Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Enzymatic-Reaction Induced Production of Polydopamine Nanoparticles for Sensitive and Visual Sensing of Urea

Nan Li, [a] Hai-Bo Wang, [a] Larissa Thia, [a,b] Jing-Yuan Wang, [b] Xin Wang*[a]

[a] School of chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, 637459, Singapore.

[b] Nanyang Environment & Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, #06-08 CleanTech One, 637141, Singapore

* Corresponding author. Tel: +65 6316 8866. Fax: +65 67947553. E-mail: WangXin@ntu.edu.sg

Figures and Tables

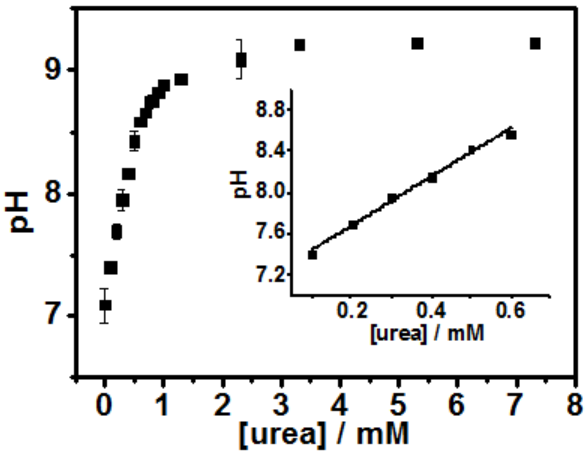

Figure S1 The pH change of urease-catalyzed hydrolysis of urea in Di-water with different concentration of urea from 0.1 to 7.3 mM at a fixed urease concentration of 0.3 mg mL^{-1}. Inset: The linear increase of pH in term of urea concentration.

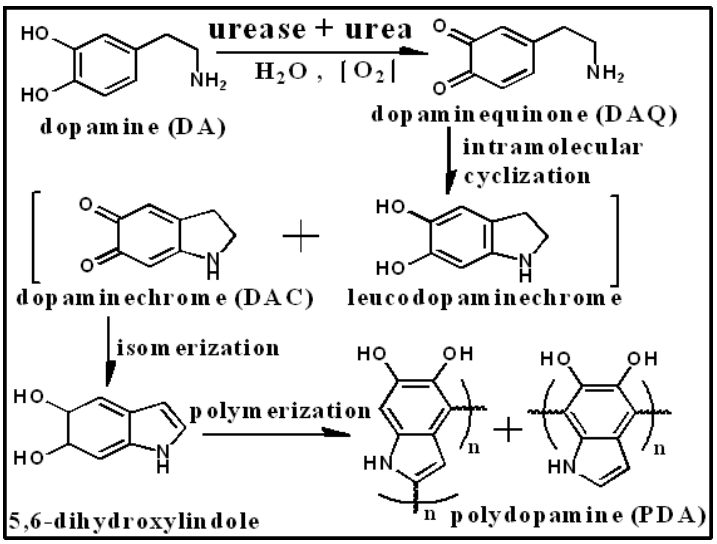

Figure S2 The proposed pathway for DA polymerization induced by urease/urea enzymatic reaction.

The urease catalytic-reaction triggered generation of PDA CNPs may occur in the following manner: (i) oxidation of the catechol group of dopamine into quinone; (ii) fast reaction of semi-quinone to dopaminequinone (DAQ); (iii) the intramolecular cyclization of DAQ leading to the more readily oxidizable dopaminochrome (DAC); (iv) isomerization of DAC to yield 5, 6 - dihydroxyindole for further polymerization and the self-assembly of small oligomers to PDA CPNs.

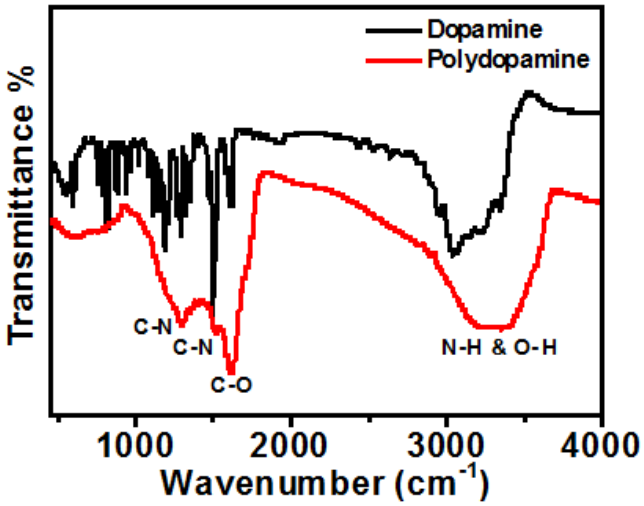

Figure S3 FTIR spectra (KBr) of DA (black, top) and PDA (red, bottom).

The large, broad band from 3200 — 3500 cm^{-1} is attributed to the stretching vibrations (O–H and N–H) of the carboxylic acid, phenolic and aromatic amino functions, as well as hydroxyl structures and water.[1]

Table S1 Comparison of performance of different methods (the data are taken from the previous reports).

Method	Principle	Linear range (M)	Detection limit (μM)	Comments	Reference
Colorimetry	PDAB as chromogenic reagent	$1.7 – 5 \times 10^{-4}$	—	low cost but low sensitivity,	Chin. J. Anal. Lab 2009, 313-315
IUE	Immobilization of urease in PPy film for amperometric sensor	$1 – 3 \times 10^{-4}$	—	responded rapidly, require of robust enzyme entrapment	Reactive Functional Polymers, 2012, 148-152.
ISE	Cover ITO electrode by $NH4^+$ selective membrane	1.3×10^{-6} to 3×10^{-2}	—	good voltage response and complex fabrication	Sensors and Actuators B, 2008, 359-366
IC	Combination of immobilized urease reaction with IC analysis	1.3×10^{-5} to 4.17×10^{-4}	3.3	good selectivity, stability, but low sensitivity	Analytical Science, 2010, 847-851
FLA	Application of urease column for fluorimetric FIA	1.0×10^{-6} to 1.0×10^{-4}	—	automatic and convenient, but complicated	Talanta, 2004, 1278-1282
PL	Detection of PL intensity of CdSe/ZnS QD	1.0×10^{-5} to 0.1	10	good sensitivity, hazardous indicator	Biosensors and Bioelectronics, 2007, 1835-1838
RS	Enhancement of RS intensity of NH_4-TPB by urea decomposition	1.25×10^{-7} to 1.5×10^{-5}	0.058	good selectivity and sensitivity	Bioprocess Biosystems Engineering, 2011, 639-645
PDA	DA polymerization induced by urease catalyzed urea hydrolysis	1.0×10^{-7} to 1.0×10^{-3}	0.1	Sensitivity, easy visualization, and no sensor fabrication	This assay

PDAB *p*-dimethylaminobenzaldehyde, *IUE* immobilized urease electrode, *PPy* Polypyrrole, *ISE* ion selective electrode, *ITO* indium tin oxide, *IC* ion chromatograph, *FIA* flow-injection analysis, *PL* photoluminescence, *QD* quantum dots, *RS* resonance scattering, *TPB* tetraphenyl boron, *PDA* DA polymerization.

(1) Dreyer, D. R.; Miller, D. J.; Freeman, B. D.; Paul, D. R.; Bielawski, C. W. *Langmuir* **2012**, *28*, 6428-6435.