30 cycles; (c) Si@CS and (d) Si@CS-g-PAAA-8:1 after 50 cycles.



**Figure S6.** Solubility test results for (a) CS (left) and CS-g-PAAA 8:1 (right) binders in 1 M CH<sub>3</sub>COOH before tilting and (b) after tilting. After tilting the parent solids sticking to the vial are visible.

**Table S3.** Comparison of the electrochemical performance for the Si electrodes fabricated by our novel binders with other representative binders.

Binder	Electrode mass loading	Current density	Electrode performance	Ref.
<b>CS-g-PAAA-8:1</b>	<b>0.67 mg cm<sup>-2</sup></b>	<b>2.1 A g<sup>-1</sup></b>	<b>1546 mAh g<sup>-1</sup> @ 100<sup>th</sup> cycle</b> <b>1301 mAh g<sup>-1</sup> @ 300<sup>th</sup> cycle</b>	<b>This work</b>
PDA-PAA-PEO	0.4 mg cm <sup>-2</sup>	2.1 A g <sup>-1</sup>	1597 mAh g <sup>-1</sup> @ 200 <sup>th</sup> cycle	1
Na-CMC	unknown	2.1 A g <sup>-1</sup>	1000 mAh g <sup>-1</sup> @ 100 <sup>th</sup> cycle	2
PAA-PEGPBI	1.0~1.3 mg cm <sup>-2</sup>	2.1 A g <sup>-1</sup>	1221 mAh g <sup>-1</sup> @ 50 <sup>th</sup> cycle.	3
PVA-PEI	3~4.5 mg cm <sup>-2</sup>	1 A g <sup>-1</sup>	1063 mAh g <sup>-1</sup> @ 300 <sup>th</sup> cycle	4
PVTES-NaPAA	0.5 mg cm <sup>-2</sup>	840 mA g <sup>-1</sup>	2077 mAh g <sup>-1</sup> @ 100 <sup>th</sup> cycle	5
NaPAA-g-CMC	0.45 mg cm <sup>-2</sup> for Si	840 mA g <sup>-1</sup>	1816 mAh g <sup>-1</sup> @ 100 <sup>th</sup> cycle	6
PAL-NaPAA	0.7 mg cm <sup>-2</sup>	840 mA g <sup>-1</sup>	1914 mAh g <sup>-1</sup> @ 100 <sup>th</sup> cycle	7
CS-CG+GA	0.4 mg cm <sup>-2</sup>	420 mAh g <sup>-1</sup>	2345 mAh g <sup>-1</sup> @ 100 <sup>th</sup> cycle	8
PAA/PANI IPN	1 mg cm <sup>-2</sup>	420 mAh g <sup>-1</sup>	2205 mAh g <sup>-1</sup> @ 300 <sup>th</sup> cycle	9
PEDOT:PSS/CMC	~1mg cm <sup>-2</sup> for Si	420 mAh g <sup>-1</sup>	1834 mAh g <sup>-1</sup> @ 100 <sup>th</sup> cycle	10
PVA-g-PAA	0.5-0.6 mg cm <sup>-2</sup>	400mAh	1315 mAh g <sup>-1</sup> @ 1000 <sup>th</sup> cycle	11
PEEM	0.2 mg cm <sup>-2</sup> for Si	375 mA g <sup>-1</sup>	3000 mAh g <sup>-1</sup> @ 50 <sup>th</sup> cycle	12
PPQ	0.8 mg cm <sup>-2</sup>	358 mA g <sup>-1</sup>	2826 mAh g <sup>-1</sup> @ 50 <sup>th</sup> cycle	13
PANi	0.3~0.4 mg cm <sup>-2</sup>	300 mA g <sup>-1</sup>	2100 mAh g <sup>-1</sup> @ 70 <sup>th</sup> cycle	14

## References

- 1 L. Lü, H. Lou, Y. Xiao, G. Zhang, C. Wang and Y. Deng, *RSC Adv.*, 2018, **8**, 4604-4609.
- 2 N. Ding, J. Xu, Y. Yao, G. Wegner, I. Lieberwirth and C. Chen, *J. Power Sources*, 2009, **192**, 644-651.
- 3 S. Lim, K. Lee, I. Shin, A. Tron, J. Mun, T. Yim and T. H. Kim, *J. Power Sources*, 2017, **360**, 585-592.
- 4 Z. Liu, S. Han, C. Xu, Y. Luo, N. Peng, C. Qin, M. Zhou, W. Wang, L. Chen and S. Okada, *RSC Adv.*, 2016, **6**, 68371-68378.
- 5 L. Wei, C. Chen, Z. Hou and H. Wei, *Sci. Rep.*, 2016, **6**, 1-8.

- 6 C. Luo, L. Du, W. Wu, H. Xu, G. Zhang, S. Li, C. Wang, Z. Lu and Y Deng, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12621-12629.
- 7 X. Zeng, Y. Shi, Y. Zhang, R. Tang and L. Wei, *RSC Adv.*, 2018, **8**, 29230-29236.
- 8 X. Yu, H. Yang, H. Meng, Y. Sun, J. Zheng, D. Ma and X. Xu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 15961-15967.
- 9 D. Shao, H. Zhong and L. Zhang, *ChemElectroChem*, 2014, **1**, 1679-1687.
- 10 P-F. Cao, G. Yang, B. Li, Y. Zhang, S. Zhao, S. Zhang, A. Erwin, Z. Zhang, A. P. Sokolov, J. Nanda and T. Saito, *ACS Energy Lett.*, 2019, **4**, 1171-1180.
- 11 J. He and L. Zhang, *J. Alloys Compd.*, 2018, **763**, 228-240.
- 12 M. Wu, X. Xiao, N. Vukmirovic, S. Xun, P. K. Das, X. Song, P. Olalde-Velasco, D. Wang, A. Z. Weber, L. W. Wang, V. S. Battaglia, W. Yang and G. Liu, *J. Am. Chem. Soc.*, 2013, **135**, 12048-12056.
- 13 S. M. Kim, M. H. Kim, S. Y. Choi, J. G. Lee, J. Jang, J. B. Lee, J. H. Ryu, S. S. Hwang, J. H. Park, K. Shin, Y. G. Kim and S. M. Oh, *Energy Environ. Sci.*, 2015, **8**, 1538-1543.
- 14 H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nat. Commun.*, 2013, **4**, 1943-1946.