

## Supporting Information

Tunichrome-Inspired Gold-Enrichment Dispersion Matrix and Its Application in Water

Treatment: A Proof of Concept Investigation

Amarendra Dhar Dwivedi <sup># a,b</sup>, Rega Permana <sup># a</sup>, Jitendra Pal Singh <sup>c</sup>, Hakwon Yoon <sup>a</sup>, Keun

Hwa Chae <sup>c</sup>, Yoon-Seok Chang <sup>a</sup>, Dong Soo Hwang <sup>\* a,b</sup>

<sup>a</sup> Division of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Pohang 37673, Republic of Korea

<sup>b</sup> Division of Integrative Bioscience and Biotechnology, Pohang University of Science and Technology (POSTECH), Pohang 37673, Republic of Korea

<sup>c</sup> Advanced Analysis Centre, Korea Institute of Science and Technology, Seoul-02792, Republic of Korea

Corresponding author:

\*Dong Soo Hwang (E-mail: dshwang@postech.ac.kr)

# Author contributions:

A.D.D. and R.P. contributed equally.

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## S1. Materials used and general procedure

N-hydroxysuccinimide (NHS), HAuCl<sub>4</sub>, KAu(CN)<sub>2</sub>, ICP gold standard (1000 ppm), gallic acid, ammonium thiosulphate, thiourea, cadmium-, cobalt-, nickel salts, sodium boro hydride, 4-nitrophenol, methylene blue, and powdered activated carbon (Darco G-60) were purchased from Sigma-Aldrich Co. Ltd. Chitin was purchased from TCI Chemicals. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC.HCl) was purchased from APExBIO. Granular activated carbon and NaOH was purchased from (Samchun Pure Chemical Co., Ltd, Republic of Korea).

Working standards were prepared from the stock solution (1000 mg/L). The pH was adjusted by the addition of 0.1 M HNO<sub>3</sub> and 0.1 M NaOH solution under agitation. To test the degree of sorption, an aliquot of the aqueous phase was removed and filtered by using a membrane filter, diluted with 2% HNO<sub>3</sub>, and metal concentrations were analyzed by inductively coupled plasma optical atomic emission spectrometer (ICP-OES) (iCAP6300 DUO ICP-OES; Thermo Scientific).

## S2. Sorption experiment and data analysis

The concentration of Au(III) retained in the CGa calculated as:

$$Q_{eqm} = \frac{(C_i - C_{eqm})V}{W} \quad (S1)$$

where,  $Q_{eqm}$  (mg/g) is the amount of gold on CGa at the equilibrium,  $C_i$  (mg/L) is the initial concentration of Au(III),  $C_{eqm}$  (mg/L) is the equilibrium gold concentration,  $V$  is the volume of solution (L), and  $W$  (g) represents the CGa dose. All studies were carried out in duplicate. Statistical data in this study were investigated using Microcal Origin software for the best-fit models. Rate controlling steps (intraparticle diffusion; eq. S2), isotherms (Langmuir; eq. S3,

Freundlich; eq. S4, Sips isotherm; eq. S5), and thermodynamic data (eqs. S6, S7) were calculated by following modelling equations:

$$Q_t = k_{ipd} \sqrt{t} + C \quad (S2)^1$$

$$q_e = Q_m k_l C_e / (1 + k_l C_e) \quad (S3)^{2, 3}$$

$$q_e = k_f C_e^n \quad (S4)^4$$

$$q_e = Q_m (k_{lf} C_e)^n / (1 + (k_{lf} C_e)^n) \quad (S5)^5$$

$$\Delta G^\circ = -RT \ln K_c \quad (S6)^6$$

$$\ln K_c = -(\Delta H^\circ)/RT + (\Delta S^\circ)/R \quad (S7)^6$$

*Abbreviations:* (Rate kinetics:  $Q_t$  is adsorption capacity at time  $t$ ,  $k_{ipd}$  represents intraparticle diffusion rate constant,  $C$  is the intercept of plot of  $Q_t$  versus  $\sqrt{t}$ . *Isotherm models:*  $q_e$  is the equilibrium adsorption capacity of Au(III) ions,  $C_e$  is the equilibrium concentration of gold ions,  $Q_m$  is the maximum sorption capacity, and  $k_l$  is Langmuir constant.  $n$ ,  $k_f$  and  $k_{lf}$  are empirical constants of Freundlich and Sips isotherms. *Thermodynamics:*  $R$  is the universal gas constant ( $8.314 \times 10^{-3}$  kJ/mol.K),  $T$  (K) is the absolute temperature,  $K_c$  is the thermodynamic equilibrium constant; standard Gibb's free energy change, enthalpy change, and entropy change are presented as  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ )

For desorption studies, the gold loaded CGa was collected via centrifugation and decantation of the supernatant. The exhausted material was eluted with a selected eluent (0.02 L) for 24 h and centrifuged it. Desorption efficacy was calculated as:

$$\text{Desorption efficacy (\%)} = \frac{\text{Released gold ions (mg.L}^{-1}\text{)}}{\text{Sorbed gold ions (mg.L}^{-1}\text{)}} \times 100 \quad (S8)$$

### S3. Catalytic and antimicrobial experiments

#### *Reduction of 4-nitrophenol*

Three mL of NaBH<sub>4</sub> solution (30 mM) was mixed with 30  $\mu$ L of PNP aqueous solution (5 mM) in a quartz cuvette at 25 °C, then, 6 mg of CGa/Au composite added to this mixture. After certain time intervals, the supernatant was analyzed for PNP concentrations by UV-VIS spectroscopy test. After completion of the reduction reaction and between each cycle, the CGa/Au catalyst could be easily separated using tweezers, washed with DI water, blotted with filter paper, and subjected to the next cycle.

#### *4-nitrophenol calibration curve*

To establish the calibration curve of 4-nitrophenol, a series concentration of 1 mM, 2 mM, 3 mM, 5 mM, and 10 mM 4-nitrophenol solutions were made accordingly from the stock solution (50 mM). The absorbance of each solution was measured using UV-Vis spectrophotometer at 400 nm, subsequently, the calibration curve was made ( $R^2 = 0.9979$ ), as in Figure S10. Moreover, the catalytic efficiency of 4-nitrophenol by CGa/Au is shown in Figure S11.

#### *Reduction of MB*

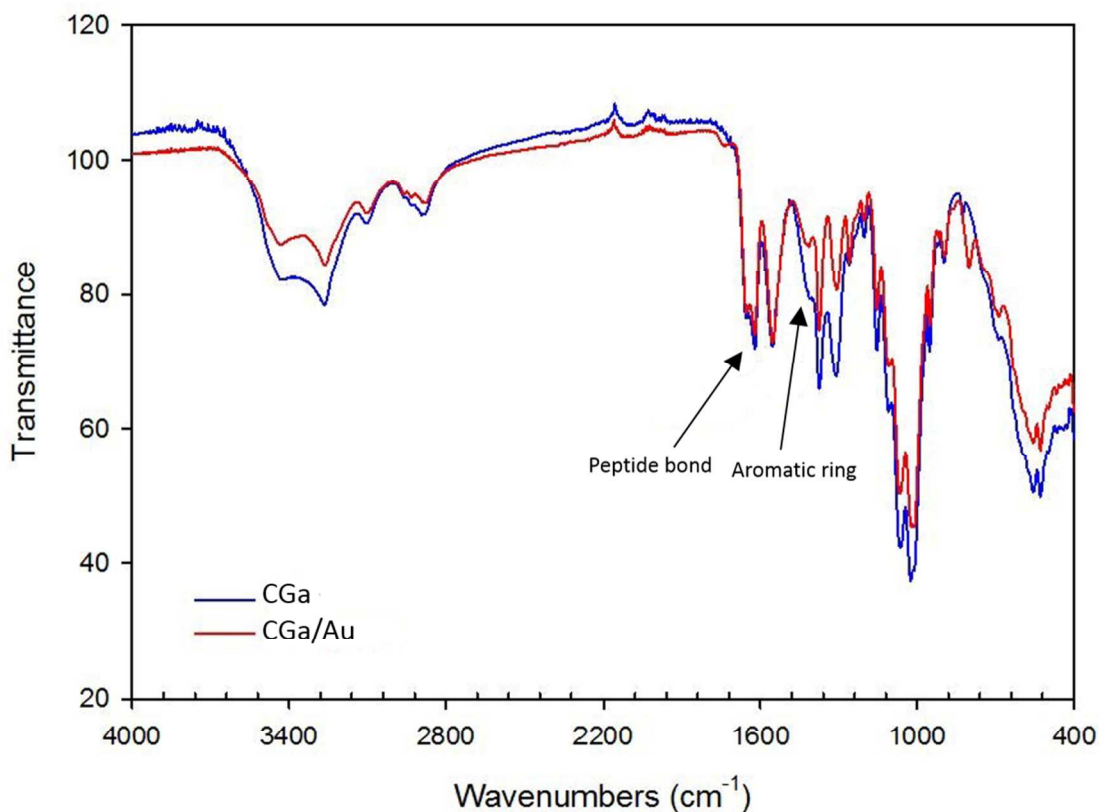
Six mg of CGa/Au composite was added to 20 mL of MB solution (50 mg/L) for 1 h stirring at 25 °C. Then, NaBH<sub>4</sub> (30 mM) was added to the solution. After reduction, the supernatant was put into a cuvette for an UV-VIS spectroscopy test.

#### *Antibacterial test*

The viability of bacterial cells was estimated using the FDA (fluorescein diacetate). *Escherichia coli* (*E. coli* DH5- $\alpha$ ) were chosen as a surrogate microorganism to test the bactericidal activity.

We pre-cultured the bacterial cells in nutrient broth. Aliquots of 20 mL of *E. coli* ( $10^6$  CFU/mL) in PBS buffer were exposed to 0.3 g/L of materials and incubated at 37 °C for 24 h. Each material and control were treated with 40 mg/L FDA. An excitation wavelength ( $\lambda_{\text{ex}}$  485 nm) and an emission wavelength ( $\lambda_{\text{em}}$  530 nm) were used to detect fluorescence spectroscopically. All experiments were performed in triplicates and the average values and standard deviations are considered.

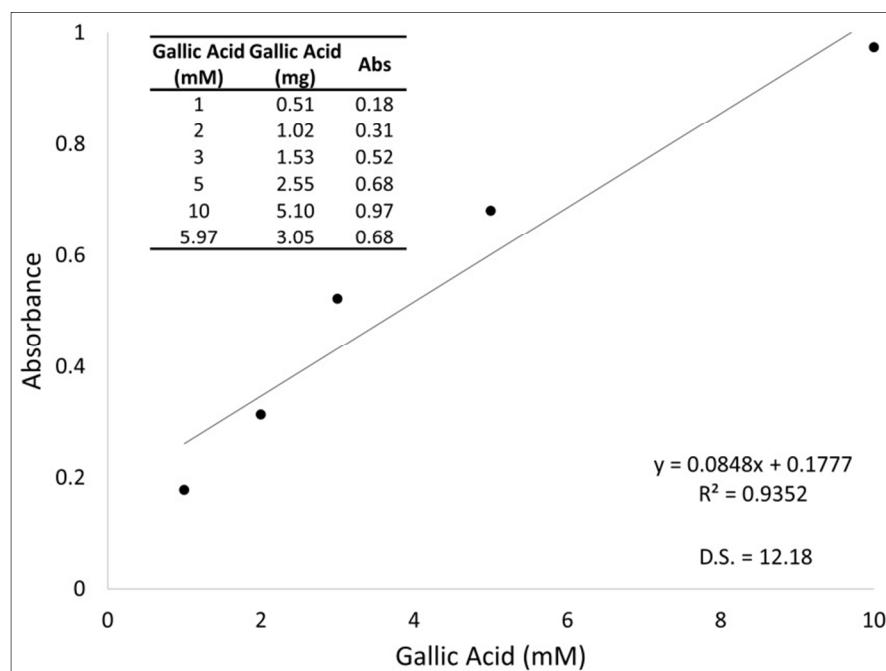
**Figure S1:** FTIR spectra of composite materials (CGa and CGa/Au)



FTIR spectroscopy was used for the qualitative identification of the chemical groups present in the materials. The vibrational bands in CGa/Au (after gold uptake) did not indicate the significant changes except the minor shifting of peaks. Gold possibly exerted relatively small effects in comparison to the larger impact of surface functional groups in CGa (as shown in spectra).

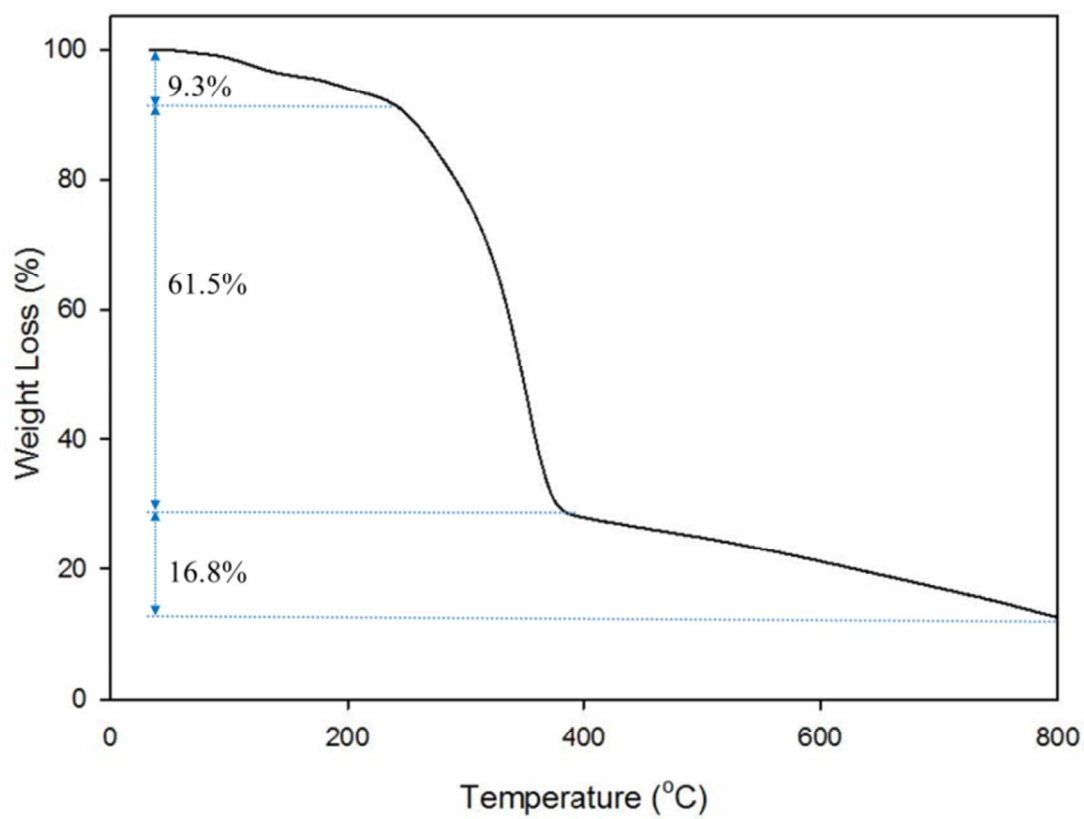


**Figure S2:** Degree of substitution of gallic acid conjugation on chitin nanofiber

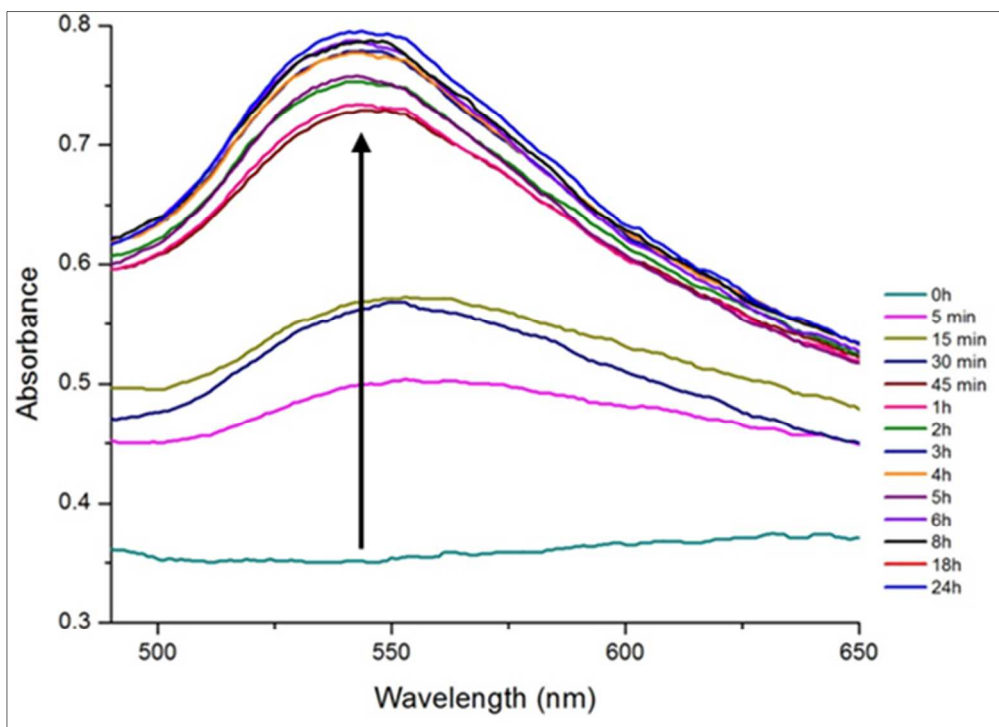


Quantification of gallic acid in the composite material was estimated using modified Arnow's assay. A series of gallic acid standard solutions were made ranging from 1 to 10 mM solutions to establish the standard calibration curve ( $R^2 = 0.9352$ ). The composite material (CGa; 25 mg) was prepared and each sample was vacuum-sealed in glass ampoules containing 1 ml of 6 M HCl with 20  $\mu$ l of phenol (to prevent oxidation) and heated up to 110°C for 24h. To each solution, 1 ml of 1.45 M sodium nitrite/0.4 M sodium molybdate solution was added to 1 ml of each sample. These solutions turned yellow. Then, 1 ml of 1 M NaOH was added to each solution, which turned dark brown-red. Light absorbance at 520 nm of each sample was recorded accordingly. The total weight of gallic acid in the sample was estimated through a series of conversions (from mM to moles and then weight in milligram).

**Figure S3:** Thermogravimetric analysis of CGa



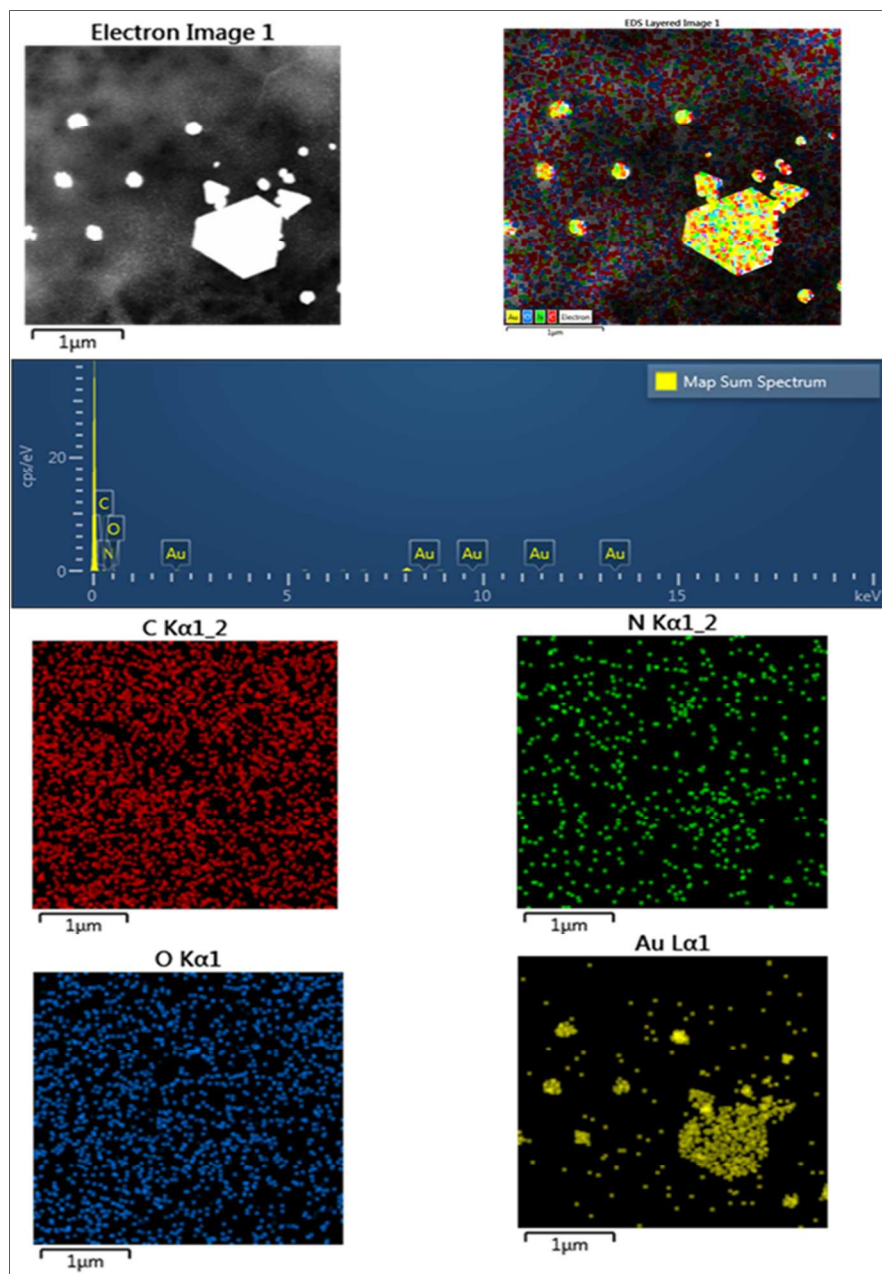
**Figure S4:** Surface plasmon resonance (SPR) band for *in situ* produced gold nanoparticle (upside arrow indicates nanoparticle formation)



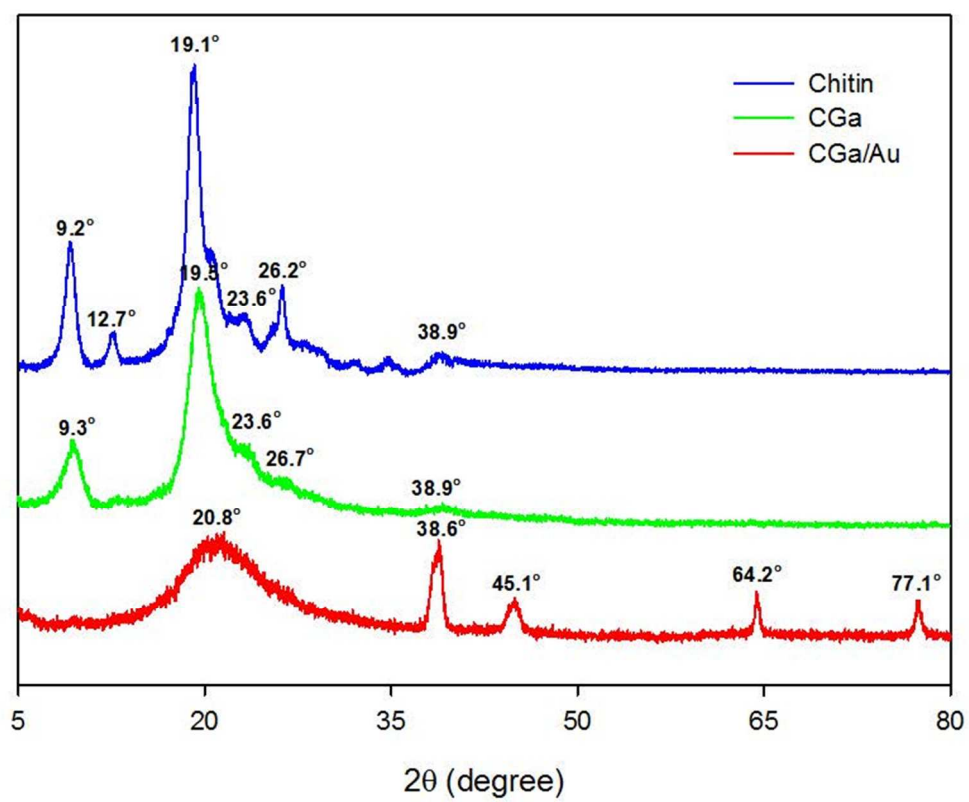
*Experimental details:*

20 mL of 100 mg/L aqueous solution of auric acid were prepared in a stoppered Erlenmeyer flask and 0.3g/L of CGa hydrogel was added to it at room temperature for 0 to 24 h time-progression, observing a yellowish to dark red-brown solution; indicating the formation of Au NPs. A noticeable spectroscopic feature of Au NP (noble metal nanoparticle) is the surface plasmon resonance, which displays a distinct absorption band (at 538 nm) in the visible range.

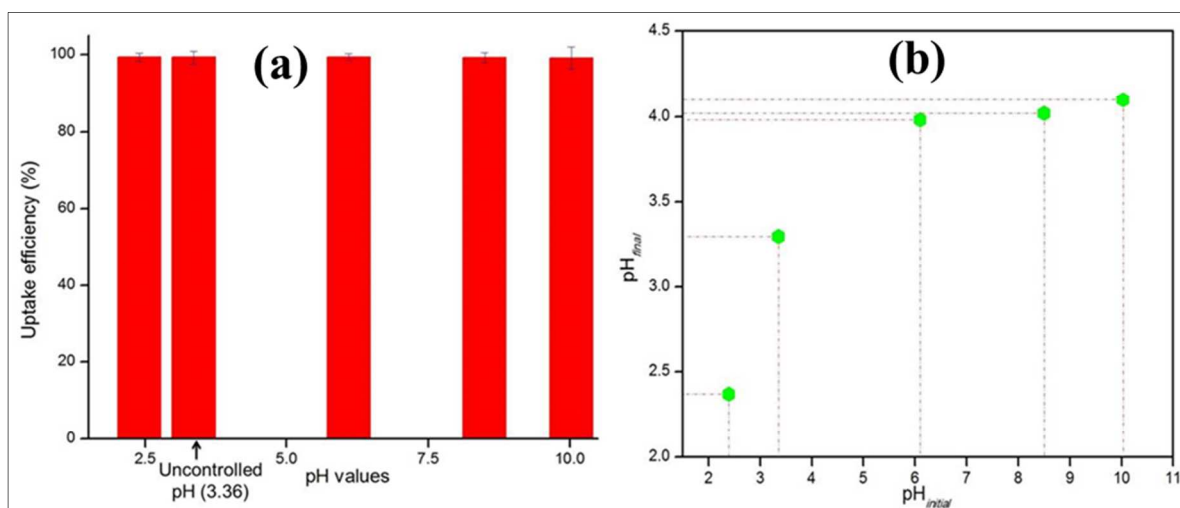
**Figure S5:** EDX spectra and elemental mapping of CGa/Au composite



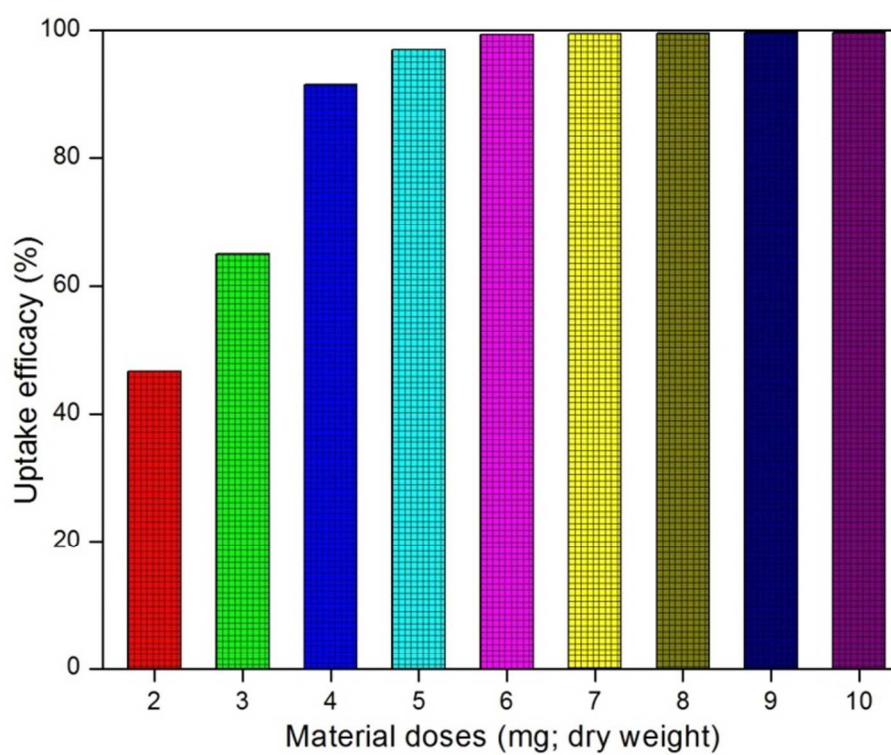
**Figure S6:** Comparative XRD patterns of native chitin, CGa, and CGa/Au composite



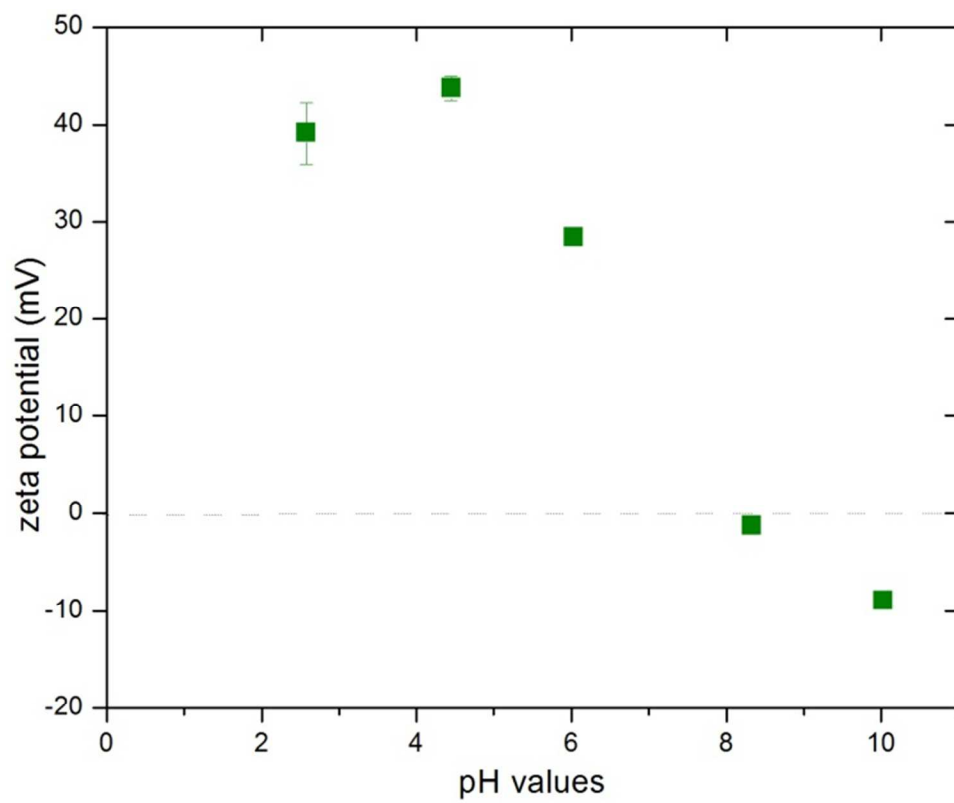
**Figure S7: (a)** Impact of different solution pHs on gold uptake efficiency (CGa doses = 0.3 g/L;  $[\text{Au(III)}]_0 = 100 \text{ mg/L}$ ; reaction time = 24 h; temperature = 298K); **(b)** correlation showing initial pH (start of experiment) versus final pH (end of experiment)



**Figure S8:** Impact of CGa doses on gold uptake ( $[V] = 0.02$  L;  $[Au(III)]_0 = 100$  mg/L; reaction time = 24 h; temperature = 298K)

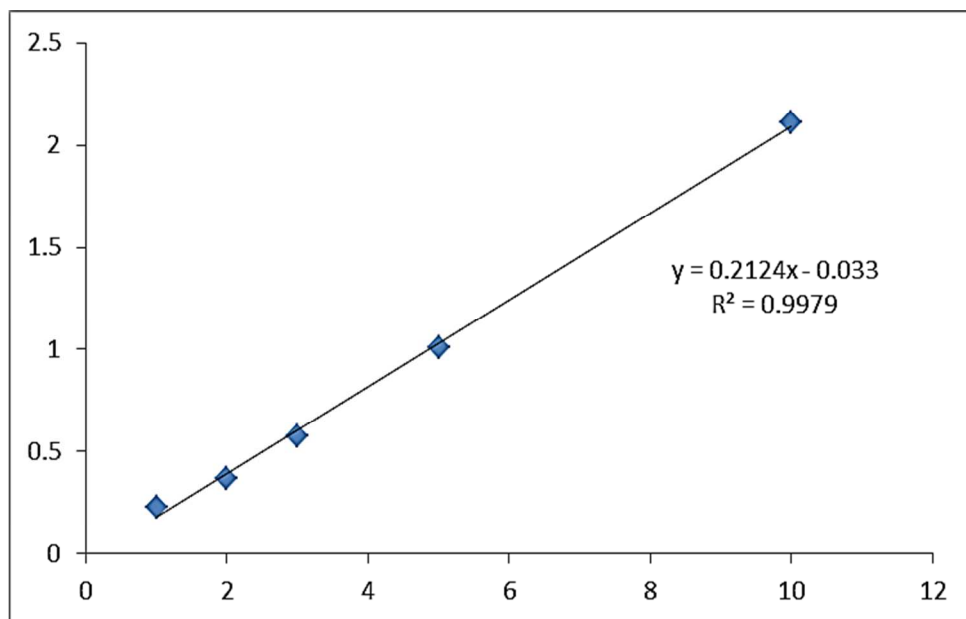


**Figure S9:** Zeta potential of CGa measured at different pH values

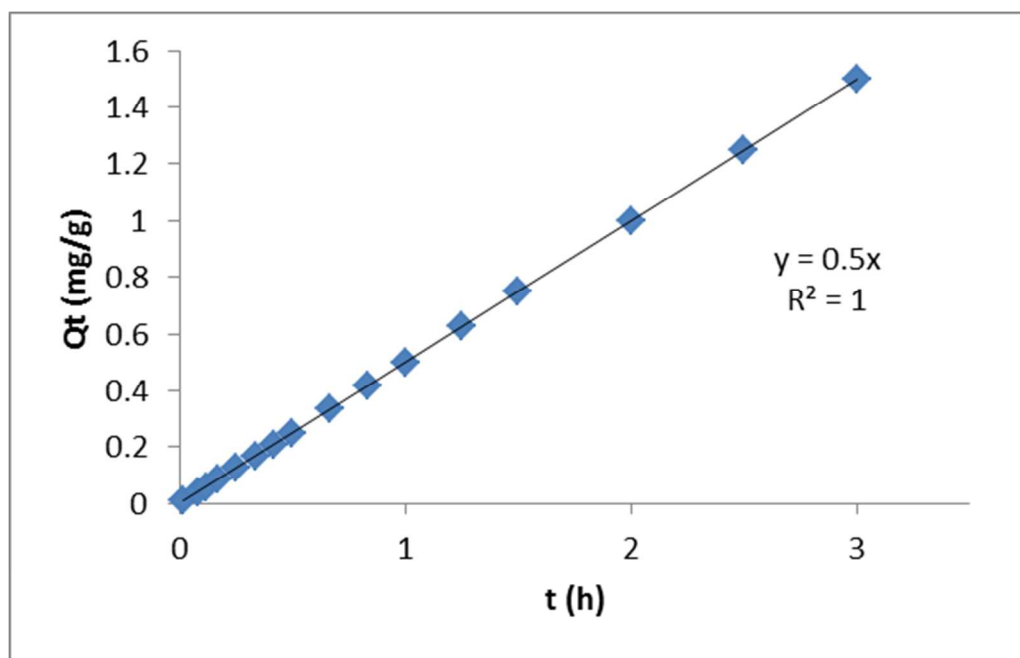




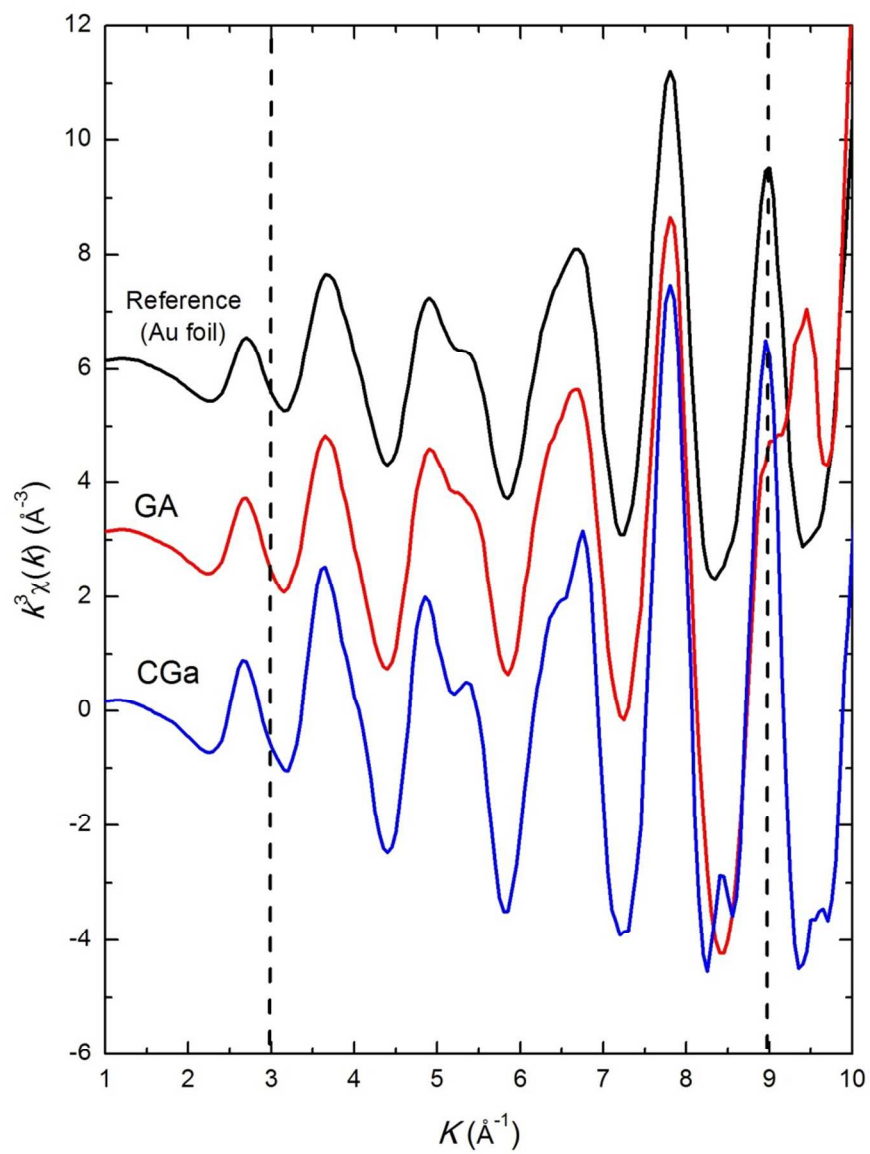
**Figure S10:** 4-nitrophenol calibration curve



**Figure S11:** Catalytic reduction of 4-nitrophenol by CGa/Au (time varied from 0.016 to 3 h; material dosing = 2 g/L;  $[\text{PNP}]_0 = 5 \text{ mM}$ ;  $Q_t$  = catalytic efficiency)



**Figure S12:**  $k^3$ -weighted EXAFS spectra of samples (dotted lines show  $k$ -fitting range)



**Table S1:** Gold isotherm data obtained from tunichrome-mimetic CGa

<b>Langmuir</b>					<b>Freundlich</b>					<b>Sips</b>				
$Q_m$ (mg.g <sup>-1</sup> )	k <sub>L</sub>	adj square	r- value	F- value	k <sub>F</sub>	n <sub>F</sub>	adj square	r- value	F- value	$Q_m$ (mg.g <sup>-1</sup> )	K <sub>s</sub>	n <sub>s</sub>	adj square	r- value
532.5	2.6	0.9516	493.4		8.5x10 <sup>16</sup>	7.1	0.877	190.8		562.9	1.4	0.6	0.9721	572.5

**Table S2:** Composition details (synthetic wastewater was made up using OECD guidelines)

Components	Concentration (mg/L)
Peptone	160
Meat extract	110
Urea	30
K <sub>2</sub> HPO <sub>4</sub>	28
NaCl	7
CaCl <sub>2</sub> ·2H <sub>2</sub> O	4
Mg <sub>2</sub> SO <sub>4</sub> ·7H <sub>2</sub> O	2
pH (~7.3±0.1), COD (~310 mg/L), and TOC (~110 mg/L)	

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