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2 Facile and Green Synthesis of Surfactant-Free ${ }_{3} \mathrm{Au}$ Clusters/Reduced Graphene Oxide ${ }_{4}$ Composite as Efficient Electrocatalyst for ${ }_{5}$ Oxygen Reduction Reaction

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11 Fig. S1 TEM image of Au clusters prepared with DMF.


2 Fig. S2 Raman spectra of GO, RGO, and Au clusters/RGO composite prepared with

3 CA.

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6 Fig. S3 EDS patterns of Au clusters/RGO composites prepared with different agents:
7 (a) CA, (b) AA, (c) $\mathrm{N}_{2} \mathrm{H}_{4} / \mathrm{NH}_{3}$, and (d) DMF. The inset shows the SEM image of
8 selected area for EDS and the contents of different elements (C, O, N, and Au).


2 Fig. S4 FTIR spectra of Au clusters and Au clusters/RGO composites prepared with
$3 \mathrm{CA}, \mathrm{AA}_{2} \mathrm{H}_{4} / \mathrm{NH}_{3}$ and DMF.

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7 Fig. S5 CV curve of RGO reduced by CA in $\mathrm{O}_{2}$ saturated 0.1 M KOH solution.
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Fig. S6 (a) TEM image of Au clusters/RGO composites (CA) prepared with different

11 ratio of Au cluster: RGO. (a) 1:1; (b) 2.5:1 and (c) 4:1.


2 Fig. S7 CV curves of Au clusters/RGO composites directly prepared in DMF solution

3 at $140{ }^{\circ} \mathrm{C}$; (b) and (c) CV curves of Au clusters/RGO composites prepared with
$4 \mathrm{~N}_{2} \mathrm{H}_{4} / \mathrm{NH}_{3}$ and ascorbic acid (AA). All the ratio of Au clusters: RGO are 5:1.


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\text { Potential(V vs } \mathrm{Ag} / \mathrm{AgCl})
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6 Fig. S8 The dependence of $n$ value for Au clusters/RGO composite (CA) on the 7 potential.


Potential (V vs Ag/AgCl)
9 Fig. S9 Comparison of the electrochemical stability of commercial $\mathrm{Pt} / \mathrm{C}$ and Au

1 clusters/RGO composite prepared with CA by continuous cyclic voltammetry in $\mathrm{O}_{2^{-}}$ 2 saturated 0.1 M KOH solution

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Table S1. Tentative band assignments of DMF protected Au clusters

| Wavenumber $\left(\mathrm{cm}^{-1}\right)$ | Assignment |
| :---: | :---: |
| 1719 | $v(\mathrm{C}=\mathrm{O})$ of carboxylic acid group |
| 1651 | amide I |
| 1557 | amide II |
| 1441,1342 | $v(\mathrm{C}-\mathrm{H})$ |
| 1403 | $v(\mathrm{C}-\mathrm{N})$ and $\mathrm{CH}_{3}$ deformation |
| 1252,1178 | $v(\mathrm{C}-\mathrm{O})$ |
| 1057,1037 | $v(\mathrm{C}-\mathrm{N})$ and $v(\mathrm{C}-\mathrm{H})$ |
| 939 | $v(\mathrm{C}-\mathrm{C})$ |

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